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NICKEL–METAL HYDRIDE BATTERIES: FROM CONCEPT TO CHARACTERISTICS

Since the development of Nickel–Metal Hydride (NiMH) batteries in the late eighties of the previous century, these batteries have become widely accepted in our present-day portable society. In the very early days of the current century this battery type has become even more popular in portable electronics than any other battery system. This is, among other things, due to their high storage capacity, good rate capability and environmental friendliness. During battery operation hydrogen shuttles from one electrode to the other. As such, this battery system can be considered as the first commercial success towards the so-called hydrogen era, which is generally accepted about to begin. This justifies reviewing this nowadays mature battery system. The basic electrochemical principles underlying the energy storage reactions and the various side reactions, occurring during (over)charging, (over)discharging and under open-circuit conditions will be discussed. In the second part of the paper the most important battery characteristics, such as charge/discharge capabilities, self-discharge behaviour and battery life are reviewed.

Batteries are energy storage devices that are able to convert chemically stored energy into electrical energy. The application of batteries to provide portable equipment with electrical energy has been rapidly growing during the last decades. Various types of commercially available batteries are used nowadays, varying from small button cells to batteries for cars and other large-scale electrical storage applications. Two classes of batteries are generally distinguished (see Table I).

In the first place there are primary cells. These types of batteries can not generally be recharged and are, therefore, denoted as non-rechargeables. The most popular member of this class, often used in many portable electronics, is the alkaline zinc–manganese dioxide cell. Another example is the zinc–air button cell, widely applied in hearing instruments. A second class of batteries is formed by secondary cells. These can be recharged once they are partly or completely discharged. During recharging electrical energy is again converted into chemical energy by means of a charging device. It is evident that for applications, which frequently need a lot of "portable energy", such as portable telephones, electrical shavers, portable CD players and (hybride) electrical vehicles (HEV), rechargeable batteries are preferred, not only for economical and environmental reasons but also for the user's convenience. Various types of rechargeable batteries are available and the number is still expanding. The most popular types are at the moment the conventional nickel–cadmium battery, the in the early nineties developed nickel–metal hydride (NiMH) and the most recent lithium (Li–ion) batteries. Numerous efforts are nowadays being made by battery manufacturers to increase the energy density of all these systems. It is to be expected, as indicated in Table 1, that future

Table 1. Open-circuit potentials and energy density values for various primary (non-rechargeable) and secondary (rechargeable) batteries

	System	Open-circuit Potential [V]	Energy density*	
			Wh/kg	Wh/l
Primary Batteries	$Zn–MnO_2$	1.6	100–140	300–400
	Zn – air	1.6	200–290	275–1000
Secondary Batteries	SLA	2.0	30 – 40	70 – 80
	NiCd	1.3	35 – 65	100 – 200
	NiMH	1.3	40 – 90	160 – 310
	Li – ion	3.8	100 – 160	200 – 390
	Li – Polymer	3.8	100 – 175	200 – 300

*Strongly dependent on discharge rate

systems, such as lithium–polymer batteries will further improve the energy density.

In this paper one of the most important battery systems will be reviewed, i.e. the NiMH battery. The electrochemical principles [1] for both the basic electrochemical storage reactions and the various side reactions, occurring under various operating conditions, will be highlighted together with the most interesting battery characteristics. For more detailed information about the materials characteristics of both the Ni and metal hydride (MH) electrode, the reader is referred to Refs. [1,2].

BASIC ELECTROCHEMICAL REACTIONS

Energy storage reactions

A schematic representation of a NiMH battery containing a hydride–forming (MH) electrode is shown in Fig. 1 [1,3]. The electrodes are electrically insulated from each other by a separator. Both separator and electrodes are impregnated with an alkaline solution that provides ionic conductivity between the two electrodes. The overall electrochemical reactions, occurring at both
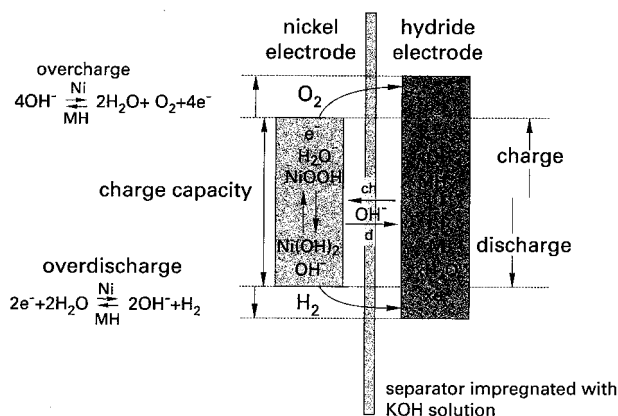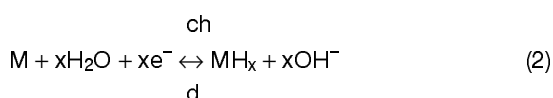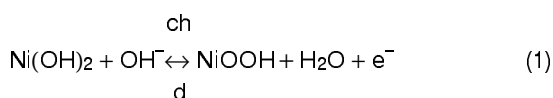
Figure 1. Schematic representation of the concept of a sealed rechargeable NiMH battery.

electrodes during charging (ch) and discharging (d) can, in their most simplified form, be represented by

$$Ni(OH)_2 + OH^- \overset{ch}{\underset{d}{\leftrightarrow}} NiOOH + H_2O + e^- \qquad (1)$$

$$M + xH_2O + xe^- \overset{ch}{\underset{d}{\leftrightarrow}} MH_x + xOH^- \qquad (2)$$

