Chem Factsheet

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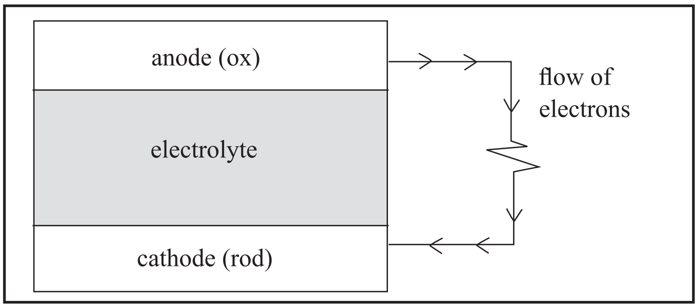
Rechargeable Batteries

To understand this Factsheet, you will need familiarity with:
- The idea of a reverse reaction
- Oxidation and reduction half-equations
- The basic principles of a voltaic cell
- Oxidation states

By the end of this Factsheet, you will have gained understanding of:
- The fundamental principles behind the design of rechargeable batteries
- The reactions occurring in three different rechargeable batteries
  - Lead-acid battery
  - Nickel-cadmium battery
  - Lithium-ion battery
- The advantages and disadvantages of rechargeable batteries

A battery is an electrochemical cell capable of discharging electrical current via a redox reaction. Batteries convert chemical energy into electrical energy that can be used to power various devices. Some types of battery may contain multiple cells connected in series.

Oxidation occurs at the anode of the cell leading to a loss of electrons and these electrons flow around an external circuit (the device) where they are used in a reduction reaction at the cathode of the cell. The flow of electrons allows work to be done.



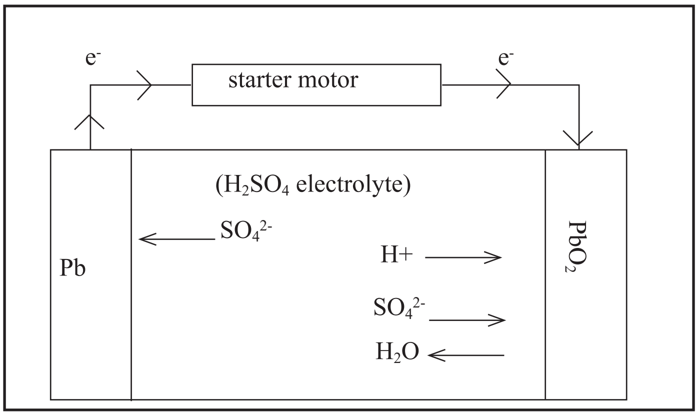
Primary and Secondary Cells

A primary cell is a battery in which the reactions occurring cannot be reversed and, hence, they are not rechargeable. The voltaic cells covered on A level and IB syllabuses (e.g., the Daniell cell) are examples of primary cells. The ubiquitous, non-rechargeable AA and AAA batteries used in electronic devices are also typical primary cells.

A secondary cell is one in which the redox reactions that occur during discharge are reversible through an input of electrical current. These cells are rechargeable. Typical examples include the lead-acid, nickel-cadmium and lithium ion batteries.

The Lead-acid Battery

Lead-acid batteries are typified by the large, heavy 12 V battery found in car starter motors. They normally comprise of six 2 V cells arranged in series. The principal components of a fully charged lead-acid battery are:
- A solid metallic lead anode
- A solid lead(IV) oxide, PbO_2, cathode
- A sulfuric acid electrolyte between the two electrodes



During discharge, the lead anode undergoes oxidation and releases electrons in the following reactions:

Oxidation half-equations (anode) –

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

or

$$Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

During these reactions, the oxidation state of lead increases from 0 to +2.

The electrons released at the anode flow through the external circuit (starting the motor) and are then involved in a reduction reaction at the cathode.

Reduction half-equations (cathode) –

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

or

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

> The sulfuric acid electrolyte contains a mixture of SO_4^{2-} and HSO_4^- ions due to the first, strong dissociation and second, weak dissociation of sulfuric acid. Either species can be represented in the relevant half-equation.

