Aqueous Electrolyte Batteries

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Aqueous electrolyte batteries

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Despite the growing interest in advanced lithium batteries, the overwhelming majority of batteries manufactured today are still based on aqueous electrolytes, mostly sulphuric acid or potassium hydroxide solution. The ubiquitous lead–acid battery is, after 150 years, still being improved as regards its design and materials of construction. Rechargeable batteries based on potassium hydroxide electrolyte have nickel oxide or silver oxide positive electrodes and negatives of zinc, cadmium or iron metal, or hydrogen in the form of hydrogen–platinum electrodes or as metal hydrides. The most common by far is the nickel oxide–cadmium battery, although others find specialized applications. Progress in the development of the various aqueous electrolyte batteries is outlined, including novel batteries not yet in production (zinc–bromine, vanadium redox). Limitations (technical, economic and environmental) to the use of batteries are mentioned. Finally, reference is made to super- and ultra-capacitors and their intermediate role between rechargeable batteries and conventional capacitors.

1. Introduction

A convenient method of classifying electrochemical power sources is according to the nature of their electrolyte. Acid electrolytes are used in the ubiquitous lead–lead oxide battery (H_2SO_4) and in the phosphoric acid fuel cell (H_3PO_4). Potassium hydroxide electrolyte is employed in alkaline batteries (alkali–manganese, nickel–cadmium, nickel–iron) and in the alkaline fuel cell. Fused salts are ideal electrolytes for high-temperature systems such as military reserve batteries and molten carbonate fuel cells, while ceramic oxide electrolytes are used in sodium batteries (sodium–sulphur, sodium–nickel chloride) and in the high-temperature solid state fuel cell. Other batteries are based on silver salts as electrolyte (e.g. $RbAg_4I_5$ in silver batteries), or organic liquids or polymers (lithium batteries). Such a diversity of electrolyte types opens up a challenging range of problems in materials science and electrochemistry. This volume aims to highlight many of these problems, to show the progress being made in overcoming them and how they interact with applied problems of engineering design and production technology.

This introductory paper to Session 1 is concerned primarily with aqueous electrolyte batteries and will summarize advances in that field and some of the problems remaining to be solved. Batteries are of two types: primary (or ‘throw-away’) and secondary (or rechargeable). Primary batteries are comparatively easy to design as they undergo only a single discharge reaction. Secondary batteries, by contrast, are often required to have a life of more than 1000 charge–discharge cycles with no appreciable loss of capacity or power output. In chemical terms, this translates into an electrochemical reaction involving the reversible and quantitative oxidation–reduction of

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the electrode materials (which are solids for aqueous electrolyte batteries) for the required operational life of the battery. These electrode reactions generally involve solid state diffusion leading to phase changes and recrystallization. From the viewpoint of the solid state chemist this is an exceedingly demanding duty schedule, unparalleled elsewhere in applied solid state chemistry. The severity of the specification is apparent when one considers the many possible side reactions leading to battery deterioration and failure. These include:

(i) densification and swelling of the electroactive material with loss of porosity;

(ii) progressive formation of inactive phases in the electrode material;

(iii) growth of metallic needles ('dendrites') at the negative electrode causing internal short circuits;

(iv) shedding of active material from electrode plates;

(v) separator dry-out through overheating, leading to electrolyte redistribution;

(vi) corrosion of current collectors resulting in increased internal resistance; and

(vii) gassing of electrode plates on overcharge causing disruptive effects.

These, and other degradation processes, may result in precipitous battery failure, through an internal short-circuit, or may lead to progressive loss in capacity and performance. Generally the degradation steps are interactive and accumulative, so that once performance deterioration sets in it accelerates and the battery becomes unusable after a few tens of charge–discharge cycles.

The precise specification required of a battery depends very much upon the application for which it is intended. Batteries are often designed to meet specific criteria, e.g. long life, high power output, wide ambient temperature range, low maintenance, etc. For this reason commonly used designations such as 'lead–acid', 'nickel–cadmium' are simply generic descriptors for a whole family of batteries designed to meet specific applications. Indeed, it is common for battery design engineers to spend their entire career designing batteries based upon a single electrochemical couple.

2. Lead–acid battery

The $Pb–H_2SO_4–PbO_2$ electrochemical cell is by far the most common type of rechargeable battery, having more than 90% of this market. It is widely used for starting, lighting and ignition (SLI) in vehicles and finds many other applications, including emergency (stand-by) power supplies, motive power batteries for electric vehicles and, in the form of sealed cells, power for portable appliances. Since its invention in 1859 it has undergone many developments involving both materials and design. Some of these have been of an essentially practical or engineering nature, e.g.