During charging divalent Ni^{II} is oxidised into the trivalent Ni^{III} state and water is reduced to hydrogen atoms at the metal (M) electrode, which are, subsequently, absorbed by the hydride–forming compound. The reverse reactions take place during discharging. The net effect of this reaction sequence is that the hydroxyl ions in the electrolyte are transported from one electrode to the other and hence no electrolyte consumption takes place during current flow. For proper functioning of the battery it is thus essential that both electrical and ionic conductivity can take place. The basic reactions are also indicated in Fig. 1. Nowadays almost all commercial NiMH batteries employ the as–denoted AB5–type hydride–forming compounds as the active negative electrode material. The development of electrochemically stable AB5–type compounds have contributed to a large extent to the realisation of NiMH batteries [1,4,5]

In general, exponential relationships are observed between the partial anodic/cathodic currents and the applied electrode potential under kinetically–controlled conditions, as depicted schematically in Fig. 2 (dashed curves). The potential scale is given with respect to a Hg/HgO (6 N KOH) reference electrode [6]. The equilibrium potential of the Ni–electrode under standard conditions is far more positive ($E^0_{Ni} = +439$ mV) than that of the MH–electrode [1]. This latter is found to be dependent on the plateau pressure of the hydride–forming battery materials used (generally E^0_{MH} ranges between –930 and –860 mV) [1,7]. This implies
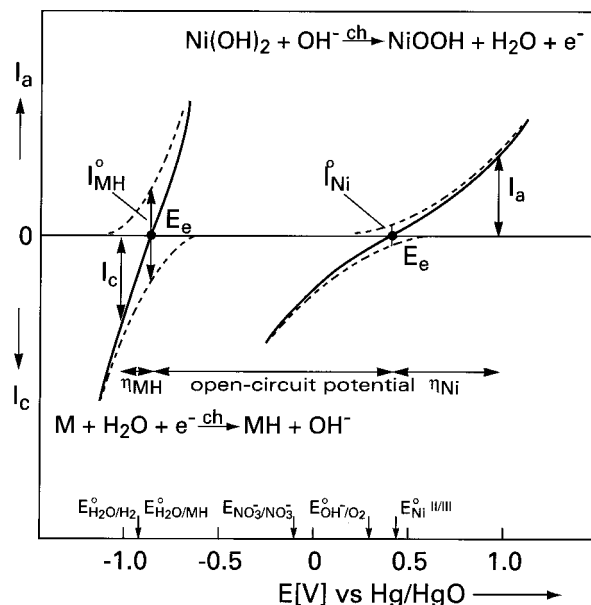

Figure 2. Schematic representation of the current–potential curves for a Ni and MH electrode (solid lines), assuming kinetically controlled charge transfer reactions. The partial anodic and cathodic reactions are indicated as dashed lines. The exchange currents (I_o) are defined at the equilibrium potentials (E_e). Potentials are given with respect to a Hg/HgO reference electrode. Besides the redox potentials (E^0) of the main electrode reactions those of some side–reactions are also indicated.

that the theoretical open–circuit potential of a NiMH battery is approximately 1.3 V, very similar to that of NiCd batteries. This makes these two different battery systems indeed very compatible, although it should be noted that some differences in performance still exist between both systems.

During galvanostatic charging with a constant current an overpotential (η) will be established at both electrodes. The magnitude of each overpotential component (η_{Ni} and η_{MH} in Fig. 2) is determined by the kinetics of the charge transfer reactions. The exchange current I_0 is generally considered to be an electrochemical measure for the kinetics of a charge transfer reaction. I_0 is defined at the equilibrium potential, E_e, at which the partial anodic current equals the partial cathodic current (see Fig. 2). In the case of the Ni–electrode, I_0 is reported to be relatively low [1], which implies that, at a given constant anodic current, I_a, the established overpotential at the Ni–electrode is relatively high (Fig. 2). In contrast, the kinetics of the MH–electrode are reported to be strongly dependent on the material composition [1]. Assuming a highly electrocatalytic hydride–forming compound, this implies that the current–potential curves, characteristic for the MH–electrode are very steep in comparison to those for the Ni–electrode, resulting in a much smaller value for η_{MH} at the same cathodic current I_c, as schematically shown in Fig. 2. It is evident that the battery voltage under current flow is a summation of the open–circuit

potential and the various overpotential contributions. This includes the ohmic potential drop (η_{IR}) caused by the electrical resistance of the electrolyte (R_e). The reverse processes occur during discharging, resulting in a cell voltage lower than 1.3 V. Clearly, since the potential of both electrodes may change considerably, the absolute values of these potentials cannot be directly deduced from the cell voltage. The use of a reference electrode is therefore inevitable in order to interpret the current–potential dependencies in an appropriate way.

