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# Non-Aqueous Battery Systems

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# Non-aqueous battery systems

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Lithium and sodium are light and highly electronegative elements which form the basis of anodes for high-energy-density battery systems. Their high chemical reactivity requires the use of ionic conductors based on non-aqueous solvents, polymers, solid electrolytes or fused salts. An associated range of cathode materials enables cells to be fabricated with open-circuit voltages from 1.5 to 4.0 V. Practical non-aqueous batteries have energies extending from 100 mWh primary button cells used to power electric watches to 20 kWh secondary batteries being developed for vehicle traction. Power output also varies dramatically with application, ranging from a cardiac pacemaker power source operating at 25–100 $\mu$W for up to 10 years, to a military lithium thermal battery delivering all of its energy in a 1 s pulse, with a specific power of 5 kW kg$^{-1}$. This wide range of applications demands diverse electrical characteristics which may include low self-discharge, extensive cyclability, prolonged shelf-life, etc., and which in turn call for many different types of battery design and materials. This paper surveys the battery chemistry, materials and design of lithium-based primary and reserve cells and of lithium and sodium-based rechargeable batteries.

## 1. Introduction

The number of practical applications for electrochemical power sources has increased significantly over the past 20 years. Most notably, the development of microelectronics has led to a major market in high-value consumer products which require easily portable primary or secondary batteries—electric watches, calculators, ‘camcorders’, mobile telephones, ‘lap-top’ computers, personal CD players, etc. At the other end of the capacity scale, electric-vehicle, industrial-traction, military and stationary applications are now demanding power sources which have both high energy density and high power density. The range of electrical characteristics required by these diverse applications can only be realized by the use of a wide variety of cell designs and materials. As high energy density is generally one of the key requirements, alkali metal-based systems, and in particular those using lithium or sodium, are likely to form the dominant technology. Lithium, for example, because of its low density, has a specific capacity of 3860 Ah kg$^{-1}$ in comparison with 820 Ah kg$^{-1}$ for zinc and 260 Ah kg$^{-1}$ for lead. Further, since the electrode potentials obtainable with alkali metal anodes are at least twice those of the transition metals, theoretical energy density comparisons favour the former even more. Environmental considerations also suggest the use of lithium or sodium over lead, cadmium and nickel.

The chemical reactivity of these highly electronegative elements precludes the use of aqueous electrolytes, and power sources therefore require ionic conductors based on organic solvents, polymers, fused salts or solid electrolytes. All of the components

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of these conductors must be electrochemically stable with respect to cell open-circuit voltages from 1.5 V to over 4.0 V depending on the cathode selected, and to even higher voltages which may be encountered during charging of secondary systems.

In this paper we consider first primary and reserve lithium batteries, then 'ambient' or low-temperature lithium secondary systems, principally low capacity cells for consumer products but also polymer electrolyte and other batteries for electric vehicle applications, and finally high-temperature rechargeable cells for traction and stationary uses.

## 2. Primary and reserve systems

Research into lithium batteries began in the late 1950s. It was soon established that lithium metal was stable from a practical point of view in a number of electrolytes, including systems based on propylene carbonate, liquid sulphur dioxide and molten salt eutectics, due to the formation of a passivating layer which prevented chemical corrosion but permitted cell discharge. This has been termed the *solid electrolyte interface* (SEI) (Peled 1983). The first commercial primary cell was introduced by SAFT in 1973. The initial emphasis was on military applications until various engineering and safety problems had been resolved. Within a further 10 years, primary cells with capacities from 5 mAh to thousands of Ah were available. This technology is now mature, with over fifty companies in the market, and development work has slowed down, although research on improving high-rate solid cathode cells continues. A number of new interesting specialist batteries based on, for example, thin (*ca.* 0.3 mm) laminated cells are still under intensive development. In addition to their superior energy density and high cell voltage, the principal advantages of primary lithium batteries include a very wide operating temperature range, flat discharge characteristics and extended shelf-lives.