(i) the replacement of early glass containers by hard rubber, and later by plastics such as high-impact polypropylene;

(ii) the development of through-the-wall cell interconnects, rather than external cell connectors;

(iii) heat-sealed plastic case-to-cover assemblies;

(iv) safety vents for sealed cells; and

(v) automatic central watering systems for traction batteries.

Other materials developments have been more science based, in particular the metallurgical alloys used in the plates.

The electrode reactions of the lead cell are unusual in that the electrolyte (H_2SO_4) is also one of the reactants, as seen in the following equations for discharge:

$$\text{negative electrode} \quad Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e^- \quad (-0.356\ \text{V})$$

$$\text{positive electrode}\quad PbO_2 + H_2SO_4 + 2H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O \quad (1.685\ \text{V})$$

$$\text{overall}\quad Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \quad (2.041\ \text{V}).$$

The theoretical energy density of the Pb–PbO_2 couple (including the mass of reactant acid) is 170 W h kg^{-1}. In practice, most lead–acid batteries deliver 30–50 W h kg^{-1}, depending upon their design and the rate of discharge. The difference represents the mass of inert lead (grids and connectors), the battery case and terminals, the cell separators and unused active material. A great deal of research has gone into improving the utilization of the active material, which can be as low as 25–30%, but with limited success. It is well understood that the available capacity is determined by mass transport and ionic diffusion within the porous electrode structures.

(a) *Positive grid alloys*

Traditionally, lead–antimony alloys (up to 8% Sb) have been employed for the positive grids in Pb–acid batteries. The role of the antimony is to harden the alloy and to improve castability and paste adherence. Also there is evidence that Sb retards positive grid corrosion. Against these desirable features must be set the fact that Sb is leached from the positive grid during corrosion, diffuses through the electrolyte and deposits on the negative plate where it reduces the hydrogen overpotential and leads to hydrogen evolution during battery charge. Also there is increased self-discharge and reduced charge efficiency, leading to gassing. At high overcharge voltages SbH_3 may be liberated. Because of these deleterious aspects, the trend has been towards reducing the antimony content, or eliminating it altogether with the substitution of other alloying agents. 'Low maintenance' batteries generally contain less than 3% Sb, thereby reducing gassing.

'Maintenance-free' batteries utilize a Pb–Ca alloy (up to 0.1 wt% Ca) or a Pb–Ca–Sn alloy. On quenching the grids during manufacture, a dispersion of Pb_3Ca forms around pure lead grains resulting in precipitation hardening. This composition alloy eliminates many of the undesirable features of Sb, in particular gassing, provided the charging voltage is controlled. Such batteries may only be used in 'float' conditions (e.g. automotive or stand-by applications) and are unsuited to regular deep discharge. Research directed to this problem is in progress.

(b) *Grid design and manufacture*

Much thought and research has gone into optimizing the design of grids so as to maximize their conductivity and their strength for minimum mass. Computer-aided design has been extensively employed.

While most grids are individually quench-cooled, a growing tendency is to use continuously cast strip which is then slit, expanded to form grids and cut to size. The combination of expanded positive grids and continuously cast negatives gives a highly materials-efficient battery.

(c) *Separators*

Many different materials have been employed as porous separators in Pb–acid batteries. Early batteries used sheets of flannel, wood, or resin-impregnated glass wool. Modern separators consist of a plastic resin (polyethylene or PVC) with an inorganic filler (SiO_2). The separator may contain three times as much silica by weight as polymer. The pore volume and pore size distribution are tightly controlled in the manufacturing process. The separator has ribs along its length to hold it away from the positive electrode where water is formed on discharge.

(d) Active materials

The electrochemically active material is made by reacting lead ingots with air in a ball-mill, or by roasting liquid lead with air in a pot furnace. This is then made into a paste with sulphuric acid and the grids are pasted, with certain inert additives to the negative electrode (expanders). After pasting, the electrodes are 'cured' by allowing them to stand in air to permit chemical reactions to take place in the paste, forming various basic lead sulphate hydrates. The electrodes are then mounted in the cell and 'formed' by charging electrochemically to convert the basic salts to PbO_2 at the positive and to spongy Pb metal at the negative.

(e) Battery design

Lead–acid batteries are of three basic designs:

(i) Flat, pasted plates as used in automotive or stand-by batteries.
(ii) Tubular positive plate batteries for deep discharge applications (e.g. traction).
(iii) Sealed, valve regulated batteries for portable power applications.

Traction batteries have a positive plate composed of vertical porous tubes made of glass- or polyester-fibre into which lead spines are inserted and packed around by active material. The tubes serve to hold the active mass in place and prevent shedding. Valve regulated lead–acid (VRLA) batteries are sealed batteries in which the gases formed on overcharge are recombined electrochemically at the negative electrode. For this to occur, provision must be made for the oxygen formed at the positive to migrate to the negative electrode by operating the cell in the 'electrolyte starved' regime (as opposed to the 'flooded' cells of the other two types). A porous glass mat separator contains the electrolyte at a saturation level of 90–95%, leaving 5–10% voidage through which oxygen passes to the negative electrode where it recombines with hydrogen.

