

# BATTERY STORAGE

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**ABSTRACT:** This paper focuses on four generic types of secondary battery – Alkaline batteries, Flow batteries, Sodium batteries, and Lithium batteries – that hold most promise for the storage of energy.

**Keywords:** Batteries of nickel-cadmium, Nickel-metal hydride, Nickel-zinc, Zinc-air, Zinc-bromine, Redox, Sodium-sulphur, Sodium-nickel chloride, Lithium-ion, and Lithium-polymer.

**RESUMO:** As baterias alcalinas, as de matérias activas exteriores, as de sódio e as de lítio constituem uma forma excelente para o armazenamento de energia química e podemos encará-las como muito promissoras para aplicações de armazenamento de energia em larga escala. Este artigo inclui alguns comentários pertinentes sobre estes sistemas recarregáveis, na sua actual fase de investigação e desenvolvimento.

**Palavras chave:** Baterias de níquel-cádmio, Níquel-hidreto metálico, Níquel-zinco, Zinco-ar, Zinco-bromo, Redox, Sódio-enxofre, Sódio-cloreto de níquel, Ião-lítio e Polímero-lítio.

## 1. INTRODUCTION

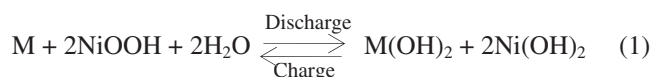
In a previous paper [1], pertinent comments on lead-acid batteries were discussed. Particularly, in its first section on general remarks, we discussed their manufacture, size types, consumer and industrial applications, required cycle-life and other criteria, degradation processes and other limitations, etc. [2-10].

Apart from the most common type of storage battery that is the ubiquitous lead-acid battery, there are more four generic types of secondary batteries that deserve some comments. These are the alkaline batteries, the flow batteries, the sodium batteries, and the lithium batteries. The general remarks made for the lead-acid batteries in our previous paper [1] also apply for the batteries to be discussed here.

## 2. ALKALINE BATTERIES

Alkaline batteries are based on an electrolyte of concentrated (~ 30 wt.%) potassium hydroxide (KOH) solution. The positive electrode is normally nickel hydroxide (Ni(OH)<sub>2</sub>), which is capable of being oxidised electrochemically to Ni<sup>3+</sup> (“nickel oxide”) during charge and reduced back to Ni<sup>2+</sup> during discharge. Occasionally, for specialised applications, this is replaced by silver oxide (AgO), although this is an expensive option. The negative electrode may be one of three metals – cadmium, iron, zinc – or a complex metal hydride.

By far the best-known rechargeable alkaline battery is cadmium-nickel-oxide, commonly termed “nickel-cadmium” or “NiCad”. The Swedish scientist Waldemar Jungner invented this battery at the end of the 19<sup>th</sup> century. At about the same time, working in the USA, Thomas Edison invented the iron-nickel-oxide (or “nickel-iron”) battery, which has very similar chemistry. The overall reaction is:



where M = Cd or Fe. The standard cell voltage is 1.30 and 1.37 V for nickel-cadmium and nickel-iron, respectively, i.e. considerably below that of lead-acid (2.048 V) [1].

Over the course of the past century, the nickel-cadmium cell proved to be more commercially successful than the nickel-iron cell and the latter is now rarely used. The principal reasons for this are that the iron electrode: (i) gases excessively on charge, which results in low electrical efficiency and higher water maintenance; (ii) suffers from a high rate of self-discharge on standing, which is caused by corrosion of the negative plate. On the other hand, the nickel-iron cell is highly robust and is capable of 2000 charge-discharge cycles at 80% DoD. Given this attribute, it was formerly used as a traction battery for industrial trucks and some railway applications where electrical efficiency was not an over-riding consideration [2].

## 2.1 Nickel-Cadmium Batteries

The practical cell voltage of traditional nickel-cadmium batteries is 1.2 V and their specific energy is 30-40 Wh kg<sup>-1</sup> (rather similar to that of lead-acid batteries), although 60 Wh kg<sup>-1</sup> has been achieved in some recent designs. Nickel-cadmium batteries often come as packs of five inter-connected cells that are series-connected to give a 6-V battery. The high-rate and low-temperature performances of nickel-cadmium are both better than those of lead-acid, and other beneficial features are: a flat discharge voltage, long life, continuous overcharge capability, and good reliability. Cells and batteries are available in many different sizes and with pocket-plate, plastic-bonded or sintered electrodes. Sealed consumer cells range in size from 10 mAh up to 15 Ah, while vented cells used as standby power units have capacities up to 1000 Ah. High-power cells, capable of delivering up to 8000 Ah are available for engine starting and are used in aircraft and some heavy vehicles. The principal disadvantages of the nickel-cadmium systems are its high cost and environmental concerns associated with the disposal of batteries that contain toxic cadmium. Nickel-cadmium batteries are gradually being replaced by nickel-metal-hydride alternatives, especially in the smaller sizes, but are holding their own for industrial applications. Particular applications include aircraft batteries, vehicle traction, and standby power. A very large nickel-cadmium system is being installed at Fairbanks, Alaska to sustain the power supply from the local utility [3].

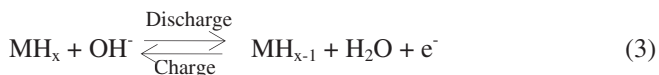
## 2.2 Nickel-Metal-Hydride Batteries

The nickel-metal-hydride battery also uses a nickel oxide positive electrode, but the negative active material is essentially hydrogen that is stored as a metal hydride. One of the popular metal hydrides is based upon a complex alloy of rare earth metals, nickel, aluminium, and other additives. An alternative alloy is based on titanium and zirconium. The electrode reactions are as follows.