### (*a*) *Low capacity cells for consumer products*

Most commercial cells use lithium metal anodes, solid cathodes such as metal oxides, sulphides or oxosalts or polycarbon fluorides, and an electrolyte such as $LiAsF_6$ dissolved in a mixed organic solvent based on organic carbonates, cyclic or acyclic ethers, lactones or esters. While a considerable effort has been expended in optimizing electrolyte systems for primaries, this has been an easier task than for lithium secondary batteries, as noted below. Button cells represent the major production type, but 'high-energy' 3 V cylindrical cells are becoming increasingly common. A typical commercial cell weighing 17 g (Sanyo CR 15400) has a nominal energy density of 230 Wh $kg^{-1}$, giving a capacity of 1.3 Ah at 3 V. Such cells are generally used for 10–100 mA rate discharges, but are capable of continuous discharge at over 1 A and pulse discharge at over 3 A. (Nohma *et al.* 1994). Iron sulphide may be used as a cathode material to fabricate excellent rate lithium primary batteries, with nominal voltages of 1.5 V which can act as direct replacements for aqueous cells, and which give up to four times higher service lifetime. AA-sized cells are currently being heavily promoted worldwide in competition with conventional alkali manganese products. It seems likely that the consumer market for low capacity applications will soon become confined to the latter (including RAM, the limited rechargeable alkali manganese system) for the most price-sensitive application where energy density is not important, and to the somewhat more expensive lithium batteries where low weight and superior electrical characteristics are critical. Already 25% of sales of Japanese primaries are lithium-based systems.

### (*b*) *Lithium primary cells for medical applications*

The advantages of lithium power sources for medical implants are their high energy density, predictable discharge behaviour, reliability and hermetic sealing. Cardiac pacemakers have been in use for 35 years, initially using 10 zinc mercury oxide cells weighing 200 g and with a lifetime of one to three years. Over 350 000 pacemakers are now implemented annually, with batteries which last for 10 years. The great majority of these use a lithium anode and an electronically conducting charge transfer complex formed by iodine and poly-2-vinylpyridene as the cathode (Greatbatch & Holmes 1992). Such cells have typically a total volume of 6 $\mathrm{cm^3}$ and a mass of 22 g. It was originally considered that the lithium iodide solid electrolyte formed initially on placing the anode and cathode in contact and subsequently on discharge, provided for lithium ion transport by simple vacancy migration. It is now known that this is a much more complex phenomenon, involving liquid-like phases formed by the polyvinylpyridine.

Demand pacemakers are very low-drain devices requiring only 25–50 $\mu$W for sensing and 60–100 $\mu$W for stimulation. Implanted ventricular defibrillators (which are now the treatment of choice rather than drug therapy for patients with cardiac fibrillation conditions) must, on the other hand, be able to deliver short electrical pulses of 25–40 J (e.g. 2 A at 2 V for 10 s) and hence require a much higher rate battery. The most common system is a lithium–silver vanadium oxide ($\mathrm{Ag_2V_4O_{11}}$) cell with a liquid organic-based electrolyte (Takeuchi & Thiebolt 1988). More than 80 000 units have been implanted. Implanted drug delivery devices also use lithium primary batteries, as do neurostimulators and bone-growth stimulators which are now at the clinical trials stage. Ventricular assist devices and liver blood pumps which are also under development will require rechargeable batteries.

### (*c*) *Higher power cells*

The highest rate lithium primary cells are based on soluble ($\mathrm{SO_2}$) or liquid ($\mathrm{SOCl_2}$, $\mathrm{SO_2Cl_2}$) cathodes. These systems can also provide very high practical energy densities.

