# Electrochemical Power Sources

## 1. Rechargeable Batteries

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**The pressing need to alleviate our urban air-quality has provided the impetus for electric vehicles. Over the years, a great deal of research and development work has been carried out, and is still underway, on all aspects of electric vehicles especially on improving the power sources, namely the rechargeable batteries, fuel cells and electrochemical supercapacitors. The developments in rechargeable batteries for electric vehicles are reflected in this part of the article while fuel cells and electrochemical supercapacitors will be described in Part 2 of the article.**

## Rechargeable Batteries

A battery is an electrical storage device. Batteries do not generate electricity, they store it, just as water tank stores water for future use. Rechargeable batteries store a fixed amount of chemical energy and may be recharged when the electrochemically active materials in them have been exhausted.

A battery comprises an anode (negative plate), a cathode (positive plate) and an electrolyte. The negative plate consists of a current collector and an active compound, which is often a metal, such as finely divided zinc, lead or cadmium. The positive plate also contains a metallic current collector and an active component which is a higher valent metallic oxide, such as $MnO_2$, $PbO_2$, $NiOOH$ or $AgO$, that is capable of being reduced. The electrodes are separated by an electrolyte that conducts ions but which must be an electronic insulator to avoid internal short-circuits. In most conventional batteries, the electrolyte is an aqueous solution, such as $ZnCl_2$, $KOH$ or $H_2SO_4$, but some advanced batteries use non-aqueous solution, ion-conducting ceramics, polymers or molten salts as electrolyte.

It is desirable that the energy delivered by a battery during discharge should be as high as possible. The energy output of a battery is dependent on the amount of active material present in the battery. Since the weight and volume of the battery are at premium for most of the applications, it is the energy density, which has to be maximized. Engineers refer to the quantity of electricity stored per kilogram of the battery as the energy density. The speed of delivery or rate of discharge is called power density. For many applications, such as traction and automotive, it is also necessary to have a high power density. For an efficient delivery of charge from battery, it is desirable that the energy density be maximized at optimum required power. Between periods of use, a loss in the available energy of the battery occurs partly due to a leakage of charge between the electrodes and partly due to consumption of charge at the electrodes by the parasitic reactions. This is commonly referred to as self-discharge. This results in a decrease in both the effectiveness of the battery as a source of energy as also its reliability for a given application during storage. Structural integrity of the battery is another important characteristic since this confers immunity from mechanical stresses such as vibrations and shocks to which batteries are often subjected to in practice. In short, a maximum energy at optimum power-density, minimum internal-resistance, maximum charge-retention, high mechanical-strength and long cycle-life are the desirable characteristics of a battery.

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In recent years, several rechargeable batteries have been proposed for electric cars. Some of the promising rechargeable batteries for electric cars are described below.

## Lead-Acid Batteries

The rechargeable battery most commonly known to us is the lead-acid battery. The lead-acid battery is one of the most successful electrochemical systems ever developed. Although it was first demonstrated as early as in 1859 by Plantè and many other rechargeable batteries have been developed since then, the
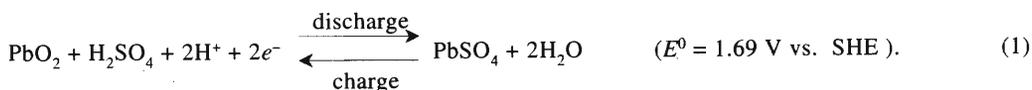
lead-acid battery is still the most widely used rechargeable battery. There are three types of lead-acid batteries in common use: (a) batteries with excess or flooded electrolyte, (b) low-maintenance batteries with a large excess of electrolyte, and (c) batteries with immobilized electrolyte and with a pressure-sensitive valve usually referred to as valve-regulated lead-acid (VRLA) or sealed lead-acid (SLA) batteries.

The conventional flooded-type lead-acid battery requires checking of specific gravity of electrolyte, periodic addition of water to maintain electrolyte above the plates and recharge soon after the battery discharge to prevent hard sulfation that causes loss of capacity. The emission of acid fumes causes corrosion of metallic parts in the vicinity of the battery. The seepage of acid on the top cover leads to leakage current resulting in increased self-discharge and ground-shunt hazards.

To overcome these problems VRLA or SLA batteries based on oxygen-recombination cycle have emerged. SLA batteries offer the freedom of battery placement, cyclability without the addition of water or checking the specific gravity, increased safety and superior performance in some instances.