At the positive electrode:



At the negative electrode:



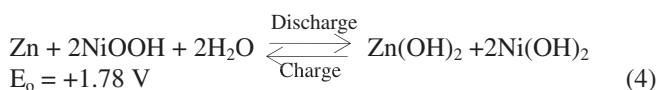
The operating voltage of a nickel-metal-hydride cell (1.2-1.3 V) is almost the same as that of nickel-cadmium, which allows ready interchangeability, and the discharge curve is quite flat. By contrast, the capacity of a nickel-metal-hydride cell is significantly greater than that of a nickel-cadmium cell of the same mass, with the result that the specific energy (60-80 Wh kg<sup>-1</sup>) is higher. Moreover, nickel-metal-hydride batteries are capable of producing pulses of very high power. The batteries are resilient to both overcharge and overdischarge, and may be operated from -30 to +45 °C. Another advantage is that there are no toxicity problems with recycling. Disadvantages associated with nickel-metal-hydride are a comparatively high cost, a higher

self-discharge rate than nickel-cadmium, and a poor charge-acceptance at elevated temperatures [4,5].

In recent years, since their development in the late 1980s, small nickel-metal-hydride cells have become extremely popular for use in portable electronic devices (e.g. mobile phones, laptop computers, cassette players, etc.), as well as in toys and workshop tools. Coin cells are manufactured for use in calculators. To a significant degree, lithium batteries are now replacing them, but the market is still vast. Large (100 Ah) prismatic cells are made for assembly into 12- and 24-V modules and these have been employed as traction batteries in a number of demonstration electric vehicles. By virtue of their high power, nickel-metal-hydride has been the battery of choice for the new generation of hybrid electric vehicles that are under development in Japan.

## 2.3 Nickel-Zinc Batteries

Zinc is the ideal material for negative electrodes in alkaline electrolyte batteries on account of its high electrode potential. It is the most electropositive of the common metals that can be plated from aqueous solution. The nickel-zinc cell has, therefore, a comparatively high standard voltage, i.e.



and a correspondingly high specific energy. A practical nickel-zinc cell discharges at ~1.6 V and can attain 90-100 Wh kg<sup>-1</sup>, while an industrial battery pack would be expected to yield 70 Wh kg<sup>-1</sup>. This performance is substantially higher than that of lead-acid, nickel-iron or nickel-cadmium, and is attractive for motive-power applications because it virtually doubles the daily range provided by lead-acid batteries.

The nickel-zinc battery has been extensively studied in recent years as a candidate traction battery for electric vehicles. Unfortunately, however, the system suffers from one serious drawback, namely the greater solubility of zinc in potassium hydroxide, compared with cadmium or iron, leads to a much reduced cycle-life. During charge-discharge cycling, the solubility causes the zinc to migrate and accumulate towards the centre of the negative plate such that the plate densifies, changes shape, and loses capacity. Also, there is a marked tendency for zinc dendrites (needles) to grow from the negative during recharging and these can penetrate the separator and cause internal short-circuits. Much research has been directed towards elucidating and overcoming these two limitations, and some success has been reported. Prototype batteries with stabilised zinc electrodes have sustained up to 500 cycles, but this is still too low for the battery to achieve commercial success as a power source for electric vehicles. If the problem of short life can be resolved, then it would appear that the nickel-zinc battery could find use in many different applications. This is one of the remaining major challenges in the field of alkaline batteries [6,7].

## 2.4 Zinc-Air Batteries

The zinc-air battery is novel in two respects: (i) it has a gaseous positive active material, viz. oxygen; (ii) although

not electrically rechargeable, it may be recharged “mechanically” by replacing the discharged product, zinc hydroxide, with fresh zinc electrodes. With these features, the battery is akin to a fuel cell, with the “fuel” being a slurry of finely divided zinc powder suspended in potassium hydroxide solution. During discharge, the zinc is converted to zincate ( $\text{Zn}(\text{OH})_4^{2-}$ ) and zinc hydroxide ( $\text{Zn}(\text{OH})_2$ ) at the negative electrode. The battery is recharged by removing the spent slurry from the cell and replacing it with fresh electrolyte and zinc powder. The spent slurry is then regenerated in a separate electrolysis unit. An alternative arrangement, for use in electric vehicles, has the zinc powder compacted onto a current-collector frame, which is inserted in a separator envelope that is flanked on both sides by air electrodes (Figure 1). The electrode assembly is in the form of a cassette that may be removed from the cell stack and conveyed to a central facility for electrochemical regeneration of particulate zinc. The overall system is composed of three units: a cell stack, a stack dismantling and refuelling machine, and a factory-based plant for fuel regeneration. A traction battery of eight modules (150 kWh) was built and tested successfully in Germany in a Mercedes Benz 410 postal van. The battery had high specific energy ( $200 \text{ Wh kg}^{-1}$ ), but only modest specific power ( $100 \text{ W kg}^{-1}$  at 80% DoD). The range of the vehicle was 300 km between recharges [8].

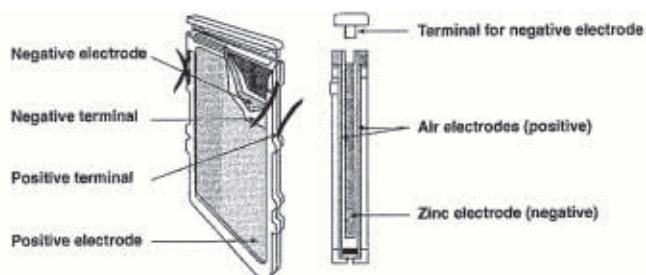


Fig. 1. Zinc-air cell and cassette system.