The lithium–sulphur dioxide cell has a lithium anode and a porous carbon current collector to enable the cathodic reaction

$$2\mathrm{SO_2(diss.)} + 2\mathrm{e^-} \rightarrow \mathrm{S_2O_4^{2-}}$$

to take place at high current levels. The high conductivity electrolyte is typically acetronitrile with dissolved lithium bromide: about 70% of the weight of the electrolyte–depolarizer solution of an undischarged cell is $\mathrm{SO_2}$. Electrical protection devices such as fuses and current limiters and/or ‘shut-down’ separators are essential in such high-power systems, since abuse can cause overheating and thermal runaway. High-power D-sized cells can deliver pulse loads of over 30 A at a voltage of 2 V. They have capacities of up to 30 Ah, and practical energy densities of over 300 Wh $\mathrm{kg^{-1}}$. Such cells are not generally available on the consumer market, although they may be built-in components of certain products; they have a wide range of military applications (Linden 1984).

Molecules such as thionyl chloride ($\mathrm{SOCl_2}$) and sulphuryl chloride ($\mathrm{SO_2Cl_2}$) can act both as a cathodic reagent and electrolytic solvent for salts such as $\mathrm{LiAlCl_4}$, and are used to form cells of the highest available practical energy densities—up to 500 Wh $kg^{-1}$. They may be configured as high-rate cells with rather lower energy density and are used mainly for military applications such as for torpedo motors, with batteries providing 50–150 kWh at 200–600 kW. Thermal management is a significant problem but various solutions have been developed including the use of 'heat pipes' for small batteries and recirculating electrolyte–seawater heat exchangers for large underwater systems (Chenebault 1994).

The 'ultimate battery' would be based on the lithium–fluorine couple which has a theoretical open-circuit potential of nearly 6 V, and a theoretical energy density of over 6000 Wh $kg^{-1}$. The reactivity of lithium and fluorine make the realization of such a cell unlikely, but systems are currently being studied which use fluorine-containing interhalogen compounds as cathodes. The most promising is $BrF_3$ which has a liquid range from 9–126 °C and significant conductivity ($8 \times 10^{-3}$ S $cm^{-1}$ at room temperature) due to self-ionization. Coupled with lithium, $BrF_3$ provides a cell with an open-circuit potential of 5.2 V and a theoretical energy density of 2680 Wh $kg^{-1}$ which is almost twice that of Li–$SOCl_2$ (Chenebault 1994).

### (*d*) *Lithium reserve batteries*

In a reserve battery, a key component of the cell, often the electrolyte, is not introduced until an activation procedure has been initiated. Reserve batteries are expected to deliver the same electrical performance before and after 25 years of storage under the harshest of environmental conditions. A number of ambient lithium cells based on the above-described liquid cathodes may be constructed as reserve systems.

For aerospace applications, thermal reserve batteries are the major form of reserve power source, providing a market of over £50M per annum. Such power sources were originally developed during the Second World War for V2 missiles. Currently they are almost exclusively based on a lithium alloy anode (LiAl, LiSi or LiTe), an iron sulphide cathode and are activated by melting a salt mixture such as LiCl–KCl, to give a very highly conductive eutectic using, say, a Fe–$KClO_4$ heat pellet ignited electrically by a Zr–$BaCrO_4$ 'fuse strip'. Batteries consist of stacks of bipolar plate cells, each having an open-circuit potential of about 2 V and with overall power ratings of several kW. Batteries of this type are constructed as 'high power' (discharge time less than 30 s) or 'long discharge' (discharge time up to 60 min).

## 3. 'Ambient'† secondary batteries

In the 1970s it was found that a number of transition metal dichalcogenides could reversibly 'intercalate' lithium according to the reaction

$$x\mathrm{Li}^+ + \mathrm{MA}_2 + xe^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li}_x\mathrm{MA}_2$$

and could therefore be used as positive plates for secondary lithium batteries. These charge–discharge processes correspond to the extraction–insertion of lithium ions from the electrolyte and compensating electrons from the current collector with only

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† Some of these batteries based on polymer electrolytes may be operated at 60–80 °C—significantly lower temperatures than the systems considered in the next section.

minimal changes to the host structure. Initially, the hosts studied were semiconducting layered compounds such as $TiS_2$ or $MoS_2$ which could accommodate the lithium in the van der Waals gap between the layers; more recently anisotropic materials such as $CoO_2$, $NiO_2$ and isotropic $MnO_2$ spinel phases have been developed (Ohzuku & Ueda 1994).