As progressive corrosion occurs, excess hydrogen is vented through the one-way valve.

3. Neutral and alkaline electrolyte batteries

(a) Primary batteries

Most commercial primary cells are based upon the Zn–MnO_2 electrochemical couple. *Leclanche cells*, first proposed in 1866, employ an aqueous solution of ammonium chloride and zinc chloride as the electrolyte, while the cathode is a mixture of manganese dioxide and carbon black. A carbon rod serves as the positive current collector and the negative is a zinc can into which the other components are placed. The MnO_2 may be a natural mineral (pyrolusite) or a synthetic product. Leclanche cells are of simple construction and are relatively cheap to manufacture. They are cost-effective for low-rate applications, or for intermittent operation with rest periods between use. The chemical reactions taking place in the cell are complex and, in outline at least, are reasonably well understood (Vincent 1984). The formation of solids such as $Zn(NH_3)_2Cl_2$, $ZnCl_2 \cdot 4Zn(OH)_2$ and $ZnO \cdot Mn_2O_3$ at high discharge rates severely limits the available capacity, unless recuperative periods are allowed for diffusion processes to take place within the cell. Leclanche cells do not perform well at low temperatures, nor is their charge retention on standing (shelf life) especially long. However, for intermittent use at ambient temperatures they provide a cost-effective power source and are still widely used.

In the so-called *zinc chloride cell* the ammonium chloride is replaced entirely by $ZnCl_2$. This simplifies the cell chemistry considerably and these cells perform better at high discharge rates and at low temperatures. Mineral MnO_2 is replaced by synthetic material prepared by the electrolytic oxidation of $MnSO_4$. The cell requires a more elaborate seal design to prevent leakage and these factors, taken together, result in a higher cost of manufacture to offset the improved performance.

The *alkaline manganese cell*, which employs concentrated potassium hydroxide electrolyte (*ca.* 30%) is a premium grade of primary battery which is taking a progressively larger market share. The cathode mix consists of electrolytic MnO_2 and graphite. The cells are usually inverted with respect to zinc–carbon cells, the cathode mix being on the outside and surrounding the zinc anode which is in powdered form. Thus the cell case is positive rather than negative and the insulating seal is at the bottom of the cell rather than the top. These cells perform better than zinc–carbon cells at high current drain and also at low temperature. Moreover, they have a shelf life of several years. They are particularly well suited to portable power applications (audio cassettes, toys, etc). Despite the warnings on battery labels, it is possible to recharge alkaline manganese cells for tens of discharge cycles *provided* the voltage is tightly controlled. On discharge it should not be allowed to fall below 0.9 V, corresponding to reduction of MnO_2 to Mn_3O_4. Reduction beyond this to MnO is irreversible. On charging, overcharge must be avoided as there is no provision for venting gases; therefore the use of voltage-limited taper current charging is essential. Rechargeable alkaline manganese batteries have a performance which combines features of both the primary cells and secondary nickel–cadmium cells. They have almost twice the initial capacity of Ni–Cd, cost less than half the price, but are capable of only 20–30 recharge cycles (cf Ni–Cd which is capable of over 200 cycles). An important environmental point is that they contain no toxic Cd or Hg to cause disposal problems. Traditionally primary batteries have had a small quantity of mercury added to the anolyte to raise the hydrogen overvoltage at the zinc anode. Recently expressed environmental concerns have led to this being replaced by less toxic additives to achieve the same goal. Market demand for rechargeable alkaline manganese batteries is rising sharply at a time when sales of small Ni–Cd cells are declining (*Batteries International*, Issue 23, April 1995).

In principle, *magnesium* or *aluminium* can be substituted for zinc in primary cells with considerable advantage. Because of their lower atomic masses (and, in the case of Al^{3+}, higher ionic charge), their specific capacities are greater, namely Zn $0.82\ \mathrm{A\,h\,g^{-1}}$, Mg $2.21\ \mathrm{A\,h\,g^{-1}}$, Al $2.98\ \mathrm{A\,h\,g^{-1}}$. Moreover, the higher electrode potentials of Mg and Al result in higher cell voltages and thus higher specific energies per unit cell mass and volume. Unfortunately, the higher electrode potentials also lead to high anodic corrosion rates. On standing on open circuit a thin protective oxide film forms on the anode which has to break down before discharge can take place. This results in a ‘voltage delay’ before discharge begins and this is commercially unacceptable. For this reason rather few primary cells with magnesium or aluminium anodes have been manufactured.