### 3. FLOW BATTERIES

Flow batteries possess certain characteristics that are typical of rechargeable batteries, but in other respects resemble fuel cells. They may be seen as a hybrid of the two. Like traditional secondary batteries, they are rechargeable and charge-discharge cycling involves the oxidation and reduction of a metal cation (or of an anion). Nevertheless, they are comparable with fuel cells in that the reagents are stored outside of the battery itself, in external reservoirs, and the capacity of the battery is determined only by the size of these reservoirs. Thus, as with a fuel cell, the energy content and the power of the battery are divorced; the latter is determined by the design and size of the cell stack. Moreover, in many designs of flow battery the cell stack is built on the “plate-and-frame” principle, as shown in Figure 2 for a bipolar fuel cell. The separator is either a microporous plastic membrane or an ion-selective polymer membrane of high ionic conductivity; the latter is similar to that used in a proton-exchange membrane fuel cell. The positive and negative electrode systems each have an electrolyte loop for the supply of reagents from the respective external reservoirs.

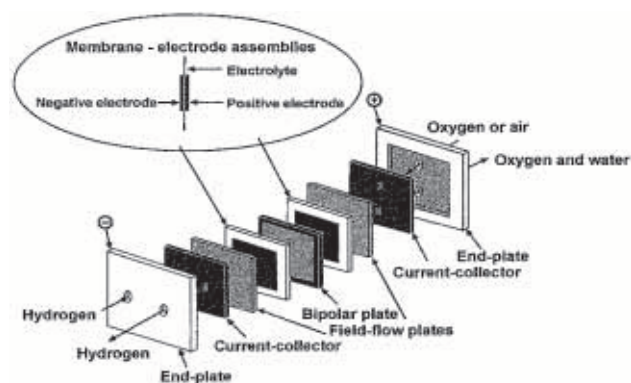
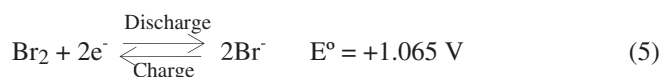


Fig. 2. Structure of a two-cell PEMFC module.

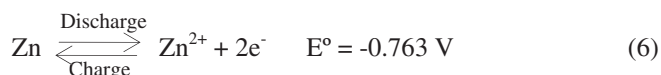
#### 3.1 Zinc-Bromine Batteries

One of the best known of these flow batteries is the zinc-bromine battery (Figure 3). In the discharged state, the electrolyte in both loops is a concentrated solution of zinc bromide ( $\text{ZnBr}_2$ ). The electrode reactions are as follows.

At the positive electrode:



At the negative electrode:



On charging,  $\text{Zn}^{2+}$  ions are reduced to zinc metal, which is deposited on the negative electrode, while  $\text{Br}^-$  ions are oxidised to bromine in the positive electrode. Because bromine is a highly volatile and reactive liquid, it is complexed with an organic reagent to form a poly-bromo compound, which is an oil and is immiscible with the aqueous electrolyte solution. The oil is separated and stored in a special storage compartment in the external reservoir of the positive electrode until needed again for discharge.

The standard cell voltage is 1.83 V, but typically falls to 1.3 V at an operating current density of  $100 \text{ mA cm}^{-2}$ . An attractive feature of this battery is that it is constructed mostly of lightweight plastic components (frames, tanks, plumbing, etc.) and is easily assembled. Research and development has been on-going in several countries for a number of years. Traction batteries have been built and tested in electric vehicles, and larger systems have been demonstrated as energy-storage facilities for electric-utility applications. The zinc-bromine battery has, however, yet to prove a commercial success. A major technical problem is the chemical reactivity of bromine towards most plastic components, while there is also concern over safety in the event of leakage of bromine vapour [9].

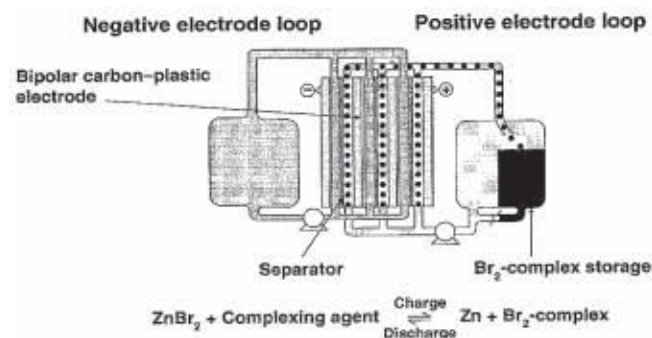
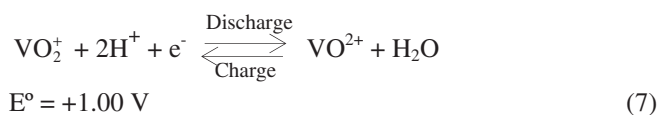


Fig. 3. Schematic of a zinc-bromine flow battery.