In conclusion we can say that the kinetics of the charge transfer reactions can generally be described by exponential relationships, denoted as the Butler Volmer equations [1]. These non–linear relationships indicate that the so–called charge transfer resistances do not have constant values but are dependent on the applied current. The Butler–Volmer relationships can simply be characterised by two parameters, i.e. the equilibrium potential E_e and the exchange current I_0. It should, however, be noted that these parameters do not have fixed values but are dependent on the concentration of the electroactive species involved in the charge transfer reactions and thus change as a function of state–of–charge (SoC). This is schematically illustrated for the current–potential characteristics of the MH electrode in Fig. 3. The anodic oxidation of stored hydrogen atoms is here shown to be dependent on the hydrogen concentration at the electrode surface for three different concentrations (bold, dashed and grey lines). On the other hand, the reduction rate of water is independent of SoC (water is considered not to be depleted at the electrode surface). As a result, the complete current–potential curves (bold, dashed and grey lines) and, hence, the indicated values for E_e and I_0, change significantly as a function of state–of–charge. This holds, of course, not only for the metal hydride electrode but also for other electrodes. This makes an appropriate mathematical description of an entire battery much more complex. It should be emphasised that the transport limitations of protons and hydrogen atoms inside both the Ni– and MH electrode, respectively, complicate the description of the complete charge transfer kinetics further. For more detailed information about these topics the reader is referred to Refs. [8,9].

Side reactions

Overcharging

To ensure the proper functioning of sealed rechargeable NiMH batteries under a wide variety of conditions, the battery is designed in such a way that the Ni electrode is the capacity–determining electrode, as schematically depicted in Fig. 1. Such a configuration forces side–reactions to occur at the Ni electrode both during overcharging and overdischarging, as will be shown below.
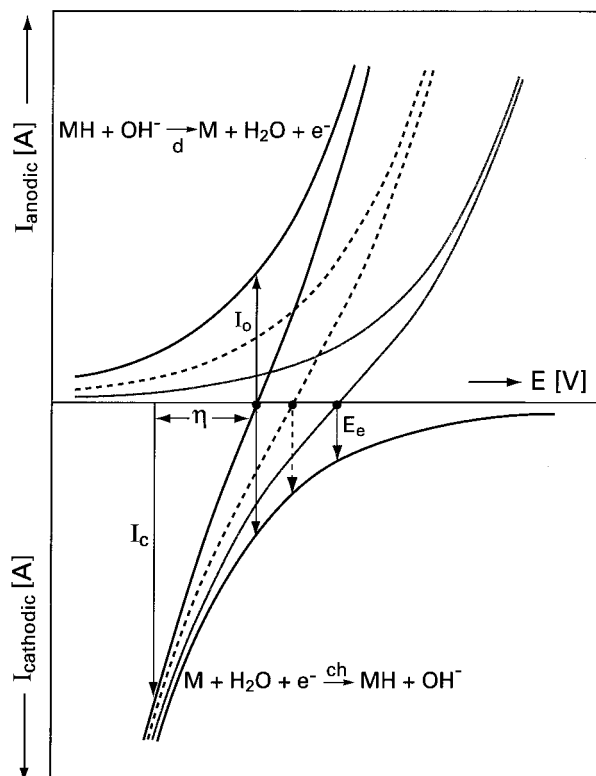

Figure 3. Schematic representation of the dependence of the partial anodic current–potential curves on the hydrogen concentration within the solid of a metal hydride electrode, i.e. at different states–of–charge. The hydride–formation is state–of–charge independent. As a consequence the overall Butler–Volmer relationships (solid lines) reveal that both the equilibrium potential (E_e) and the exchange current (I_0) change as a function of the state–of–charge.

During overcharging OH^- ions are oxidized at potentials more positive with respect to the standard redox potential of the OH^-/O_2 redox couple (about 0.3 V with respect to the Hg/HgO reference potential) and oxygen evolution starts at the Ni electrode, according to

$$\overset{Ni}{4OH^- \rightarrow O_2 + 2H_2O + 4e^-} \qquad (3)$$
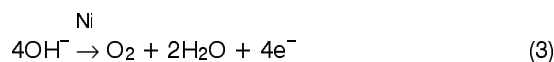
Again, an exponential relationship between the current and the potential is to be expected when no transport limitation of OH^- towards the electrode surface occurs, as schematically shown in curve (a) of Fig. 4. A more or less constant oxygen overpotential (η_{O2}) will be established at the Ni electrode. As a result, the partial oxygen pressure inside the sealed cell starts to rise. Advantageously, oxygen can be transported to the MH electrode, where it can be reduced at the MH/electrolyte interface in hydroxyl ions at the expense of the hydride–formation reaction (2):

$$\overset{MH}{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-} \qquad (4)$$
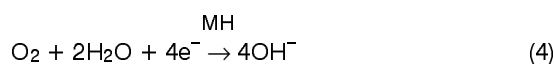
When this reduction reaction is kinetically controlled an exponential dependence is also to be

expected for this reduction reaction, as shown in curve (b) of Fig. 4. It should, however, be noted that the steepness of this curve not necessarily need be the same for the oxygen evolution (curve (a)) and oxygen recombination reaction (curve (b)). It is even very unlikely that the kinetics of both reactions are similar since the oxidation and the reduction reactions take place at chemically different electrode surfaces, resulting in different values for the exchange current density. Moreover, since the overpotential for the recombination reaction at the MH electrode is high it is even more likely that the rate is controlled by the oxygen supply via the electrolyte. All together, the above mechanism ensures that the partial oxygen pressure inside the battery will be kept low, assuming that the recombination mechanism is functioning properly.