Other *cathode materials* which have been employed in zinc primary cells are mercury oxide (HgO) and silver oxide ($AgO–Ag_2O$). These are used in miniature or ‘button’ cells which find applications in watches and in portable electronic equipment. Notable features of these cells are their high volumetric capacities, up to $400\ \mathrm{A\,h\,l^{-1}}$ for mercury cells and even higher for silver cells, and their flat discharge curves. They are particularly well suited to low-drain constant-voltage applications such as

Table 1. *Characteristics of alkaline batteries*

cell	voltage	specific energy (W h kg^{-1}) theoretical	specific energy (W h kg^{-1}) practical[a]
Fe–NiOOH	1.25	267	40–60
Cd–NiOOH	1.20	210	30–40
Zn–NiOOH	1.60	326	70–100
Fe–Ag_2O_2		not used	
Cd–Ag_2O_2	1.3/1.1	274	50–80
Zn–Ag_2O_2	1.8/1.5	432	90–150

[a] Dependent upon discharge rate.

hearing aids. On account of the environmental concern over mercury disposal and the cost of silver, they are rapidly being replaced by primary lithium cells.

(*b*) *Secondary batteries*

Secondary (rechargeable) batteries with alkaline electrolytes have one of three metals as the anode (Cd, Fe or Zn) and either nickel (III) oxide or silver oxide as the cathode. In addition to these six electrochemical couples, whose characteristics are summarized in table 1, there are the fuel cell–battery hybrids. These have either an air cathode or a hydrogen anode; they are discussed further later.

The *cadmium–nickel oxide cell* (generally referred to as 'nickel–cadmium') was invented by Jungner in Sweden in 1899 and is by far the best known secondary alkaline battery. The overall cell reaction is

$$\mathrm{Cd} + 2\mathrm{NiOOH} + 4\mathrm{H_2O} \rightleftharpoons \mathrm{Cd(OH)_2} + 2\mathrm{Ni(OH)_2}\cdot\mathrm{H_2O}, \quad \textsc{ocv} = 1.30\ \mathrm{V}.$$

The Ni–Cd battery is manufactured in a wide variety of styles and sizes. Its applications include starting batteries for aircraft and large vehicles, stand-by power supplies and, in the smaller sizes, many domestic uses (shavers, power tools, toys, etc.). The positive features of Ni–Cd cells are an almost constant discharge voltage (1.2 V), long cycle life, high rates of discharge and charge, good low-temperature performance, continuous overcharge capability, low maintenance requirements and reliability. On the negative side are its comparatively high cost, environmental concerns over the use of cadmium and a phenomenon termed the 'memory effect'. The battery tends to 'remember' its recent cycling history and, if it is cycled without periodic deep discharge, it is no longer capable of yielding its full capacity. The explanation of this behaviour is still incomplete.

The negative electrode may contain 20–25% iron mixed with the cadmium (for cheapness), while the positive electrode has a few per cent cobalt hydroxide added to the nickel hydroxide to improve cell capacity and cycle life. The electrolyte, typically 25–30 wt% KOH, contains a little LiOH to aid charge acceptance by the cathode. Electrodes are fabricated in one of two ways.

(1) *Pocket plate electrodes.* Perforated steel strip is preformed as channels into which the active mix (often briquetted) is inserted. The filled channels (or pockets) are sealed and linked together horizontally to form the battery plate.

(2) *Sintered electrodes.* Sintered electrodes are made from fine nickel powder mixed with a volatile binder (e.g. ammonium carbonate), coated on to a nickel current collector, lightly pressed and sintered. The loss of the volatile material ensures a highly porous matrix (80–90% voidage) into which the active ingredients are impregnated as salt solutions and then decomposed, either thermally or cathodically, to yield the active mass. Variants of this technique employ preformed nickel sponge or reticulated foam as the supporting matrix. Sintered electrodes tend to give better performance than pocket plate electrodes, but are considerably more expensive to manufacture.

Other types of Ni–Cd battery are spirally wound cells and hermetically sealed cells for use in portable appliances.

The *iron–nickel oxide cell* ('nickel–iron') was developed by Edison in USA around 1900. It is similar to the Ni–Cd cell in many respects (voltage, specific energy, etc.), but the iron negative is cheaper than cadmium and also non-toxic. The Ni–Fe battery is capable of 2000 charge–discharge cycles at 80% depth of discharge and is highly robust, being undamaged by substantial overcharge and repeated total discharge. For these reasons Ni–Fe batteries have been employed in electric traction (industrial trucks, etc.) and in railway applications. The two major problems with the Ni–Fe battery both stem from the iron anode, namely:

(i) heavy gassing on charge due to preferential hydrogen evolution; this results in a requirement for frequent maintenance (water addition) and in low electrical efficiency (60–80% current efficiency); and

(ii) rapid self-discharge on standing due to corrosion of the negative plates.