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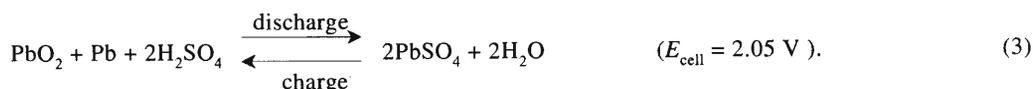**Box 1. Electrochemistry of the Lead-Acid Battery.**

At the positive plate:

$$PbO_2 + H_2SO_4 + 2H^+ + 2e^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4 + 2H_2O \qquad (E^0 = 1.69 \text{ V vs. SHE}). \qquad (1)$$

At the negative plate:

$$Pb + H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} PbSO_4 + 2H^+ + 2e^- \qquad (E^0 = -0.36 \text{ V vs. SHE}). \qquad (2)$$

The net cell reaction is accordingly given by,

$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O \qquad (E_{cell} = 2.05 \text{ V}). \qquad (3)$$

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The charge and discharge processes in a lead-acid battery are shown schematically in *Figures* 1 and 2, respectively. The positive plate in a lead-acid cell accepts the charge less efficiently than its negative counterpart. Therefore, during the recharge of a lead-acid battery, $O_2$ and $H_2$ are evolved non-stoichiometrically with $O_2$ evolution occurring prior to $H_2$ evolution. The $O_2$ evolved at the positive plate is constantly
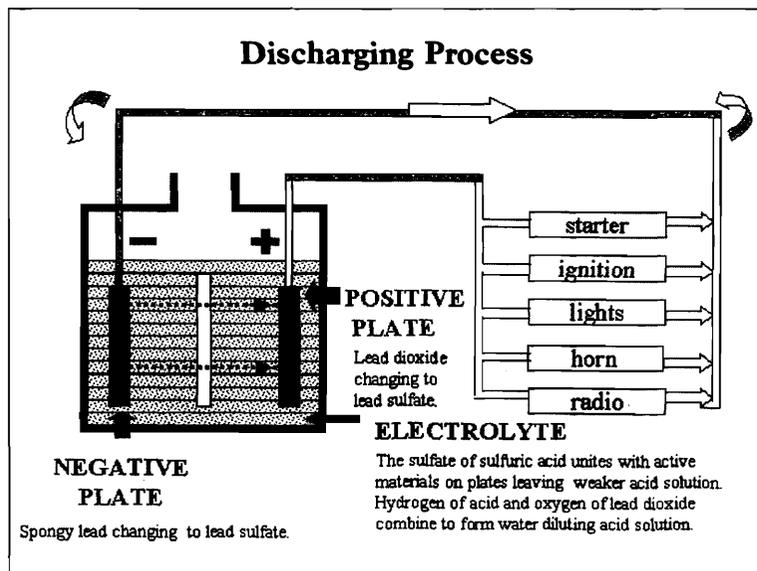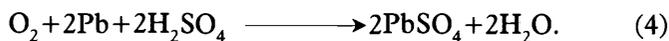


Figure 2. Discharging process of a lead-acid battery.

reduced at the negative plate as follows.

$$O_2 + 2Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O. \qquad (4)$$

The $PbSO_4$ generated during reaction (4) is retrieved as active Pb during the charging process according to reaction (2) (*Box* 1). This feature is the main stay in the design of SLA batteries.

The key issues, which in the past have made the lead-acid batteries fail, are short-life, high-maintenance, and inadequate energy density. Additional issues such as safety, environmental impact and material recyclability are becoming more critical than in the past. Keeping these factors in mind, manufacturers of rechargeable batteries are exploring other technologies.
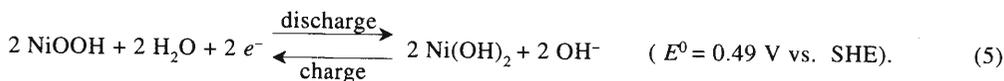
## Nickel-Cadmium Batteries

At present, nickel-cadmium (Ni-Cd) batteries represent the best balance between specific energy, specific power, cycle-life and reliability. The Ni-Cd battery has a positive plate of nickel oxy-hydroxide (NiOOH), a negative plate of cadmium (Cd), and an aqueous solution of potassium hydroxide (KOH) for the electrolyte. The battery can endure a lot of abuse both physically and electrically. Also, the alkaline electrolyte does not enter into the discharge reaction as the acid does in the lead-acid battery and hence does not get depleted as the battery discharges. During discharge, NiOOH in the positive plate is converted to $Ni(OH)_2$. This reaction results in a change in the Ni-oxidation state from $+3$ to $+2$. During the cell recharge, NiOOH is retrieved. The cadmium of the negative plate is converted to $Cd(OH)_2$ during the cell discharge and retrieved during the cell charge.