So far as the negative plate is concerned, lithium ions are readily formed from lithium metal on discharge and replated on charge. As noted previously, however, the key to the kinetic (and hence practical) stability of lithium is its ability to form a passivating surface layer by homogeneous reaction with components of the electrolyte. In secondary cells this process may cause acute problems in cycling, which can be responsible for cell failure or safety hazards, as described below. Two alternative approaches have been taken: (i) use of insertion hosts for both positive and negative electrodes or (ii) selection of systems where the electrolyte reacts to only a very limited extent with the lithium.

### (*a*) *Lithium metal*–$MA_2$ *cells*

When lithium is recharged in cells with most organic solvent-based electrolytes, especially when 'reactive' anions such as $AsF_6^-$, $PF_6^-$, $CF_3SO_3^-$, etc., are present, there are several consequences.

(i) Some of the newly plated lithium may be 'lost' due to electronic isolation of the grains from the lithium electrode by the passivating layer formed around them.

(ii) The effective surface area of the electrode may become progressively larger with cycling.

(iii) The uniformity of the deposit may become poor, leading to overheating, dendrite formation and internal short circuits.

The formation of high surface areas may be reduced if stack pressure can be generated in suitably designed cell structures (e.g. a spiral construction). Lithium loss can be compensated for by designing the cell with an initial stoichiometric excess: figures of merit (FOM) for lithium cycling of 50–100 have been demonstrated. A FOM of 50 would require a fourfold excess to permit 200 cycles. The safety record of early secondary cells with lithium metal electrodes was, however, not good and safety considerations led to product recall in the case of the 'Molicel' Li–$MoS_2$ AA-sized power source which was the first commercial cell of its type.

While most manufacturers are now concentrating on cells which do not involve metallic lithium (as considered next), prototype lithium metal cells have recently been demonstrated which are based on electrolytes with minimum reactivity and which can survive electrical, mechanical and thermal abuse even after extensive cycling. Such Li–$MA_2$ cells have exceptionally good charge retention at open circuit in comparison with all other ambient secondary batteries, and superior energy density.

### (*b*) $Li_xC_6$–$MA_2$ *cells*

In the *lithium ion, rocking chair* or *swing* cell, both electrodes are based on insertion materials. Since the host for the negative plate must have a potential similar to that of pure lithium, this has in practice restricted the choice to graphite or graphite-like phases. Such electrodes can reversibly insert lithium according to the reaction

$$x\mathrm{Li}^+ + 6\mathrm{C}(s) + x\mathrm{e}^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li}_x\mathrm{C}_6$$

for $x \leqslant 1$. Most carbons used in commercial cells have much more complex structures than graphite, with turbostratic disorder in which successive layers are rotated with respect to one another, staging faults, and regions which are 'disorganized'. The detailed structure of the carbon host has a critical influence on the electrochemical behaviour, and determines *inter alia* the capacity, voltage and reversibility of the electrode, in addition to controlling solvent cointercalation.

The use of carbon insertion electrodes greatly improves the cyclability and the rate of recharge of ambient lithium secondary cells, but self-discharge losses are significantly greater. The driving force for the replacement of metallic lithium in practical cells is, however, undoubtedly the improved safety. As a material, $LiC_6$ is not inherently safer than lithium, but on cycling carbon-based negatives, the increase in contact area between electrode and electrolyte phases observed with the metal does not occur. Further, dendrites are not likely to form under normal charging conditions. During the first charge of a carbon electrode, some of the lithium formed reacts irreversibly to form a thin ionically conducting, electronically insulating solid electrolyte interface around the carbon particles. Unlike the situation with metallic lithium, there is no further film formation on subsequent cycles. There is therefore a much reduced probability of thermal runaway caused by the reaction of a large lithium surface with the electrolytes. Note, however, that such problems are likely to reappear if carbons of very large surface area were to be used.