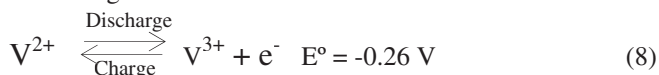
### 3.2 Redox Batteries

Other flow batteries are of the redox type in which ions are oxidised and reduced but remain in solution, with no solids, gases or immiscible liquids being formed. One such battery – the vanadium redox system – is being investigated in Australia. This depends for its operation on the fact that vanadium exists in several different valence states. In the charged state, the positive-electrolyte loop contains a solution of  $V^{3+}$  and the negative loop contains a solution of  $V^{2+}$ . On discharging, the former solution is reduced to  $V^{4+}$  and the latter is oxidised to  $V^{3+}$ , as follows.

At the positive electrode:



At the negative electrode:

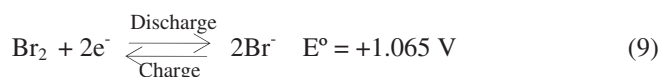


The standard cell voltage is 1.26 V. Under actual operating conditions, however, a concentrated electrolyte is used (2M vanadium sulphate in 2.5M sulphuric acid) and the open-circuit cell voltage is 1.6 and 1.4 V at 100 and 50% SoC, respectively. Since both electrolyte loops contain vanadium, any leakage across the ionically conducting membrane separator will not cause a significant loss in cell performance. There are four storage tanks external to the battery: two for the reagents in the charged state and two for the discharged state. A 12-kWh vanadium redox battery was constructed in 1994 for use in the storage of solar energy. More recently, a 450-kW, 1-MWh facility has been built as a demonstration system for load-levelling service at the Kansai Electric Power Plant in Japan, as well as several other 25-kW units for wind energy storage and other stationary services. The latter units have reported a life of more than 16 000 cycles. The advantage seen for this technology over lead-acid lies in its indefinite cycle-life, which is limited only by the materials of construction and not by the reactants in solution. It should be noted, however, that the vanadium redox battery has a low specific energy (typically, 25 Wh  $kg^{-1}$ ), and is therefore unlikely to find application in electric road vehicles.

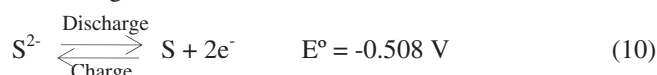
The latest flow battery that has been under intensive development is known as the Regenesys® system. This differs from other flow batteries in that no metal cations are

involved in its electrode reactions. Rather, anions are oxidised and reduced at both electrodes. The cell, which is again built on bipolar plate-and-frame principle, uses a membrane separator that is permeable to sodium ions but not to sulphide anions. During discharge, the reaction at the positive electrode is the reduction of bromine dissolved in sodium bromide (NaBr) solution to bromide ions, while the reaction at the negative electrode involves the oxidation of sulphide ions to sulphur, which is contained in sodium polysulphide solution. The electrode reactions are as follows.

At the positive electrode:



At the negative electrode:



Thus, the standard cell voltage is 1.57 V.

A schematic of this battery, which is also considered to be a type of “regenerative fuel cell” [10], is shown in Figure 4(a). The system has been developed by RWE nPower, a UK utility company for large-scale energy storage at power stations and within the electricity-supply network itself. The plant is constructed on a modular basis; the individual modules have an output power of 100 kW (Figure 4(b)). A 10-MW plant would use 100 of these modules joined together electrically, and have reservoirs to give a stored energy capacity of 100 MWh. Until recently, two prototype plants were under construction – one at a power station in the UK and the other in the USA. These would have been among the largest batteries ever to be constructed but, in early 2004, both projects were postponed for commercial reasons [9-11].

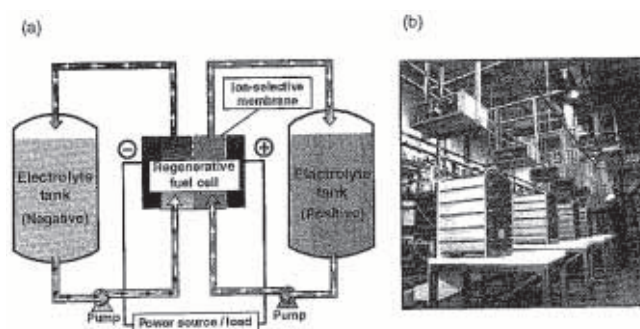


Fig. 4. Regenesys® flow battery: (a) schematic of operating principle; (b) 100-kW modules.

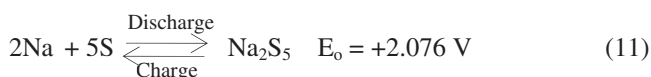
## 4. SODIUM BATTERIES

### 4.1 Sodium-Sulphur Batteries

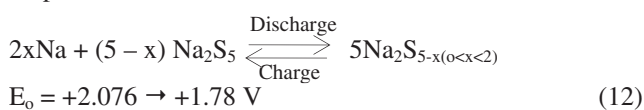
Sodium is a highly reactive metal that can ignite or explode when treated with water; it is therefore not an obvious candidate as an electrode in a battery. On the other hand, it has some attractive features, namely, it: (i) has a high electrochemical reduction potential (-2.71 V, compared with -0.76 V for zinc); (ii) is abundant and low cost; (iii) is non-toxic.

The possible use of sodium in a battery became a practical proposition in 1967 when scientists working at the Ford Motor Company in the USA discovered that a solid ceramic material, sodium  $\beta$ -alumina, is an exceptionally good conductor for sodium ions at temperatures above about 300 °C. This opened up the possibility of a high-temperature battery based on liquid sodium as the negative active material. The same group of scientists also devised the idea of using liquid sulphur as the positive active material – and so was born the sodium-sulphur battery. This battery operates at 300-400 °C and is contained in a heated, insulated enclosure. The cell discharges in two steps as  $\text{Na}^+$  ions pass from the sodium negative electrode through the  $\beta$ -alumina electrolyte, to the sulphur positive electrode, i.e.