The mechanism of the electrode reaction (5) (*Box* 2) involves diffusion of protons through the solid-state lattices of $Ni(OH)_2$ and NiOOH so that there is a continuous change in the composition of the active material between $Ni(OH)_2$ and NiOOH. As the transformation of $Ni(OH)_2$ to NiOOH and vice-versa is a bulk feature, the process is homogeneous in nature. By contrast,
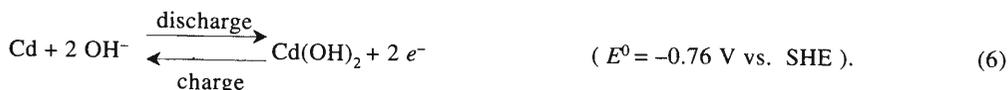
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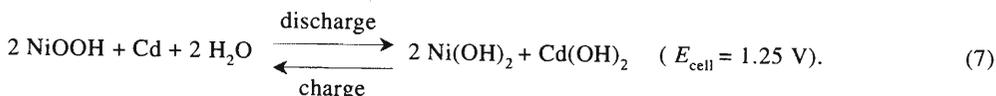**Box 2. Electrochemistry of the Nickel-Cadmium Battery**

At the positive plate:

$$2\ NiOOH + 2\ H_2O + 2\ e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} 2\ Ni(OH)_2 + 2\ OH^- \qquad (E^0 = 0.49\ V\ vs.\ SHE). \qquad (5)$$

At the negative plate:

$$Cd + 2\ OH^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Cd(OH)_2 + 2\ e^- \qquad\qquad (E^0 = -0.76\ V\ vs.\ SHE). \qquad (6)$$

Accordingly, the overall charge and discharge reactions for the cell are:

$$2\ NiOOH + Cd + 2\ H_2O \underset{charge}{\overset{discharge}{\rightleftarrows}} 2\ Ni(OH)_2 + Cd(OH)_2 \quad (E_{cell} = 1.25\ V). \qquad (7)$$

reaction (6) (*Box* 2) involves both solid and liquid phases, and hence is heterogeneous in nature.

Due to their high cranking-power, lower weight and corrosion-free atmosphere, nickel-cadmium batteries have found ample applications in defence and space. Nickel-cadmium batteries are produced mainly in sintered plate and pocket-plate configurations. Recently, fiber nickel-cadmium batteries, which employ fibers of foam nickel, have been developed and commercialized. Nickel-cadmium batteries are generally designed to be positive limited and, akin to lead-acid batteries, can be sealed by utilizing the oxygen-recombination cycle wherein the oxygen evolved at the positive plate during the battery charging diffuses to the negative plate, and combines with active cadmium to form Cd (OH)$_2$ according to the reaction below.

$$Cd + \tfrac{1}{2}\ O_2 + H_2O \longrightarrow Cd(OH)_2 \qquad (8)$$

The generated Cd(OH)$_2$ is concomitantly converted to active cadmium during the battery charging according to reaction (6) (*Box* 2).

Nickel-cadmium batteries however suffer from the memory effect, which burdens the user with having to at least occasionally follow a time-consuming recharging regime in order to

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maintain their rated capacity. The effect appears to be due to the growth of abnormally large crystals on cadmium electrode. These crystals reduce the surface area of the cadmium electrode thereby increasing the battery's effective internal resistance. Besides, nickel-cadmium batteries store only slightly more energy per unit weight than lead-acid units and have a fairly high rate of self-discharge at high temperatures. Worst of all, cadmium is an awful poison that can contaminate the environment.
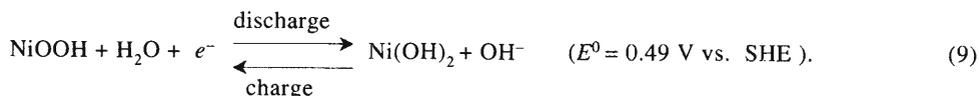
## Nickel-Metal Hydride Batteries