Although thermodynamically more favourable ($E_{Ni}^o > E_{O2}^o$), the parasitic oxygen evolution reaction (Eq. 4) only takes place at significant rates at more positive potentials than the range in which the basic Ni reaction generally occurs (Eq. 1). This is fortunately due to the much poorer kinetics of the oxygen evolution reaction ($i_{O2}^o < i_{Ni}^o$) compared to those of the Ni reaction. This generally results in a rather sharp increase of the battery voltage at the end of the charging process, at the point where the overcharging process takes over. This is indeed confirmed experimentally, as Fig. 5 reveals. It is also clear from this figure that the pressure inside the battery sharply rises at the end of the charging process, around 100% SoC, and tends to level off at higher SoC. This pressure rise is, in fact, dictated by the competition of the oxygen evolution reaction and the Ni reaction and

is found to be strongly dependent on the rate at which the NiMH battery is charged. In the steady–state during overcharging, the amount of oxygen evolved at the Ni electrode, represented by I_{O2} in curve (a) of Fig. 4, is equal to the amount of oxygen recombining at the MH electrode (I_{rec} in Fig. 4), resulting in a constant gas pressure. This situation is almost attained in Fig. 5 at higher SoC values. Evidently, under this steady–state condition all of the electrical energy supplied to the battery during overcharging is completely converted into heat. It is clear from Fig. 4 that the complete battery voltage is used under this condition to build up the two oxygen overpotential contributions.

Besides the gas pressure build–up inside NiMH batteries, the development of the battery temperature is also of considerable importance and influences the thermodynamics and kinetics of the various processes. In addition, the temperature may also induce secondary effects, such as for example, a reduced cycle life. The formation of heat (W) inside a battery can be represented by

$$W = I \left\{ \Sigma \left[\frac{-T\Delta S_i}{nF} \right] + \Sigma |\eta_i| + IR_e \right\} \qquad (5)$$

where I is the current flowing through the battery, T the temperature, n the number of electrons involved in the overall charge transfer reaction (summation of Eqs. (1) and (2)) and F is the Faraday constant [1,9]. The factors which contribute to the evolved heat during current flow can be easily recognised in Eq. (5): (i) the entropy changes (ΔS_i) brought about by the various electrochemical reactions, (ii) the various overpotential components (η_i) and (iii) the internal battery resistance, the contribution of which may be significant, especially when high currents are applied, as the heat evolution due to this effect is proportional to the square of the current. As long as the basic electrochemical reactions (Eqs. (1) and (2)) proceed inside the battery, the
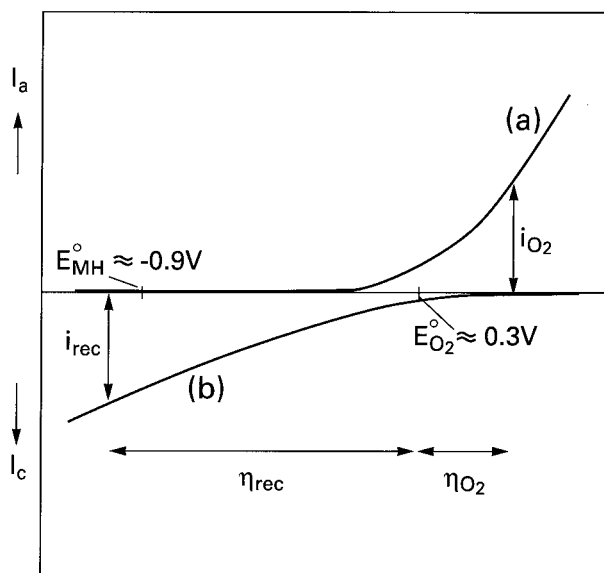

Figure 4. Schematic representation of the overcharging process inside a NiMH battery. The anodic oxygen evolution reaction (curve (a)) takes place at the Ni electrode whereas the cathodic oxygen recombination reaction (curve (b)) occurs at the MH electrode.
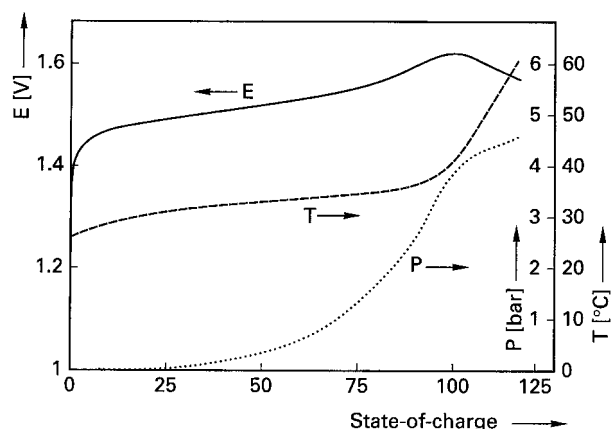

Figure 5. Development of the cell voltage (E), the internal gas pressure (P) and the cell temperature (T) as a function of state-of-charge for a NiMH battery during charging and overcharging with a high (3 A) current. The battery is then fully charged within 20 min.