Step 1:



Step 2:



Thus, the standard cell voltage is constant at 2.076 V for the first part of the discharge, i.e. as far as the production of  $\text{Na}_2\text{S}_5$ , after which it declines linearly to 1.78 V. The electrolyte is in the form of a ceramic tube that holds the liquid sodium, while the liquid sulphur is contained within an outer annulus between the electrolyte tube and the cell housing. Since liquid sulphur is a non-conductor, it is held in the interstices of graphite felt that is packed around the outside of the tube. The felt, therefore, provides electrical contact between the electrolyte tube and the outer cell casing. The cell is sealed hermetically so as to insulate the electrodes from each other and to exclude the atmosphere.

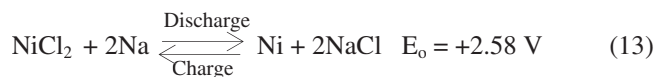
While this concept sounds simple enough, in practice it proved to be incredibly complex. Teams of battery researchers in Germany, Japan, the UK and the USA worked on the developing the sodium-sulphur battery as an electric-vehicle battery for over 20 years. Finally, in the late 1980s, most of these teams were disbanded as the technical and safety problems were deemed to be intractable. This was despite the fact that the first electric vehicle to be equipped with a sodium-sulphur battery (a 50-kWh unit) was driven in England as early as 1973. The Japanese, however, continued their programme of research and development, but with the emphasis on load-levelling duty. Prototypes of rather large utility batteries have been constructed and tested in Japan by the Tokyo Electric Power Company. It is not clear how the Japanese workers may have overcome the technical problems of durability, reliability and safety that others have found to be insurmountable for electric-vehicle applications [11,12].

#### 4.2 Sodium-Nickel-Chloride Batteries

Drawing upon the research conducted on sodium-sulphur batteries, a new sodium-based battery was invented by workers in South Africa and the UK in the late 1970s. They recognised that many of the technical problems of the sodium-sulphur battery arose from the sulphur electrode and

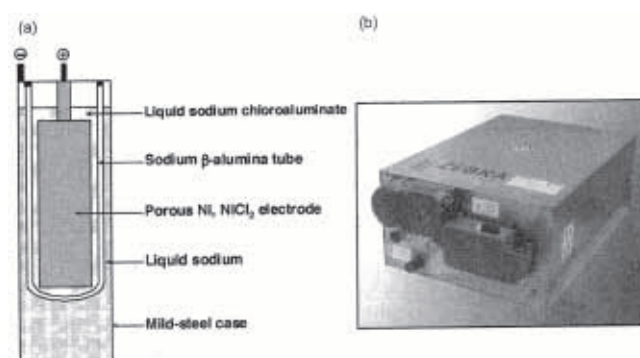
that if any alternative could be found, a high-temperature sodium battery was still a possibility. After some exploratory work, the researchers eventually settled on nickel chloride as the positive active material to give the sodium-nickel-chloride battery, popularly known as the ZEBRA battery in acknowledgement of its South African origins [9,11,13].

The reaction is very simple:



The cell retains the  $\beta$ -alumina electrolyte tube and liquid sodium as the negative electrode but, in this case, the sodium surrounds the outside of the electrolyte tube and the nickel chloride is on the inside (see schematic in Figure 5(a)). Further work showed that this cell only works satisfactorily when assembled in the discharged state. There is then no need to purify and handle sodium metal; rather, it is formed in situ during charging as sodium ions pass through the electrolyte from the positive to the negative electrode. The battery operates over a wide temperature range from 175 to 400 °C. Because the starting materials of the positive electrode (nickel, sodium chloride) are both solid, it is necessary to add a liquid in the positive compartment to make electrical contact with the ceramic electrolyte. The liquid used is molten sodium chloroaluminate ( $\text{NaAlCl}_4$ ). A traction battery consists of many such cells, wired in series and contained within a double-walled, thermally insulated, battery box.

A 17.8-kWh sodium-nickel-chloride battery that operates at either 278 or 557 V, depending upon the internal wiring configuration, is shown in Figure 5(b). Over the past 25 years, many of these batteries have been built in the UK and Germany and used in electric vehicles, which include buses and popular cars (Renault “Twingo” and “Clio”; Opel “Astra”; Mercedes-Benz “190” and “A” class; BMW “3 Series”). These trials have proved highly successful and have demonstrated that ZEBRA batteries are robust, reliable, and safe in operation. Also, they require no maintenance. The vehicles have good ranges of at least 160 km between charges and the driving characteristics are almost indistinguishable from these of the internal-combustion engine versions. Given the encouraging performance obtained from these batteries, a factory has been built in Switzerland for their manufacture.



**Fig. 5.** (a) Schematic diagram of a sodium-nickel-chloride cell;. (b) ZEBRA electric-vehicle battery (278 V, 17.8 kWh).

A limitation to the possible applications for ZEBRA batteries lies in the requirement to keep them hot [13]. The batteries can be cooled and re-heated, but this requires care and would not be a regular practice. They are best suited to vehicles that are used daily on a regular schedule, such as buses and delivery trucks. When not in use for more than a few hours, the pack would normally be plugged into the mains for recharging and for maintaining the temperature by means of heaters incorporated in the battery box. The heat loss is small and the battery may be left unattended and disconnected for at least 48 hours. A major advantage of high-temperature batteries is that their performance is independent of the ambient temperature and, therefore, they can withstand variations in the latter that conventional batteries would find intolerable.