The unpopularity of cadmium has encouraged the development of nickel-metal hydride (Ni-MH) batteries, which are not only cadmium-free but can also store more energy than comparatively sized nickel-cadmium units. Similar to nickel-cadmium batteries, the Ni-MH units also employ nickel-positive plates with NiOOH as the active material and an aqueous KOH electrolyte. The main difference is that the active material in the negative plate is hydrogen absorbed in a metal alloy. The metal alloys in which hydrogen is stored fall into two categories: (a) the $AB_5$-alloys based on mixtures of nickel and rare earth, and (b) the $AB_2$-alloys based on nickel commonly blended with titanium, vanadium, and zirconium. A typical composition of the $AB_5$-alloy that has been documented to be a promising electrode material is Mm (Mm = Misch metal: 25 wt.% La, 50 wt.% Ce, 7 wt.% Pr, 18 wt. Nd) $Ni_{3.2} Co_{1.0} Mn_{0.6} A_{10.11} Mo_{0.09}$, which has $CaCu_5$-type crystal structure. Among the $AB_2$-type alloys, $Ti_{0.51} Zr_{0.49} V_{0.70} Ni_{1.18} Cr_{0.12}$ has been found to be an attractive electrode material, which has ^{14}C-Laves crystal structure. Although, in the beginning, $AB_5$-type alloys were employed as battery electrodes, but at present, $AB_2$-type alloys are preferred electrode materials for Ni-MH batteries. It is found that while $AB_2$-type alloys yield superior energy densities, the $AB_5$-alloys are able to hold hydrogen better thus lowering the self-discharge rate of the battery. It is noteworthy that the metal-hydride electrode offers an important advantage for materials engineering and optimization in relation to negative electrodes of other nickel-based batteries.

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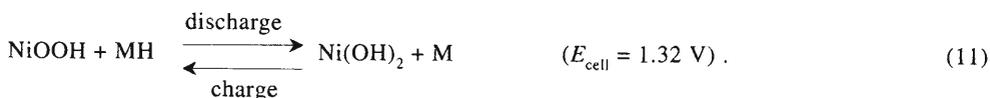**Box 3. Electrochemistry of the Nickel-Metal Hydride Battery**

At the positive plate:

$$NiOOH + H_2O + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Ni(OH)_2 + OH^- \qquad (E^0 = 0.49 \text{ V vs. SHE}). \qquad (9)$$

At the negative plate:

$$MH + OH^- \underset{charge}{\overset{discharge}{\rightleftarrows}} M + H_2O + e^- \qquad (E^0 = -0.83 \text{ vs. SHE}). \qquad (10)$$

Accordingly, the net cell reactions during its charge and discharge are given as

$$NiOOH + MH \underset{charge}{\overset{discharge}{\rightleftarrows}} Ni(OH)_2 + M \qquad (E_{cell} = 1.32 \text{ V}). \qquad (11)$$

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As a consequence of (9) and (10) (*Box* 3), there is no net change in the electrolyte quantity or concentration over the charge-discharge cycles. This is an attractive feature of Ni-MH batteries over nickel-cadmium batteries wherein water is generated during charge and consumed during discharge. On the down side, Ni-MH batteries deliver less power, have a faster self-discharge and are less tolerant to overcharge like the nickel-cadmium batteries.

## Zinc-Air Batteries

Very recently rechargeable zinc-air battery technology that uses a rechargeable air-electrode is claimed to have moved from the research laboratory to the market. A zinc-air battery can store much larger energy in relation to a comparatively-sized Ni-MH battery but zinc-air units require an air-management system to ensure the appropriate flow of air into the battery to generate the required power. Also, there is need to remove carbon dioxide from air to avoid carbonation of the KOH electrolyte. Another weak point of these batteries is their sensitivity to electrical abuse. The batteries cannot be quick charged and if these are discharged below about 0.9 V/cell (operating cell-voltage ranges
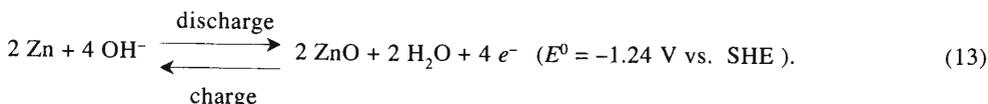
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**Box 4. Electrochemistry of the Zinc-Air Battery**

At the positive plate:

$$O_2 + 2\,H_2O + 4\,e^- \xrightarrow[\text{charge}]{\text{discharge}} 4\,OH^- \qquad (E^0 = 0.4\ \text{V vs. SHE}). \qquad (12)$$

At the negative plate:

$$2\,Zn + 4\,OH^- \xrightarrow[\text{charge}]{\text{discharge}} 2\,ZnO + 2\,H_2O + 4\,e^- \quad (E^0 = -1.24\ \text{V vs. SHE}). \qquad (13)$$

Accordingly, the net cell reactions during the charge and discharge of a rechargeable zinc-air unit are given by,

$$2\,Zn + O_2 \xrightarrow[\text{charge}]{\text{discharge}} 2\,ZnO \qquad (E_{cell} = 1.64\ \text{V}). \qquad (14)$$

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between 1-1.2 V), these batteries could be permanently damaged.