Also the battery's low-temperature performance is poor compared to Ni–Cd. Unless and until these materials problems are overcome it is unlikely than Ni–Fe batteries will enjoy increased popularity, although in France they have been fitted as traction batteries to some of the new generation of small electric cars.

Zinc–nickel oxide batteries. Zinc is the ideal anode material for use in alkaline electrolyte batteries on account of its high electrode potential. It is the most electropositive of the common metals which can be plated from aqueous solution. The Ni–Zn cell therefore has a comparatively high voltage

$$\mathrm{Zn} + 2\mathrm{NiOOH} + 4\mathrm{H_2O} \rightleftharpoons \mathrm{Zn(OH)_2} + 2\mathrm{Ni(OH)_2}\cdot\mathrm{H_2O} \quad \textsc{ocv} = 1.78\ \mathrm{V}$$

and a correspondingly high energy density. A practical nickel–zinc cell can achieve 90–100 $\mathrm{W\,h\,kg^{-1}}$ and a battery pack 70 $\mathrm{W\,h\,kg^{-1}}$. This is an extremely interesting figure for electric vehicle traction as it would virtually double the range of present day EVs. powered by lead–acid batteries. The problem lies in the structural instability of the zinc anode. On cycling, the anode changes its shape ('slumps'), densifies, recrystallizes and forms zinc dendrites (needles) which can penetrate the separator and cause a short circuit. All these problems stem from the amphoteric nature of zinc and its relatively high solubility in KOH compared to Cd or Fe. Much research has been directed to these problems and partial success has been achieved, to the extent of making experimental batteries which may be cycled *ca.* 100 times. However, this is still a factor of 5–10 too low for commercial success as a traction battery. The development of a fully recyclable zinc electrode is one of the major remaining challenges in the alkaline battery field.

Silver batteries. The silver oxide electrode discharges in two steps, namely, $\mathrm{Ag^{2+}} \rightarrow \mathrm{Ag^{+}}$ and $\mathrm{Ag^{+}} \rightarrow \mathrm{Ag}$. giving the potential for higher energy density batteries than with the nickel oxide (one electron) positive. Rechargeable silver–zinc and silver–cadmium batteries find their application where high specific energy and power levels are critical and where cost is a secondary consideration. This is principally in the military sphere. The Ag–Zn battery offers the highest energy density of any commercially available rechargeable battery (150 W h kg^{-1} and 200 W h l^{-1}), coupled to a wide operating temperature range (−20 to +70 °C). However, its useful life is limited to a few tens of charge–discharge cycles at best, although it may be stored up to five years in the dry state. The Ag–Cd battery has a lower specific energy (up to 80 W h kg^{-1}) but a longer cycle life (up to 300 cycles). The problem with the silver oxide cathode is much the same as that of the zinc anode, namely its solubility in KOH and consequent physico-chemical effects. In the case of the Ag–Zn battery, both electrodes suffer from this solubility effect and so the useful battery life is short.

4. Battery–fuel cell hybrids

A fuel cell differs from a battery in that both the fuel (hydrogen) and the oxidant (oxygen–air) are gases which are stored outside of the cell. The capacity of the cell is determined only by the availability of the reactants and therefore specific energy is not a meaningful term. Rather, specific power is used. Two types of battery–fuel cell hybrid have been developed, one in which the metal oxide positive has been replaced by an oxygen or air cathode (the 'metal–air' battery) and one in which the metal negative has been replaced by a hydrogen–platinum fuel cell anode (the 'nickel–hydrogen' battery).

(a) *Metal–air batteries*

Metal–air batteries all employ alkaline electrolytes and may have zinc, iron or aluminium anodes. The best known commercial battery is a small size zinc–air primary cell for use in hearing aids, although considerable research has been conducted on rechargeable batteries. Two concepts have been explored: (i) conventional electrical recharging of zinc–air cells and (ii) mechanical recharging, in which the exhausted electrolyte containing zinc oxide slurry is discharged from the battery and replaced by fresh electrolyte and new zinc anode plates. The exhausted electrolyte would then be returned to a central factory where the zinc anodes and the electrolyte would be recovered for recycling. Mechanically rechargeable zinc–air batteries are being developed in Israel for EV traction. Battery modules, each of 11 kW h stored energy, are assembled into a battery of 110–150 kW h suitable for powering a commercial vehicle. A specific energy of 208 W h kg^{-1} is claimed for this battery, with an air electrode life of more than 1800 cycles (*Batteries International*, Issue 21, October 1994). The zinc anode consists of a removable cassette containing the zinc plate, surrounded by a Zn–ZnO slurry. A great effort is going into building a pilot battery production line and also an automated refuelling machine which removes cassettes from an exhausted battery and replaces them with reconditioned units.