ZEBRA batteries should also be satisfactory for standby duties, for instance in a telephone exchange or mainframe computer installation. The battery would be floated at 2.58 V per cell until called upon for service. A small input of mains electricity to the built-in heaters would serve to keep the battery at operating temperature. Taken all round, the ZEBRA battery remains a strong candidate for electric vehicles and also for other applications where a medium-to-large battery is required.

## 5. LITHIUM BATTERIES

Lithium is the lightest of all metals. This fact, together with its high electrochemical reduction potential (-3.05 V), makes it particularly attractive as an active material for negative electrodes. The stored energy, expressed as Wh kg<sup>-1</sup>, is higher than for any other metal. Lithium, like sodium, is chemically reactive and cannot be used in conjunction with an aqueous electrolyte. Possible non-aqueous electrolytes are fused salts, organic liquids, polymers, and ceramics. Unfortunately, the lithium analogue of sodium  $\beta$ -alumina is not a satisfactory ion conductor and no lithium-sulphur or lithium-nickel-chloride battery based on a ceramic electrolyte has been demonstrated. Considerable research has been in fact carried out on lithium fused-salt electrolytes, but progress to date has been limited. Attention has therefore focused on the use of organic liquid and polymer electrolytes.

Small, primary lithium batteries based on organic liquid electrolytes have been manufactured for several decades for use in pocket calculators, and as memory back-up displays for computers, televisions, video cassette recorders, and cameras. These are normally in the form of 3-V coin cells. The negative electrode is lithium metal foil, there are various possible positive electrodes (MnO<sub>2</sub>, CF<sub>x</sub>, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, etc.) and the electrolyte is a solution of a salt in an organic solvent. These primary cells are in widespread use on account of their attractive features, which include high voltage, high specific energy, low self-discharge rate, and a wide temperature range of operation [14-17].

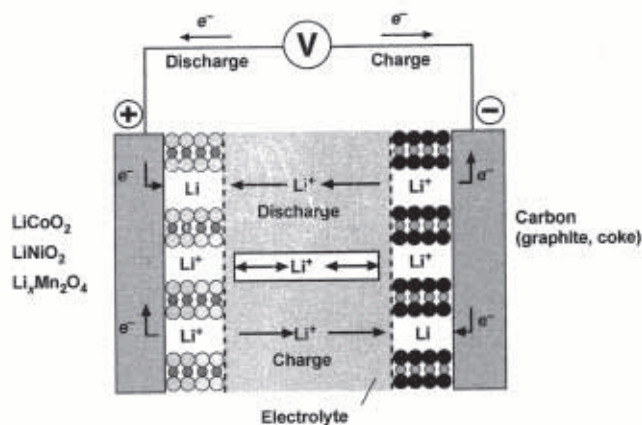
Initially attempts to develop rechargeable cells did not meet with much success. The problems were found to lie in the re-plating of lithium metal from organic solution during recharging. Generally the lithium was laid down as a mossy deposit, which after a few cycles often led to an internal

short-circuit or even a fire. Furthermore, the freshly plated lithium was not chemically stable with respect to the electrolyte. Lithium is only stable in a primary cell containing an organic electrolyte by virtue of the formation of a thin film of corrosion product on its surface, which acts as a solid electrolyte and offers protection from further reaction with the organic solvent. Various attempts were made in the 1980s, both in the USA and Japan, to manufacture and market secondary lithium cells that used negative electrodes of lithium metal, but eventually these cells were withdrawn as a result of safety-related concerns [18-20].

### 5.1 Lithium-Ion Batteries

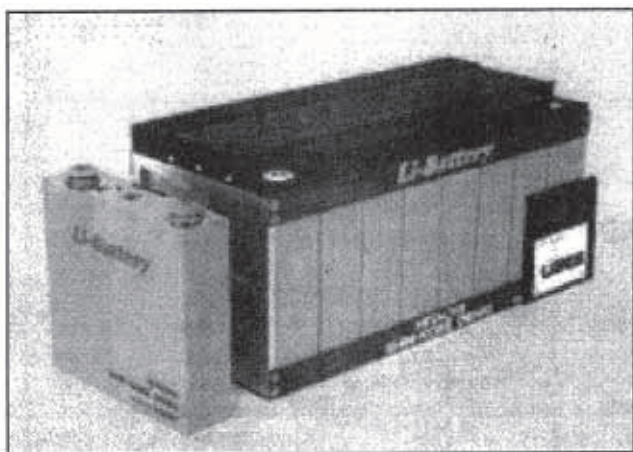
A significant advance was made in 1979 with the discovery at the Oxford University, UK, that the compounds LiCoO<sub>2</sub> and LiNiO<sub>2</sub> possess a layer structure and that Li<sup>+</sup> ions may be electrochemically withdrawn from the structure and replaced reversibly. This discovery opened up the possibility of using either of the compounds as the active material for a positive electrode in a rechargeable cell. Because these are 4-V electrodes with respect to lithium metal, it is possible to intercalate the Li<sup>+</sup> ions into a suitable negative active material, such as graphite, and still have a 3.5 to 4-V cell. In 1990, the Sony Corporation in Japan announced the "lithium-ion battery" that was based on this concept. This was the first rechargeable lithium battery to contain no lithium metal, but to depend entirely on the difference in electrochemical potential of lithium-ions intercalated in LiCoO<sub>2</sub> and in graphite.