overpotentials established at both the Ni and MH electrode are relatively small (see Fig. 2). This implies that the heat contribution, resulting from the electrode reactions is limited. The temperature rise during the normal charging procedure is therefore limited, as Fig. 5 reveals. However, this situation changes drastically as soon as the oxygen recombination cycle starts at the MH electrode. Since the MH electrode potential is at least 1 V more negative with respect to the standard redox potential of the OH$^-$/O$_2$ couple (see Fig. 4), this implies that the established overpotential for the oxygen recombination reaction is extremely high (> 1.2 V). Considering Eq. (5), it is therefore to be expected that the heat evolved inside a battery will sharply increase as soon as the oxygen recombination cycle starts. This is indeed in agreement with the pronounced temperature increase found during overcharging in the experiments (see Fig. 5). Although the recombination cycle moderates a considerable pressure rise inside the NiMH battery, it is essential to avoid prolonged overcharging in order to prevent a considerable temperature rise, which may negatively affect other electrode properties. In conclusion we may say that, depending on the kinetics of the oxygen recombination reaction, i.e. depending on the competition between reaction (2) and (4), the gas pressure and/or temperature of the battery will rise during overcharging. In fact the gas pressure and the temperature rise 'counterbalance' one another: when the recombination rate is very poor, the large pressure rise will be combined with a small temperature increase. On the other hand, when the recombination rate is excellent, the internal pressure will be limited while the temperature increase will be rather pronounced. Under extreme charging conditions both effects do have a negative influence on battery performance. It should, however, be emphasised that charging at high rates will lead to an exorbitant pressure rise, which may be fatal for the battery performance once the safety vent, with which rechargeable batteries are always equipped, has been opened. The reason for this is that not only the surplus of gases but, simultaneously, a significant amount of electrolyte is released from the battery during venting. This has a negative influence on, for example, the battery cycle life and recombination kinetics.

Overdischarging

Protection against overdischarging is another factor of importance, especially when NiMH batteries, which inevitably reveal small differences in storage capacities, are used in series. This implies that some batteries are already completely discharged while others still contain small amounts of electrical energy. Continuation of the discharge process induces overdischarging to occur of the already fully discharged batteries. Under these circumstances water is forced to be reduced at the Ni electrode, according to

$$\text{Ni}$$
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (6)$$
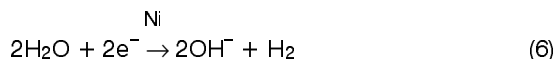
which also results in a pressure build–up inside the battery when no precautions are taken (also see Fig. 1). This decomposition reaction takes place at rather negative potentials at the Ni electrode, i.e. more than 1.3 V more negative with respect to the Ni^{II}/Ni^{III} redox potential, as is indicated in curve (a) of Fig. 6. As the (electro)chemical affinity of the metal hydride electrode towards hydrogen gas is, in principle, excellent, it is evident that this gas can be again converted into water at the MH electrode during overdischarging, according to

$$\text{MH}$$
$$H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \qquad (7)$$
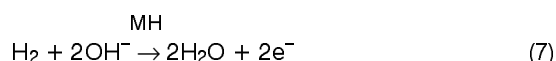
Whether the conversion of molecular hydrogen occurs directly at the MH electrode or atomic hydrogen is oxidised indirectly after chemical adsorption and/or absorption has taken place, is not clear. It is, however, obvious that in both cases high demands are put on the physical properties of the electrode/electrolyte interface. Electrochemical oxidation also occurs close to the H$_2$/H$_2$O redox potential (curve (b) of Fig. 6). This means that the cell voltage of NiMH batteries is expected to be close to 0 V under these overdischarging conditions or even invert to some extent when the overpotential contributions of both reactions are taken into account. The experimental result of such a process is shown in Fig. 7 and is in agreement with these expectations. During normal discharging, the battery voltage is around 1.2 V and drops towards an inverted voltage of
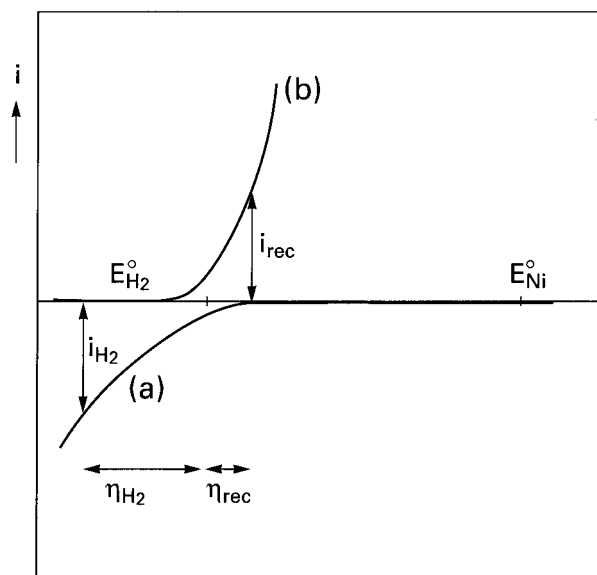

Figure 6. Schematic representation of the overdischarging process inside a NiMH battery. The hydrogen evolution reaction occurs at rather negative potentials at the Ni electrode (curve (a)) and oxidation of hydrogen occurs at the MH electrode (curve (b)) in the same potential region, resulting in a battery voltage close to 0 V.
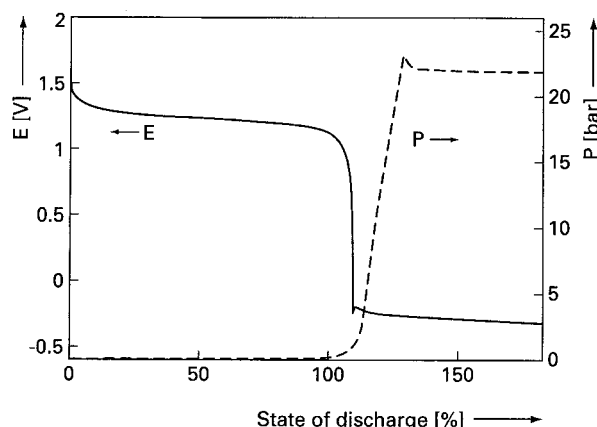
Figure 7. Experimental result of the development of the cell voltage (E) and the gas pressure (P) as a function of state-of-discharge for a NiMH battery during discharging and overdischarging.