Considerable research has been carried out in USA on the mechanically rechargeable *aluminium–air battery* for use as a vehicle traction battery. (The possibility of electrical recharging of aluminium in aqueous solution does not exist.) The attractions of aluminium as an anode material are manifold: it is cheap, non-toxic, easily fabricated, readily available, lightweight and undergoes a three-electron reaction. The last two properties result in an extremely high theoretical specific capacity for aluminium (2980 A h kg^{-1}). If an aluminium–air vehicle traction battery could be developed, and the logistical problems of mechanical recharging be solved, it would revolutionize the prospects for electric vehicles which would then have a range comparable to conventional vehicles between refuelling. Unfortunately, the materials science and engineering problems are by no means simple. The approach adopted in USA was not to use cassettes, but to feed aluminium sheet continuously from a spool through the battery. The difficulty with this approach is that the thickness of the plate lessens as it dissolves away and provision has to be made for keeping the inter-electrode separation constant by having wedge-shaped counterelectrodes. There are also problems with separating the discharge product (hydrated alumina) from the electrolyte.

The materials problems of the *air–oxygen* electrode are identical to those encountered in the alkaline fuel cell so far as discharge is concerned, although recharge poses new problems arising from the reactivity of nascent oxygen. The oxygen reduction reaction is a four-electron two-step process, only the first of which is reversible:

$$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$$

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-.$$

The reaction is catalytic and necessitates solid, liquid and gas all interacting at a point. The current collector is generally a porous conducting matrix of nickel, or carbon coated with a catalyst, which is treated so that both electrolyte and air enter the pores to contact the catalyst. The design of the electrode, so as to minimize polarization through oxygen depletion or flooding and to maximize the reaction kinetics, is a sophisticated exercise in physico-chemical engineering. The use of pure oxygen rather than air gives significantly higher current densities and avoids the problem of CO_2 poisoning of the electrolyte. However, this defeats the prime advantage of the metal–air battery, namely that air is freely available and does not have to be carried around. Electrical recharge of the zinc–air cell tends to result in corrosion of the positive electrode and also gives rise to different conditions within the pores to those present during discharge. Secondary cells have not been commercialized.

(*b*) *Hydrogen–nickel oxide batteries*

‘Nickel–hydrogen’ (Ni–H_2) batteries employ a platinum–hydrogen anode in conjunction with a nickel oxide cathode. They have been developed primarily for use in satellites where they are now displacing Ni–Cd batteries on account of their higher specific energy, their longer cycle life and their great reliability. The battery is a key component in a satellite, without which communication and control is impossible. Battery reliability is paramount since it is generally impossible to exchange units, and battery failure leads to the loss of an expensive satellite. Specific energy is also an important parameter since the storage battery is one of the satellite’s heavier components and launching costs per kg are high.

The Pt–H_2 electrode is a fully reversible electrode in alkaline media and when combined with a nickel oxide positive forms an excellent cell of potential 1.25 V. The cell reactions are as follows:

$$\text{anode} \quad H_2 + 2OH^- \rightleftharpoons 2H_2O + 2e^-$$

$$\text{cathode} \quad 2NiOOH + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^-.$$

During discharge water is formed at the anode and consumed at the cathode so that the overall electrolyte concentration remains constant. There is a counterflow of water molecules and OH^- ions across the separator. As the negative active material is a gas (H_2) there is a potential storage problem. The solution adopted is to construct the electrode stack inside a lightweight sealed inconel pressure vessel. This is cylindrical in shape, with hemispherical end caps. Optimization of the cell volume and overall mass leads to an internal pressure of *ca.* 40 bar in the charged state, falling to *ca.* 2 bar in the discharged state for a 50 A h cell. Such a cell has a specific energy of *ca.* 50 W h kg^{-1}.

Early cells used an asbestos separator, but this has since been replaced by a woven cloth of stabilized zirconia. Cell stacks are assembled with electrodes in the 'back-to-back' configuration using sintered nickel positive plaques, electrochemically impregnated with active nickel hydroxide. The hydrogen electrode is a standard fuel cell type electrode; platinum black supported on a porous lightweight carbon matrix. The cell may be overcharged without harm as oxygen generated at the positive diffuses to the Pt–C negative where it recombines with excess hydrogen. On standing at open circuit these cells do experience some self-discharge through chemical reduction by H_2 and are normally kept on trickle charge.