The mode of operation of the lithium-ion cell is shown schematically in Figure 6. The cell is assembled in the discharged state. During charge, Li<sup>+</sup> ions are withdrawn ("de-intercalated") from the structure of LiCoO<sub>2</sub>, transported across the electrolyte, and then "intercalated" into the structure of the carbon. This process is reversed on discharge. In effect, the lithium ions "rock" back and forth between the electrodes and hence the technology is sometimes referred to as a "rocking-chair" cell. This 3.8 V cell soon went into mass production in Japan, mostly in small sizes, and is now widely employed in camcorders, laptop computers, and mobile phones. Because of their much higher voltage than nickel-metal-hydride cells (1.2 V), lithium-ion cells store more energy and so provide longer run-times between charges. For this reason, they have usurped some of the markets for nickel-metal-hydride despite being more expensive. Many companies are manufacturing lithium-ion cells with either LiCoO<sub>2</sub> or LiNiO<sub>2</sub> positive electrodes and the growth in sales, starting in 1991, has been phenomenal. It is estimated that well in excess of 500 million cells are now produced per year worldwide. Ideally, manufacturers would like to replace cobalt (expensive) and nickel (moderately priced) by manganese (cheap and less toxic). Unfortunately, lithium manganese oxide (LiMnO<sub>2</sub>) is a complex entity that is more difficult to prepare and less stable structurally. Considerable research is presently being devoted to developing a satisfactory intercalation electrode based on manganese and the compound LiMn<sub>2</sub>O<sub>4</sub> has been employed commercially.



**Fig. 6.** Schematic of mode of operation of a lithium-ion battery.

Lithium-ion cells are not, however, without their problems. Aside from relatively high cost, considerable care has to be exercised in controlling the voltage during charge. Overcharging or heating above about 100 °C leads to decomposition of the positive electrode. When cells are coupled in series, or a series-parallel array to form a battery-pack, it is necessary to incorporate battery-protection circuits to avoid overcharge and the possibility of fires resulting from the presence of lithium metal. Much larger cells have been constructed, including experimental batteries for electric vehicles and stationary energy storage, but these are not yet commercially available. A 2-kWh battery module produced in Japan and made up of eight 250-Wh cells based on Li-rich  $\text{LiMn}_2\text{O}_4$  positive electrodes is shown in Figure 7. For these larger batteries to become feasible for motive-power or standby duties, their cost will have to be substantially reduced and they will have to be safe under all conditions of operation [21-23].



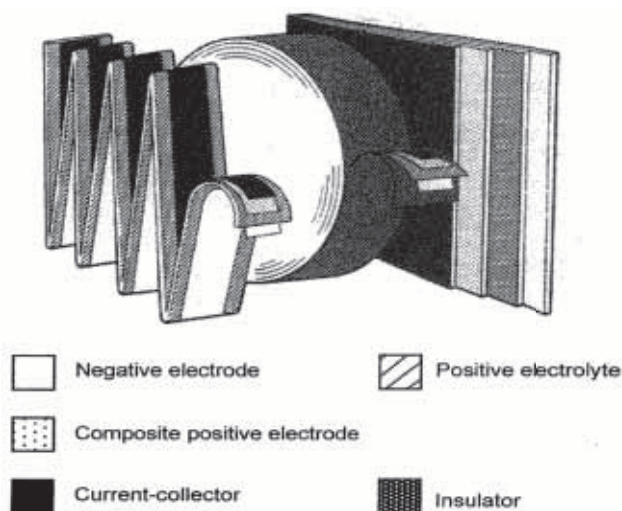
**Fig. 7.** Lithium-ion battery module (8 cells, 2 kWh).

**5.2 Lithium-Polymer Batteries**

Research on ionic conduction in polymers was undertaken at the University of Grenoble (France) in the 1970s. It was found that polymers with a relatively high dielectric constant, such as polyethylene oxide, could dissolve lithium salts. At ambient temperature, the resulting conductivity was too low for this material to be considered as a possible solid electrolyte, but at about 60 °C there was a transition

from a partially crystalline state to a fully amorphous state with an increase of several orders of magnitude in the conductivity. At 80-100 °C, the ionic conductivity was still low compared with conventional battery electrolytes, but this could be compensated if the electrolyte was in the form of a sufficiently thin film. Calculations showed that for an acceptable voltage drop of 10 mV across the electrolyte, the thickness of the polymer would need to lie in the range 10-100  $\mu\text{m}$ . It was well known that polymers could be cast in thin films, as used in packaging, and it was soon found possible to make these new electrolytes as films of appropriate thickness. Small cells were then assembled with negative electrodes made of lithium foil, and with positive electrodes that consisted of an intimate mixture of the polymer electrolyte, finely divided carbon and a suitable electroactive material such as manganese dioxide ( $\text{MnO}_2$ ) or vanadium oxide ( $\text{V}_2\text{O}_5$ ). Early experiments in the 1970s demonstrated that these small rechargeable cells had some remarkable properties and exciting prospects [24-26].

With an ionic conductivity that is low even at 100 °C, it is necessary not only to use thin electrolyte films, but also to restrict the current density of the cell to less than 1  $\text{mA cm}^{-2}$ . This poses no great problems, at least in principle, since within a given volume it is possible to pack a large surface-area of cell, typically many square metres. Although the current density is low, the total cell current may be quite high when account is taken of the large surface area. Thus, the manufacturing challenge is to make many square metres of electrolyte film and then apply a coating of the positive electrode mixture. Technologies used in the plastic films and the coated paper industries were adapted for this purpose. It was then necessary to add the thin lithium-foil negative and a positive current-collector, and finally to laminate the sandwich together to form an all solid-state cell. Such operations have to be conducted in a dry-room because of the sensitivity of the components to moisture. Once the laminate has been made, it may be configured in many different ways, as shown in Figure 8. Small flat-plate cells are packaged in composite aluminium-plastic envelopes (e.g. of the type used to hold powered foodstuffs that are moisture sensitive). Cells of larger area can be rolled into cylinders, or folded, as indicated in Figure 8.