–0.2 V when the overdischarge reactions take over. Fig. 7 also reveals that the pressure rise due to hydrogen evolution may be considerable. In the example given, the pressure was quickly built up to the critical level of approximately 20 bar. At that level the safety vent was forced to open, which can be recognised by the small pressure decrease. Since the overpotentials of both the hydrogen evolution and hydrogen recombination reaction are relatively low during overdischarging (see Fig. 6) their contribution to the heat evolution will be rather limited. This strongly contrasts to the overcharging situation described in the previous section.

In conclusion we can say that a hydrogen recombination cycle controls the pressure rise inside NiMH batteries under overdischarging conditions. As hydrogen evolution and hydrogen oxidation at both electrodes take place in the same potential region (Fig. 6), it is obvious that the battery voltage is very close to zero volts under these conditions.

Self–discharge

It is well known that charged NiMH batteries, similar to NiCd batteries, loose their stored energy under open–circuit conditions to a certain extent. Typical self–discharge rates at room temperature are of the order of 1 or 2% of the nominal storage capacity per day. The self–discharge rates are, however, strongly dependent on external conditions, such as SoC and temperature [9]. Various mechanisms contribute to the overall self–discharge rate. These mechanisms are all electrochemical in nature. The mechanisms operative in NiMH batteries occur mainly via the gas phase and can be divided into processes initiated by the Ni or MH electrode. The most important mechanisms, contributing to the overall self–discharge rate, are:

(i) Considering the redox potentials of the Ni electrode (+439 mV) and that of the competing oxygen

evolution reaction (+300 mV; see Fig. 2)), it is obvious that trivalent Ni^{III} is thermodynamically unstable in an aqueous environment. As a consequence, NiOOH will be reduced by hydroxyl ions at the open–circuit potential, according to

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \qquad (8)$$

$$\overset{Ni}{4OH^- \rightarrow O_2 + 2H_2O + 4e^-} \qquad (9)$$
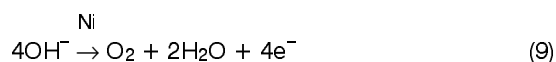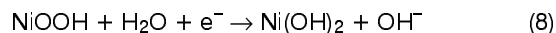
These reactions, occurring at the Ni electrode at a rate determined by both individual exchange currents, are represented by curves (a) and (b) in Fig. 8. The electrons released by the OH– ions are transferred to the Ni electrode at the electrode/electrolyte interface. Although the Ni^{III} species are principally unstable, electrical charge can, however, be stored in large quantities in the Ni electrode. As discussed, before this is due to the fact that the kinetics of the oxygen evolution reaction are relatively poor, so that it takes quite a while before appreciable capacity is lost due to battery self–discharge. Subsequently, the produced oxygen gas can be transported to the MH electrode, where it can be reconverted into OH– ions at the expense of charge stored in the MH electrode, i.e.

$$\overset{MH}{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-} \qquad (10)$$

$$MH + OH^- \rightarrow M + H_2O + e^- \qquad (11)$$

These reactions, also occurring at the open–circuit potential at the MH electrode, are represented by curves
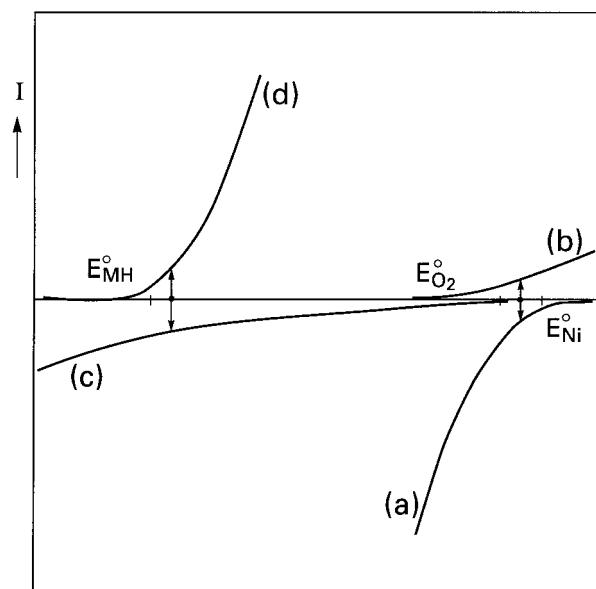

Figure 8. Schematic representation of the "oxygen gas phase shunt", partly responsible for the self–discharge behaviour under open–circuit conditions of aqueous rechargeable batteries, like NiMH. Oxygen evolution (curve (a)) is initiated at the Ni electrode which is simultaneously discharged (curve (b)) at the open–circuit potential. Consequently, O_2 can be reduced at the MH electrode (curve (c)) at the expense of electrochemically stored hydrogen (curve (d)).

(c) and (d), respectively, in Fig. 8. Evidently, under open–circuit conditions when no external current flows, all the reaction rates are equal. Furthermore, Fig. 8 indicates that the battery open–circuit voltage will be around 1.2 V. The ultimate result is that stored charge in both the Ni and MH electrode is slowly released through a gas–phase shunt, in this case oxygen gas.