During the reduction reactions, the oxidation state of lead decreases from +4 to +2.

The overall redox reaction occurring in the lead-acid battery can be created by combining appropriate oxidation and reduction half-equations.

Overall: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

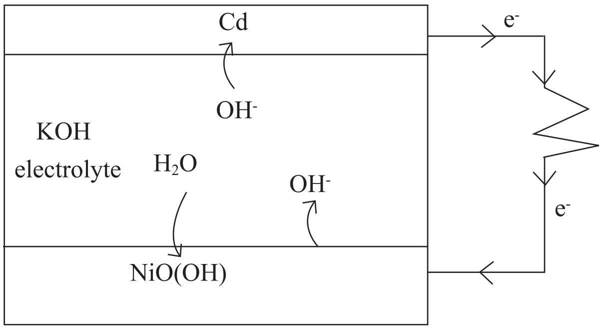
The battery can be recharged, converting lead(II) sulphate back into lead and lead(IV) oxide, by supplying an electrical current to the battery. In a vehicle engine, this is done via the alternator which converts the kinetic energy produced by the moving engine parts into electrical energy for recharging the battery and powering the vehicle's electrical devices.

Nickel-cadmium Battery

Nickel-cadmium batteries (NiCad for short) are the common rechargeable AA and AAA-sized batteries (though they can come in a variety of sizes) that power numerous small electronic devices such as toys, calculators, clocks, etc. They typically produce 1.2 V per battery.

NiCad batteries have been superseded by nickel-metal hydride (NiMH) batteries in recent years, due to their superior storage and reduced environmental impact.

When fully charged, a NiCad battery comprises:
- A solid metallic cadmium anode
- A solid nickel(III) oxide hydroxide, $NiO(OH)$, cathode
- An alkaline electrolyte such as potassium hydroxide, KOH.



During the discharge process, the cadmium anode releases electrons (oxidation) and combines with hydroxide ions from the electrolyte to form solid cadmium(II) hydroxide.

Oxidation half-equation (anode) –

$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$

In this oxidation reaction, the oxidation state of cadmium increases from 0 to +2.

The electrons recombine with the nickel(III) oxide hydroxide cathode in a reduction reaction forming solid nickel(II) hydroxide.
Reduction half-equation (cathode) –

$NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

During this reduction reaction, the oxidation state of nickel decreases from +3 to +2.

The overall redox equation can be created by combining the individual oxidation and reduction half-equations. The stoichiometry of the reduction reaction must be doubled to ensure the number of electrons involved is equal.

Overall: $Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

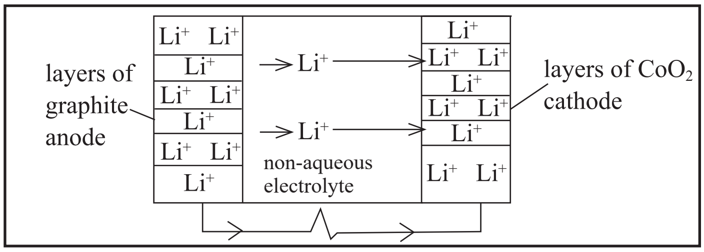
As with all rechargeable batteries, the input of electrical current can reverse both reactions, regenerating the starting materials for the electrodes. For NiCad batteries, this is typically done using a special charging device that inserts into the mains power supply, or the charging process occur within the electronic device itself when it is connected to the mains power supply.

The Lithium-ion Battery

The lithium-ion battery has become ubiquitous in recent years due to its superior performance compared to other types of rechargeable battery (see later section). Lithium-ion batteries are now commonplace in portable electronic devices such as mobile phones, laptop computers and tablets. A typical lithium-ion battery can produce a potential difference of 3-4 V.

Lithium-ion batteries are not to be confused with lithium primary cells, sometimes known as button batteries; these small lithium-based batteries are not rechargeable.