**Fig. 8.** Alternate configurations for large-area, lithium-polymer cells.

The limitations of these cells were found to be the requirement to operate in the temperature range 80-120 °C and the comparatively short charge-discharge cycle-life of early models. Nevertheless, the attractions foreseen for thin, flexible cells based on polymers have encouraged research groups throughout the world to pursue the concept vigorously. One line of approach has been to bring the operating temperature down to ambient by using an organic liquid electrolyte immobilised in a gel polymer, a so-called “gelionic” electrolyte. When optimised, such electrolytes have most of the mechanical properties of a solid-polymer film and are essentially dry, but provide better conduction of lithium ions. A second approach is to investigate alternative polymers that dissolve lithium salts to give solid solutions that are amorphous (i.e. have good conductivity) at ambient temperature. Yet a third is to abandon the lithium-metal negative electrode and aim for the polymer analogue of the lithium-ion cell. This involves a trade-off in accepting some loss of voltage in return for the claimed better rechargeability and improved safety of lithium-ion cells.

Although operation at ambient temperature is a pre-requisite for small batteries employed in portable electronic equipments, this is not necessarily the case for large industrial batteries. For example, batteries that operate at 100 °C may be ideal for electric and hybrid electric vehicles. It should be a simple matter to package and maintain a traction battery at this temperature, and so be independent of the prevailing ambient temperature. For operation at extremes of ambient temperature, where aqueous electrolyte batteries are unsuitable, polymer batteries would then be acceptable. A consortium working in the USA and Canada has produced prototype traction modules based on lithium-foil negative electrodes, which have a capacity of 119 Ah, an output of 20 V, and a specific energy as high as 155 Wh kg<sup>-1</sup>. The modules are said to have a life in excess of 600 cycles and to be safe under all conditions of abuse. If these figures are substantiated, the prospects for lithium-polymer batteries are bright, assuming that the manufacturing costs are reasonable.

## 6. PROSPECTS FOR BATTERIES

In our previous paper [1], and in the above sections, a brief account has been given of five main types of batteries that could possibly be used for the storage of electrical energy for applications that range from portable consumer electronic devices to bulk electricity storage at power stations [27-40]. In practice, many of these batteries are at various stages of development and have significant failings, as well as attractive features. Only two, lead-acid and nickel-cadmium, are commercially available today in sizes to fit large installations and at prices likely to be acceptable. Others, which are commercially available in small or medium sizes (e.g. nickel-metal-hydride and lithium-ion), could be scaled-up if the demand existed, although their cost may be a deterrent. Some of the important parameters of the various battery chemistries are summarised in Table I.

Although stored energy and peak power per unit mass are the most commonly cited numerical values for advanced batteries, it should be emphasized that these are not necessarily the most important criteria for particular

applications. Even more significant considerations may be initial cost, overall electrical efficiency, reliability and freedom from maintenance, performance under fluctuating ambient temperatures, and effective lifespan under deep-discharge cycling [41-50].

Table 1. Summary of battery characteristics

Battery	Specific energy (Wh kg <sup>-1</sup> )	Peak power (W kg <sup>-1</sup> )	Status
Lead-acid	35-50	150-400	Widely used, cheapest available
Nickel-iron	50-60	80-150	Low electrical efficiency
Nickel-cadmium	40-60	80-150	Commercially available, but costly
Nickel-metal-hydride	60-80	200-300	Available in small-to-medium sizes; used in hybrid electric vehicles; costly
Nickel-zinc	70-100	170-260	Short cycle-life
Zinc-bromine	70-85	90-110	Under development
Zinc-air	100-200	80-100	Mechanically rechargeable only
Vanadium redox	20-30	110	At demonstration stage for stationary energy
Regenesys®	n.a.	n.a.	Development programme postponed
Sodium-sulphur	150-240	230	Development almost ceased
Sodium-nickel-chloride	90-120	130-160	Electric vehicle battery applications
Lithium-ion	80-180	200-1000	Commercially available in small sizes; careful control of recharging required

What are the prospects of further advances in battery technology? The theoretical limit to the specific energy of a battery is set by the free energy of the electrochemical reaction (which determines the cell voltage), the number of electrons transferred in the reaction, and the mass of the electrodes. Generally, the theoretical cell energy, calculated in this way, is three to five times that which is practically achievable. The reason for this huge discrepancy is that the practical value has to take account of the mass of all the other cell components (electrolyte, separators, container, current-collectors, terminal posts, etc.) as well as the coulombic inefficiencies arising from side-reactions such as corrosion and self-discharge, and voltaic inefficiencies associated with overpotential and resistive loss. Most of the inorganic electrochemical couples that are likely to be economically and commercially feasible have now been investigated, with the possible exception of new intercalation electrodes and electrolytes for lithium batteries, and it appears unlikely that radically new electrochemical couples will emerge. Nevertheless, there is still enormous scope for further improving the batteries already in existence by means of advanced materials and better methods of construction and quality control. Even the lead-acid battery, after about 150 years of history, is still being improved.



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