(ii) A different type of gas–phase shunt is initiated by the MH electrode and is caused by the presence of hydrogen gas inside the battery. As the storage capacity of the MH electrode is considerably larger than that of the Ni electrode (see battery concept in Fig. 1) and the MH electrode contains a certain amount of 'precharge' in the form of hydride, a minimum partial hydrogen pressure is inevitably established inside the NiMH battery, according to the chemical equilibrium

$$MH \leftrightarrow M + 1/2H_2 \uparrow \qquad (12)$$

The partial H_2 pressure is dependent on the condition (e.g. battery life and temperature) of the battery and is mainly determined by the hydrogen plateau pressure, which is a characteristic parameter for many hydride–forming compounds [1,3]. As a result, H_2 is inevitably in contact with the Ni electrode. Since the standard redox potential of the H_2/H_2O redox couple is much more negative than that of the Ni^{II}/Ni^{III} couple, hydrogen can in principle be oxidised at the Ni electrode, whereas the Ni electrode is simultaneously reduced, according to

$$\overset{Ni}{H_2 + 2OH^- \rightarrow 2H_2O + 2e^-} \qquad (13)$$

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \qquad (14)$$
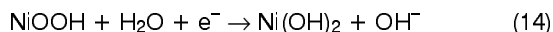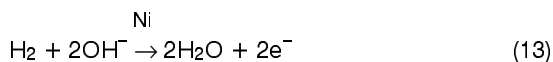
Since the oxidation of hydrogen gas takes place more than 1.2 V more positive with respect to its standard redox potential and the kinetics of this reaction are very favourable, it is likely that the hydrogen oxidation reaction at the Ni electrode becomes diffusion–controlled. This implies that the oxidation current, which generally reveals an exponential dependence on the voltage, will level off to become constant at higher voltage levels. This diffusion–controlled oxidation process, as represented by Eq. (13), is schematically indicated in curve (a) of Fig. 9. The Ni reduction reaction (Eq. (14)) is represented by curve (b). The overall electrochemical process occurs under open–circuit conditions at the Ni electrode and will be strongly influenced by the partial hydrogen pressure inside the battery. It has indeed been reported that the self–discharge rate at the Ni electrode is proportional to the partial hydrogen pressure [10]. For this reason it is important that the hydrogen pressure inside the battery is kept as low as possible, i.e. to employ hydride–forming compounds which are characterised by a relatively low hydrogen plateau pressure. Again, according to Eqs. (12) and (14), the chemical energy stored in both the MH and Ni electrode is 'wasted' by a gas–phase shunt and can no longer be employed for useful energy supply.

(iii) A third self–discharge mechanism is related to the fabrication process of a sintered–type Ni electrode. In this case these solid–state electrodes are prepared by the electrolytic reduction of an acidic salt electrolyte, often $Ni(NO_3)_2$ [1,11]. During this process NO_3^- ions are reduced to NH_4^+ ions. This results in a significant increase in pH near the electrode/electrolyte interface. The solubility product of $Ni(OH)_2$ will be exceeded and, as a result, $Ni(OH)_2$ will subsequently precipitate on the substrate. A consequence of this process is that, despite the fact that the as–prepared electrodes are thoroughly washed after preparation, a certain amount of nitrate ions are inevitably incorporated in the Ni electrodes, which can be leached out during the battery cycle–life. These NO_3^- ions, dissolved in the electrolyte, form the basis of this third self–discharge mechanism. These ionic species can be reduced to lower oxidation states [11]. It is generally assumed that a so–called nitrate/nitrite shuttle is operative in alkaline rechargeable batteries [12]. The standard redox potential of the nitrate/nitrite redox couple [11] is much more positive than that of the MH electrode ($E_{NO_2^-/NO_3^-} = -91mV$ vs Hg/HgO, see also Fig. 2). This implies that NO_3^- ions delivered by the Ni electrode can be reduced at the MH electrode under open–circuit conditions, according to
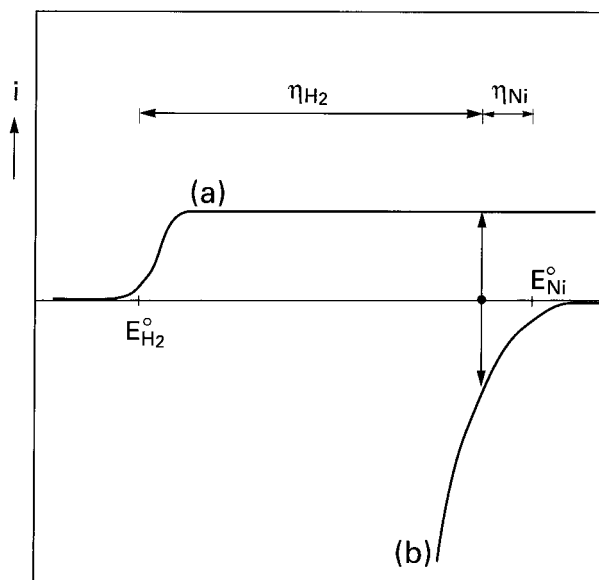

Figure 9. Schematic representation of the "hydrogen gas phase shunt" occurring during self–discharge inside a NiMH battery under open–circuit conditions. The hydride stored in the MH electrode is inevitably in equilibrium with hydrogen in the gas phase. H_2 gas can be oxidised at the Ni electrode (curve (a)) at positive potentials where NiOOH is simultaneously reduced (curve (c)). The oxidation current is shown to be diffusion–controlled, resulting in an anodic current plateau. It has indeed been shown that the self–discharge rate is proportional to the partial hydrogen pressure inside NiMH batteries.