## Secondary Lithium Batteries

The most promising system among the lithium secondary batteries is the lithium-ion battery, which is better known as lithium-ion rocking chair battery. In the unit, both the electrodes comprise intercalation materials with structure in which guest species are inserted and extracted with little structural modification of the host. The fully-charged negative plate is made of lithiated carbon which is about 10% lithium by weight and has nearly the same potential as metallic lithium. The discharged positive-plate employs one of the intercalation compounds among $LiCoO_2$, $LiNiO_2$, $LiMnO_2$ or $LiMn_2O_4$, each of which develops a voltage between 3.5-4 V with respect to lithium.
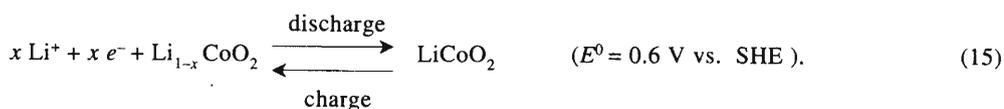
Unlike conventional acidic and alkaline rechargeable batteries, rocking-chair cells employ non-aqueous electrolytes comprising a lithium salt dissolved in an organic solvent. The main issues in selecting an electrolyte are its compatibility and thermal stability up to about 80 °C. If the negative electrode consists

> The most promising system among the lithium secondary batteries is the lithium-ion battery.

of lithiated graphite then the choice of the electrolyte is restricted to systems based on ethylene carbonate since those based on other solvents tend to cause exfoliation of the graphite. The use of lithiated coke for the negative plate provides a much wider choice with diethyl carbonate, propylene carbonate, dimethyl carbonate, and many other solvents that may be used simply or in combination. The favourite solute is lithium hexafluorophosphate ($LiPF_6$) but other lithium salts may as well be used. The ionic conductivity of these mixtures is about two orders of magnitude lower than that of aqueous electrolytes but is high enough to make practical batteries for use at or above room temperatures. Actually, even at 0 °C the ionic conductivity of $10^{-3}$ S cm$^{-1}$ for these electrolytes suffices for the practical batteries. The conductivity however varies quite appreciably with temperature, and ranges from $0.2 \times 10^{-3}$ at –40 °C to $1.5 \times 10^{-2}$ S cm$^{-1}$ at 40 °C for $LiPF_6$ dissolved in 1:1 volume mixture of ethylene carbonate and propylene carbonate. During the cell operation, lithium ions move back and forth between the two plates across the electrolyte as the unit is alternatively charged and discharged.

The lithium-ion cell is not the ultimate in the lithium secondary
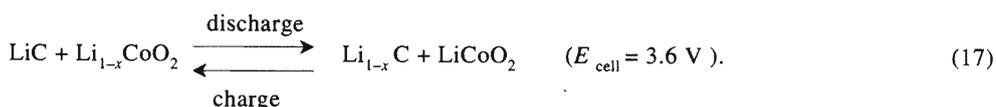
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**Box 5. Electrochemistry of the Lithium-Ion Battery**

At the positive electrode:

$$x\,Li^+ + x\,e^- + Li_{1-x}CoO_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} LiCoO_2 \qquad (E^0 = 0.6 \text{ V vs. SHE}). \qquad (15)$$

At the negative electrode:

$$LiC \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Li_{1-x}C + x\,Li^+ + xe^- \qquad (E^0 = -3.0 \text{ V vs. SHE}). \qquad (16)$$

Accordingly, the net cell reactions during the charge and discharge processes of the cell are written as below.

$$LiC + Li_{1-x}CoO_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Li_{1-x}C + LiCoO_2 \qquad (E_{cell} = 3.6 \text{ V}). \qquad (17)$$
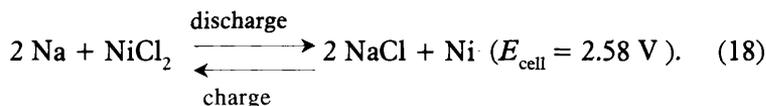
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## Suggested Reading

[1] D A J Rand, R Woods, and R
   M Dell, *Batteries for Electric
   Vehicles*, Research Studies
   Press, Trauton, UK and
   Wiley, New York, 1998.
[2] C A Vincent and B Scrosati,
   *Modern Batteries*, 2nd Edi-
   tion, Arnold, London 1997.