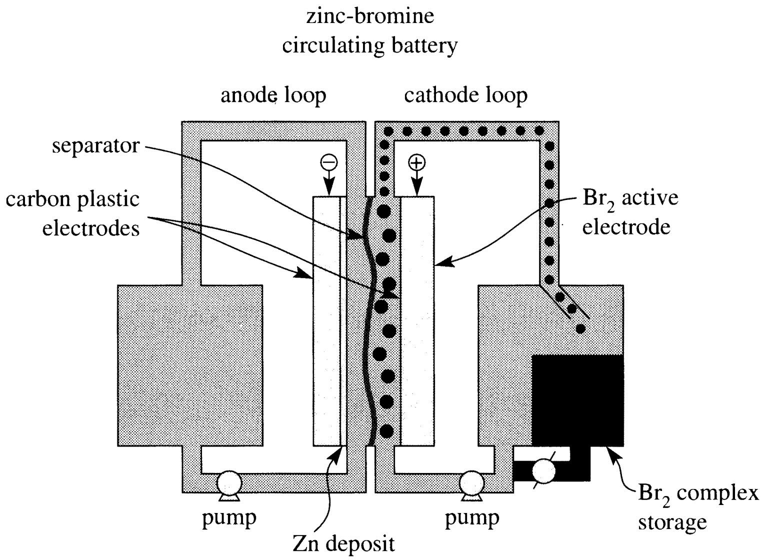
Nickel–hydrogen aerospace cells, while expensive, are highly reliable and capable of exceptionally long cycle lives. For telecommunications applications (geosynchronous orbit) the battery is used mostly in periods of eclipse and a life of 1000 cycles is adequate. However, for meteorology and other Earth observation uses (low Earth orbit), where the battery is discharged and charged during each orbit, a life of over 20 000 deep discharge cycles is sought. At present only the Ni–H_2 battery has the potential to approach such a formidable target.

A later variant of the nickel–hydrogen battery stores the hydrogen as a metal hydride which decomposes and reforms reversibly during discharge and charge. For the battery to operate effectively at ambient temperature it is necessary to select a metal hydride with a suitably high dissociation pressure (say, 0.2–2 bar) over the temperature range 0–30 °C. Of the simple metal hydrides the most suitable is $LaNi_5H_{6.5}$ which has a dissociation pressure of 1 bar at 15 °C and is made simply by hydriding the alloy $LaNi_5$. Several hydride–dehydride cycles are needed to break up and activate the alloy. Pure lanthanum is too expensive for commercial use and so Ni–MH_x batteries generally employ a 'mischmetall' alloy, prepared from unseparated rare earth oxides with other additives to adjust the dissociation pressure to the desired value. Nickel–metal hydride cells are now coming into commercial use and replace Ni–Cd in certain applications. However, their life is limited by the slow irreversible oxidation of the rare earth metals.

5. Zinc–halogen batteries

Several serious attempts were made during the 1970s to develop a rechargeable *zinc–chlorine battery* in which the chlorine was stored as the solid hydrate $Cl_2 \cdot 6H_2O$ which is stable below 9.6 °C and crystallizes out on charging. Because of the complex chemical engineering involved these batteries could only be contemplated as large units, such as required for load levelling or vehicle traction. These projects appear now to have been abandoned as too difficult, coupled with concerns over the environmental effects of the accidental release of chlorine gas.

Attempts to develop a large *zinc–bromine battery* have been more successful. Several industrial groups in USA, Austria and Australia are working on this battery. The basic concept (figure 1) is that of pumped circulating systems for both the anolyte and catholyte, which are separated by a microporous membrane permeable to Zn^{2+} ions. The electrodes are of vitreous carbon, bonded by plastic into flexible



electrochemical reactions: $Zn^0 \rightleftharpoons Zn^{++} + 2e^-$

$Br_2 + 2e^- \rightleftharpoons 2Br^-$

self-discharge: $Zn^0 + Br_2 \longrightarrow ZnBr_2$

Figure 1. Zn–Br_2 battery concept.

sheets, and the electrolyte is a concentrated solution of zinc bromide. A quaternary ammonium salt is added to the catholyte and this forms a polybromo-complex with free bromine; this is a dense oily liquid, insoluble in the aqueous $ZnBr_2$ solution, which may be separated into a storage compartment outside of the battery stack. On charging the battery, Zn^{2+} ions diffuse through the separator and are electroplated on to the carbon anode, while the free bromine liberated at the cathode forms the polybromo complex. The reverse occurs on discharge.

The battery is constructed of lightweight plastic components as regards the storage tanks, plumbing and the battery stack itself, which is of the 'plate and frame' type used in fuel cells. Either monopolar or bipolar designs are possible. Preferred materials of construction are polyvinylidene difluoride (PVDF) or polytetrafluorethylene (PTFE), which are resistant to attack by bromine, but expensive. Cheaper plastics are less resistant and tend to swell. Also the inorganic 'fillers' used in plastics can cause problems. For the gaskets which seal the plates it is necessary to find a stable elastomer which does not deform or crack in the bromine environment.