### (*c*) *Electrolytes*

The most common electrolytes are based on (i) dipolar aprotic organic solvents similar to those used in primaries, (ii) coordinating polymers and (iii) gel or 'hybrid' polymer–solvent combinations.

Liquid electrolyte formulations are generally based on salts dissolved in mixtures of solvents which provide maximum conductivity together with electrochemical stability. The latter, being a kinetic property, is not easy to rationalize and there has been much development by trial and error methods. Special attention is being paid to oxidative stability because of the use of 'high-voltage' positives in lithium-ion cells.

Polymer electrolytes are ionically conducting solid phases formed by dissolution of salts by ion coordinating macromolecules. The archetypal polymer host is poly(ethylene oxide), $(\text{–}CH_2CH_2O\text{–})_n$, known as PEO. More sophisticated copolymers, which have a similar ability to form multiple intrapolymer coordinate bonds with cations, have superior mechanical and electrical properties. Polymer electrolytes permit the design of practical all-solid-state cells which have numerous advantages, e.g. continuous production of cell laminate for flat stack, cylindrical or flat-roll design, ease of fabrication of bipolar configurations and miniature cells, absence of flammable/toxic/high vapour pressure liquids, high energy density, good thermal management, etc. (Gray 1991). By adopting a thin-film configuration, cells with reasonable power capabilities may be realized despite the lower conductivity of polymer electrolytes ($10^{-3}$–$10^{-4}$ S cm$^{-1}$) in comparison with low molar mass liquid systems. In spite of considerable progress, the quest for a sufficiently conductive 'true' polymer electrolyte for high-power applications such as traction, is still continuing. In particular, there are major efforts to produce practical polymers which have the counter anion chemically bonded to the host and thus to realize a cell which would have no concentration polarization. To improve the conductivity there are two options: (i) to persevere with the development of true polymer electrolytes, e.g. by using 'plasticizing' anions or other plasticizers, by heating the cell to modest temperatures, etc., or (ii) to use non-aqueous gels formed by networks of structural polymers such as poly(acrylonitrile), PAN, to form gel films with salts and conventional non-aqueous solvents. Both options are currently being pursued. A typical aim is to produce a 20 kWh battery with a capacity of 200–500 Ah with a peak power of 40 kW.

## 4. High-temperature batteries

High-temperature batteries exploit the very high ionic conductivity of molten salts or solid electrolytes to enable a combination of high power density and high energy density to be achieved. Cells based both on lithium and on sodium are being developed, primarily for electric vehicles and industrial traction, but they are also being studied for load levelling and other stationary applications. Both forms of sodium cell being developed commercially employ solid beta-alumina electrolytes; the lithium cell uses a molten eutectic LiCl–LiBr–KBr electrolyte. The sodium-based *Zebra battery*, discussed in detail elsewhere in this volume operates in the range 250–350 °C, the sodium–sulphur cell or *Beta battery* at somewhat higher temperatures (300–400 °C), while current versions of the lithium-ion sulphide cell operate at 400–425 °C (original designs operated in the 450–500 °C range). At these temperatures materials problems become acute and represent one of the greatest current challenges in battery technology.

### (a) *Lithium–iron sulphide batteries*

Cells using liquid and then solid alloy lithium negatives, sulphur, and then iron sulphide positives and LiCl-rich molten salt electrolytes have been under development at the Argonne National Laboratory for over 30 years (Henriksen & Vissers 1994). Work there now continues together with SAFT America under the auspices of USABC.