Lithium-ion battery technology is quite different from that of the lead-acid and NiCad batteries, though it still works via the same principles of oxidation and reduction at different electrodes. When fully charged a lithium-ion battery comprises:
- A graphitic carbon anode containing coordinated lithium atoms, LiC_6.
- A solid cobalt(IV) oxide cathode, CoO_2.
- A non-aqueous electrolyte containing a lithium salt and an organic solvent.



The structures of both the anode and cathode permit the movement of lithium ions into and out of the electrodes in processes called intercalation or insertion and de-intercalation or extraction.

During discharge, lithium atoms within the graphitic anode (represented as C_6) will lose electrons forming lithium ions. These ions then flow through the electrolyte to the cathode.

Oxidation half-equation (anode) –

$LiC_6 \rightarrow Li_{1-x}C_6 + xLi^+ + xe^-$

The use of the unknown x is to show that only some of the coordinated lithium atoms will oxidise and de-intercalate from the anode. For each lithium atom that undergoes this process, one lithium ion and one electron is formed.

The oxidation state of lithium increases from 0 to +1 for those atoms that undergo oxidation.

The lithium ions migrate through the electrolyte and recombine with electrons and the CoO_2 cathode forming lithium cobalt oxide, Li_xCoO_2.

$xLi^+ + xe^- + CoO_2 \rightarrow Li_xCoO_2$
In this reduction reaction, the oxidation state of cobalt decreases from +4 to +3.

The overall redox process is:
$LiC_6 + CoO_2 \rightarrow Li_{1-x}C_6 + Li_xCoO_2$

During the charging process, current is used to move the lithium ions back from the cathode in to the graphitic anode.

Advantages and Disadvantages of Rechargeable Batteries

Advantages	Disadvantages
Can be used many times before replacement is needed	Initial purchase cost is high relative to non-rechargeable alternative
NiCad and Li-ion batteries are small and lightweight	Often use toxic substances, e.g., cadmium, lead, nickel
Li-ion batteries have a very high power-to-mass ratio	Require specialist disposal
Lead-acid batteries can be used as emergency electrical power supplies	Lead-acid batteries are very heavy and have a low power-to-mass ratio
Cheaper than non-rechargeable alternatives over the lifetime of the product	Possibility of overcharging, particularly in Li-ion batteries, leading to overheating
Capable of generating large voltages	

Questions

1. Nickel-metal hydride (NiMH) batteries operate in a similar way to NiCad batteries, but instead of a cadmium anode they contain a hydrogen-absorbing alloy, M, at the **cathode**. The reaction occurring at the cathode is:
   $M + H_2O + e^- \rightarrow MH + OH^-$

   The reaction occurring at the anode is the reverse of the reaction that occurs at the cathode in a NiCad battery:
   $Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$
   Construct an overall equation for the redox reaction taking place in a NiMH battery.

2. Suggest a reason why it is important that the products of both discharging and recharging processes are solids.

3. Suggest a reason why NiMH batteries have a smaller environmental impact than NiCad batteries.

4. One type of experimental rechargeable battery is the lithium-sulphur battery. At one of the electrodes, polysulphides undergo the following transformations:
   $S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3$

   By determining the oxidation state of sulphur in each of the species above, deduce whether the process shown represents oxidation or reduction and, hence, at which electrode the process occurs.

Answers

1. $M + Ni(OH)_2 \rightarrow MH + NiO(OH)$

2. Lowers risk of leakage of (hazardous) solutions if damaged / material must be physically attached to the electrode in order for reaction to be reversed.

3. NiMH batteries do not contain highly toxic cadmium which can cause contamination of the environment if NiCad batteries are incorrectly disposed.

4. S_8 zero
   Li_2S_8 -0.25
   Li_2S_6 -0.33
   Li_2S_4 -0.5
   Li_2S_3 -0.67

   Oxidation state decrease so REDUCTION
   Reduction occur at the CATHODE

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