This battery was invented in 1985 by Coetzer in Pretoria (South Africa) and hence the name zebra battery. The technical name for the battery is Na-NiCl$_2$ battery.

battery technology as far as the capacity is concerned. In principle, cells with negative electrodes of metallic lithium can store about ten-times more energy per unit weight than those with negative plates of lithiated carbon. The trouble is that the lithium electrode has a tendency to react with any liquid electrolyte creating a passive film. The reaction would have little effect if it happened only once but every time lithium is stripped away and then recharged, a fresh metal surface is exposed to the electrolyte and new film is formed. This process would use-up a lot of lithium. Partially because of these difficulties, research is being focussed on lithium batteries with solid-polymer electrolytes, which would be backed by highly conducting current-collector. These cells will be less than a half mm in thickness. A layered structure of this type, if realized, would have many attractions. Batteries of such cells could be made in almost any desired shape and size. The lack of liquid would make them fairly safe and these would have the highest specific energy rating among any known battery, and would also hold their charge for years with little loss.

### High-Temperature Zebra Batteries

Over the years, significant modifications have also been made in the high-temperature sodium-sulfur (Na-S) batteries. The problem of dendritic-sodium growth in Na-S batteries has been cleverly circumvented in the zebra[1] batteries with the use of NaAlCl$_4$ in conjunction with Na+-β-alumina ceramic electrolyte. The battery operates at about 300 °C and the charge-discharge reactions during the cell operation are as follows.

$$2\,\text{Na} + \text{NiCl}_2 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\,\text{NaCl} + \text{Ni} \quad (E_{\text{cell}} = 2.58\ \text{V}). \quad (18)$$

Since the zebra batteries operate at ~300 °C, there are no detrimental effects resulting from their use at extremely cold or hot ambient-temperatures. For conventional battery systems, extreme temperatures require more elaborate thermal-manage-

| Cell type | Nominal Voltage (V) | Specific Energy (Wh/kg) | Energy Density (Wh/l) | Specific Power (W/kg) | Power Density (W/L) | Self Discharge (%/month) | | Cycle life |
|---|---|---|---|---|---|---|---|---|
| Lead-acid | 2.0 | 35 | 70 | ~200 | ~400 | 4-8 | 250-500 | |
| Lithium-ion | 3.6 | 115 | 260 | 20-250 | 400-500 | 5-10 | | 500-1000 |
| Lithium-Polymer | 3.0 | 100-200 | 150-350 | >200 | >350 | ~1 | | 200-1000 |
| Nickel-Cadmium | 1.2 | 40-60 | 60-100 | 140-220 | 220-350 | 10-20 | | 300-700 |
| Nickel-Metal Hydride | 1.2 | 60 | 220 | 130 | 475 | 30 | | 300-500 |
| Zinc-air | 1.2 | 146 | 204 | 150 | 190 | ~5 | | ~200 |
| Zebra | 2.6 | 100 | 160 | 150 | 250 | ~1 | | ~1000 |

ment or result in reduced battery performance. Besides, because of their high-temperature operation, zebra batteries allow for the use of latent heat for fast cabin heating or window defrosting. But the thermal management needs for the high-temperature zebra batteries are not ideal for electric vehicle-drive-systems. When not in use, zebra batteries typically require being plugged into wall plug, or tethered, in order to be ready for use when needed. If shut down, a reheating process must be initiated that requires about one to two days to restore the battery pack to the desired temperature, and fully charging the batteries. This reheating time can however vary depending on the state-of-charge of the batteries at the time of their shut down, battery-pack temperature, and power availed for reheating. If shut down of the battery pack is desired, three to four days are usually required for a fully-charged battery pack to lose its significant heat.

*Table 1. A comparison of the most promising rechargeable batteries for electric cars.*

The power and energy density parameters of the storage batteries discussed above are given in *Table* 1. It is noteworthy that the vanadium redox and zinc-bromine flow batteries have also been projected as possible contenders for vehicular traction. These batteries, however, have problems of excessive self-discharge. Besides, vanadium and bromine are highly toxic.

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