The overall cell reaction may be written for the two sulphides with lithium aluminium alloy as

$$2\mathrm{LiAl} + \mathrm{FeS} \rightleftharpoons \mathrm{Li_2S} + \mathrm{Fe} + 2\mathrm{Al},$$
$$4\mathrm{LiAl} + \mathrm{FeS_2} \rightleftharpoons 2\mathrm{Li_2S} + \mathrm{Fe} + 4\mathrm{Al}.$$

Flooded electrolyte prismatic cells and, more recently, ‘electrolyte-starved’ bipolar plate cell configurations have been produced.

The development of this high-temperature battery illustrates well the prime importance of advanced materials. While the active components of the cell, lithium–aluminium alloy (in the $\alpha$, $\beta$ two-phase region) and iron sulphide are relatively inexpensive, as are the components of the electrolyte, the separators, seals and current collectors all require highly engineered specialized materials. The problem with the selection of materials for separators (and also for feedthrough insulators for this battery) is the high reactivity of lithium at elevated temperatures and the thermodynamic stability of $\mathrm{Li_2O}$ which excludes the use of common ceramics such as $\mathrm{Al_2O_3}$ and $\mathrm{SiO_2}$. In addition, the separator must withstand the high sulphur activity of the metal sulphide electrode and the corrosive environment of the molten salt. A number of thermodynamically acceptable alternatives were found to form electrically conducting surface layers or to contain reactive impurities in grain boundaries and were therefore rejected. Boron nitride (BN) and yttria ($\mathrm{Y_2O_3}$) proved suitable, and cells were successfully operated using woven BN cloth separators with $\mathrm{Y_2O_3}$

felt retainers for LiAl and FeS electrodes and $ZrO_2$ felt for $FeS_2$ electrodes. Rigid porous separators of $Si_3N_4$ and AlN have also been studied, as has non-woven BN felt, but the cost of such materials is excessive and a new inexpensive MgO separator has recently been developed for use in electrolyte-starved cells. This is fabricated by cold-pressing high surface area magnesia powder with finely ground electrolyte. Complex feedthrough components are also required, using for example, a compacted BN powder sealant, a lower solid BeO insulator and upper solid $Al_2O_3$ insulator in a mechanical compression seal.

Implementation of a battery configuration employing bipolar cells (where the current collector of the cathode of one cell also serves as the current collector of the anode of the neighbouring cell) required the development of an entirely new metal–ceramic bonded electrically insulating seal. A corrosion-resistant chalcogenide structural ceramic which has 10 times the bond strength of borosilicate glass has recently been patented. The new seals which are formed in a single thermal processing step at 1100 °C are gas tight and may be thermally cycled between 25–400 °C without loss of strength. For the bipolar plate, steel is acceptable on the LiAl side at temperatures below 500 °C, above which reaction with the lithium–aluminium alloy to form an intermetallic iron–aluminium compound occurs. At the high sulphur and chlorine activities encountered with $FeS_2$, however, corrosion becomes a serious problem and alternatives to steel such as molybdenum must be used. Steel coated with titanium nitride (TiN) using high-temperature multilayer chemical vapour deposition has also been investigated.

### (*b*) *Sodium–sulphur batteries*

The concept of a high-temperature sodium–sulphur cell with liquid electrode phases and a solid sodium-ion conductor based on beta-alumina, which acts both as electrolyte and separator, was first described in 1967. It is considered particularly suitable for electrical vehicle, industrial traction and load-levelling applications because of its potential high power and the low cost of the cell components. A number of designs have been developed across the world and pilot plant production has resulted in 10–36 kWh batteries for road testing, 100 kWh modules and the design of 100 MWh batteries for stationary systems.