The Zn–Br_2 battery has an open circuit voltage of 1.83 V at 25 °C, typically falling to 1.3 V at an operating current density of 100 mA cm^{-2}. The specific energy attainable is 65–70 W h kg^{-1} in battery modules of 20 kW h size. The volumetric energy density is only moderate (80–85 W h l^{-1}), as is also the overall electrical energy efficiency (65–70%) Unlike most batteries, regular deep discharge is positively beneficial to cycle life as it prevents the build-up of zinc dendrites on the anode which would cause internal short circuits. 1000-cycle operation of this battery has been achieved and it is now being developed for both electric vehicle traction and load-levelling applications. A 100 kW h load-levelling battery is under construction in California and a 400 kW h unit planned in Australia.

6. Redox batteries

Redox batteries operate on the principle of the oxidation and reduction of metal cations in solution. They differ from conventional batteries in that no solid phases are involved in the electrode reactions, an enormous simplification. Precisely for this reason, however, the thermodynamic energy changes involved are modest and the gravimetric and volumetric energy densities correspondingly low. Redox batteries therefore have no future for portable or traction applications, but are of interest for stationary applications (stand-by, load levelling, etc.).

Common metal ions which show variable valency in solution are the 3d elements Ti, V, Cr, Mn and Fe. One redox battery which has been investigated is the iron–chromium battery:

$$\text{negative} \quad \mathrm{Cr^{2+} \rightleftharpoons Cr^{3+} + e^-},$$

$$\text{positive} \quad \mathrm{Fe^{3+} + e^- \rightleftharpoons Fe^{2+}},$$

$$\text{overall} \quad \mathrm{CrCl_2 + FeCl_3 \rightleftharpoons CrCl_3 + FeCl_2},$$

$$1.2\ \mathrm{V} \underset{\text{declining}}{\longrightarrow} 0.95.$$

One of the problems with the redox battery is the need to employ an expensive anion exchange membrane as the separator to avoid the diffusion of cations from one electrode compartment to the other. This problem is less serious in the *vanadium redox battery* which depends on the fact that vanadium has three soluble valence states and may be used in both electrode compartments, namely

$$\text{negative} \quad \mathrm{V^{3+} \rightleftharpoons V^{4+} + e^-},$$

$$\text{positive} \quad \underset{\text{charged}}{\mathrm{V^{5+}}} + \mathrm{e^-} \rightleftharpoons \underset{\text{discharged}}{\mathrm{V^{4+}}},$$

Redox batteries are pumped systems in which there are four storage tanks external to the battery, two for the reactants in the charged state and two in the discharged state. In this respect they are more akin to a fuel cell than a battery, in that the capacity is limited only by the size of the storage tanks.

The vanadium redox battery is being actively developed at the University of New South Wales (Australia) for the storage of solar generated electricity. A demonstration solar house has been built incorporating a 12 kW h vanadium redox battery.

7. Super- and ultra-capacitors

Super-capacitors have come to prominence during the past decade. They differ from conventional electrolytic capacitors in that the electrical charge is stored by ions adsorbed on high surface area electrodes, generally carbon, rather than by electrons on metallic electrodes. As ions move more slowly than electrons, the time constants for charge and discharge are correspondingly longer. In a super-capacitor no Faradaic reactions take place, but the extended surface area permits the build-up of a far greater charge than for an electronic capacitor, albeit at a much lower voltage. In this respect the super-capacitor begins to take on the character of a battery. The electrolyte employed with carbon electrodes is generally sulphuric acid.

The ultra-capacitor, of even more recent origin, stores energy by virtue of both the ionic double-layer capacitance effect and surface redox processes. The redox process is a Faradaic reaction, thereby enhancing the amount of stored energy, but because

Table 2.

characteristic	battery	electrolytic capacitor	super-capacitor	ultra-capacitor
stored energy ($\mathrm{W\,h\,l^{-1}}$)	50–250	0.05	0.1–5	1–10
peak power ($\mathrm{W\,l^{-1}}$)	150	$> 10^8$	$> 10^5$	$> 10^5$
discharge time	hours	< 1 s	s	< 1 min
cycle life	10–1000	$> 10^6$	$> 10^5$	$> 10^5$

it is a surface reaction it is fully reversible and the long cycle life associated with capacitors is maintained.

The characteristics of the different energy storage devices are summarized in table 2.

It will be seen that electrolytic capacitors contrast with batteries in that they store very little energy, but can produce high power output for very short periods. They have long cycle lives. The contrast is so great that the applications for batteries and electrolytic capacitors are entirely different. Super-capacitors, and especially ultra-capacitors, lie between batteries and conventional capacitors in their properties. It is this that makes them of such technological interest. For many applications, such as electric vehicle traction, batteries may lack the peak power output required; a battery–ultra-capacitor hybrid system, capable of boosting peak power for short periods, may provide the answer. The same may be true in providing ‘spinning reserve’ in the electricity supply system to meet sudden peak power demands for short periods. The investigation of super- and ultra-capacitors is still in its infancy and further advances may be expected.

References

Vincent, C. A. 1984 *Modern batteries.* London: Edward Arnold.