The chemistry of the sodium–sulphur cell or *Beta battery* is well understood. Sodium metal is oxidized during discharge and the ions formed migrate through the solid electrolyte to produce, initially, $Na_2S_5$ in the positive compartment, which forms a two-phase mixture with the sulphur. The sulphur phase is consumed and the $Na_2S_5$ is progressively converted into single-phase $Na_2S_3$. The discharge is not permitted to proceed further to the $Na_2S_3$–$Na_2S_2$ stage. Such cells have virtually no self-discharge processes and operate with essentially 100% coulombic efficiency. However, great care is necessary to prevent overcharge or overdischarge. The open-circuit voltage of the cell is 2.08 V and the cut-off 1.6 V. Practical cell energy densities of 150 Wh $kg^{-1}$ have been reported.

The main problem with such systems has been the failure of individual cells within battery modules, caused by electrolyte cracking or the breaking of the seals either between the beta-alumina and a ceramic insulating ring or between this ring and the stainless steel container. Recent designs for sodium–sulphur cells now being tested in electric vehicles use shorter electrolyte tubes with smaller diameters. Such designs improve the performance at high rates and minimize the effect of cell failure.

### (*c*) *Sodium–nickel chloride and related batteries*

Cells in which a sodium ion-conducting beta-alumina tube separates a liquid sodium electrode from molten sodium tetrachloroaluminate containing a dissolved cathode phase such as $SbCl_3$ or $NiCl_2$ (or S (IV) in acidic melts, i.e. with excess $AlCl_3$) have been studied for many years. The *Zebra battery* using $NiCl_2$ has now been developed to the pilot-line production stage and is seen as a very strong competitor for automotive and industrial traction applications (Sudworth 1994). Batteries have a practical energy density approaching 100 Wh $kg^{-1}$ and a power density of 150 W $kg^{-1}$ for a fully charged battery. Such cells have many advantages, including modest operating temperatures (250–350 °C) and the ability to be formed in a discharged state.

The overall cell reaction is

$$2\mathrm{Na} + \mathrm{NiCl_2} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \mathrm{Ni} + 2\mathrm{NaCl}.$$

The sodium is first formed by a priming reaction involving aluminium added to the positive compartment:

$$\mathrm{Al} + 4\mathrm{NaCl} \rightarrow 3\mathrm{Na} + \mathrm{NaAlCl_4}.$$

Normal charging involves initially the reaction of nickel powder with NaCl in the melt:

$$\mathrm{Ni} + 2\mathrm{NaCl} \overset{\text{charge}}{\rightleftharpoons} 2\mathrm{Na} + \mathrm{NiCl_2}.$$

The quantity of NaCl added is sufficient to react on charge with greater than or equal to 30% of the nickel originally added. After this an overcharge reaction takes over:

$$\mathrm{Ni} + 2\mathrm{NaAlCl_4} \overset{\text{overcharge}}{\rightleftharpoons} 2\mathrm{Na} + 2\mathrm{AlCl_3} + \mathrm{NiCl_2}.$$

Practical energy densities for automotive batteries approaching 100 Wh $kg^{-1}$ have been demonstrated with power levels of 150 W $kg^{-1}$ when fully charged. However, an increase in the internal ohmic resistance during discharge in current cell configurations causes a decrease in available power.

## 5. Conclusions

The materials that constitute both the active electrodes and the passive components of non-aqueous battery systems are clearly of critical importance in determining cell characteristics and performance (Vincent 1994). For high energy densities it is necessary to use very electronegative anodes and electropositive cathodes which, in turn, require development of electrolytes, separators (including 'shut-down' systems) and other cell components with extreme chemical and electrochemical stability. The technology is now available to produce a wide variety of primary systems for both low- and high-rate applications. The situation with secondary systems, especially for high-power (e.g. electric vehicle) applications is less clear. Whereas the basic active materials are generally well understood, successful application of these systems (and replacement of conventional aqueous batteries) requires further developments in engineering design and/or a deeper understanding of details of the electrochemical processes involved in cell charge and discharge. Combination of secondary cells in parallel–series arrangements to provide high-capacity–high-power systems represents a further challenge to ensure balanced cell behaviour and minimization of the effects of individual cell failure.

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