$$MH$$
$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (15)$$

$$MH + OH^- \rightarrow M + H_2O + e^- \qquad (16)$$
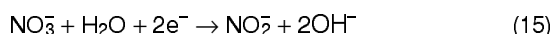
These reactions are schematically indicated in Fig. 10 by curves (a) and (b), respectively. The produced nitrite ions can diffuse to the Ni electrode. As the electrode potential of the Ni electrode is more positive than the standard redox potential of the nitrate/nitrite couple, NO_2^- can be reconverted to nitrate (curve (c) of Fig. 10) while NiOOH is simultaneously reduced (curve (d)), according to

$$Ni$$
$$NO_2^- + 2OH^- \rightarrow NO_3^- + H_2O + 2e^- \qquad (17)$$

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \qquad (18)$$
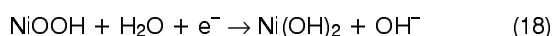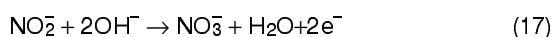
This reaction sequence can proceed continuously because the electroactive nitrate and nitrite species are continuously produced at both electrodes and are not effectively consumed. The final result is again that the charge stored in both the MH and Ni electrode is consumed and is no longer available for useful energy supply.

BATTERY CHARACTERISTICS

As described in the previous section, the sealed rechargeable NiMH battery is a technology with characteristics similar to those of the sealed NiCd battery. The MH electrode has almost the same potential, but has a significantly higher energy density compared to that of the cadmium electrode. Therefore NiMH batteries combine a compatible voltage with a higher storage capacity. A closer look will, however, reveal other differences and both types are therefore not always interchangeable.

Evidently, one of the most crucial characteristics of batteries is its energy content or capacity. This is, however, not a simple device property because the battery capacity depends on many parameters such as battery system, battery type, size, history and (dis)charging conditions. For example, the battery voltage depends strongly on these latter conditions. Consequently, an average voltage is used to compare the energy density of different battery systems in Wh. It is, however, more common to use the amount of stored charge (mAh) as a measure for the battery capacity. In the following sections various battery characteristics, such as battery type, (dis)charging conditions, storage and cycle life will be considered in relation to this storage capacity. All these parameters influence the capacity. Consequently, different batteries can only be compared under identical operating conditions. Most values in catalogues are therefore determined under more or less standardized conditions at 20 or $25^\circ C$ and at a 0.2C discharge rate.
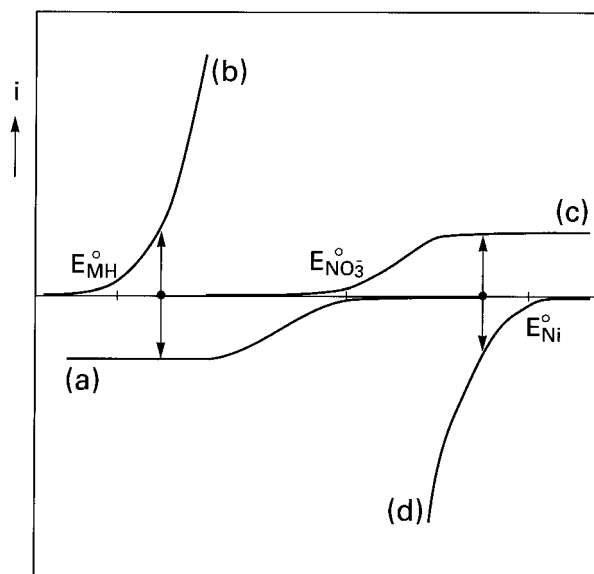

Figure 10. Schematic representation of the so–called nitrate/nitrite (NO_3^-/NO_2^-) shuttle which takes place in the electrolyte phase. This "electrolyte shunt", induced by leaching out the Ni electrode, starts with NO_3^- reduction at the open–circuit potential of the MH electrode (curve (a)), at which the stored hydrogen is simultaneously oxidised (curve (b)). The produced NO_2^- ions are transported and converted again to NO_3^- (curve (c)) at the Ni electrode which itself is reduced (curve (d)).

Battery type

The storage capacity of NiMH batteries depends on both the applied technology and battery size. A larger size induces a relatively high storage capacity, due to the more favorable ratio between the active and inactive materials, such as the battery casing. The technology determines the total battery performance and is obviously related to the chemistry and morphology of the applied electrodes. Different technologies are adopted for different fields of application. In addition to the general standard type, special types have been developed. These are, for example, optimized towards a high storage capacity, a high or low temperature performance or to resistance against overcharging. This has, among other things, been realized by applying different kinds of electrodes, e.g. pasted–, sintered– or sponge metal–type electrodes. The battery performance is, for example, also affected by the capacity ratio between the positive and negative electrode and the amount of electrolyte.

Table II shows an overview of the storage capacity of different types of NiMH batteries produced by the same manufacturer. The bold figures clearly reveal the effect of the increasing energy density with increasing battery size. This table also shows the sometimes pronounced differences between cells of the same size, as can be explained by the application of various battery technologies.

Table 2. Dimensions, capacity and energy density of various types and sizes of NiMH batteries [13]. The bold numbers refer to the standard type NiMH batteries of different size.

Type	Diameter [mm]	Length [mm]	Capacity [mAh]	Energy density [Wh/kg]	[Wh/l]
AAA	10.5	44.5	590	**59**	**184**
AAA	10.5	44.5	640	59	199
L–AAA	10.5	50	700	60	194
L–AAA	10.5	50	740	59	205
LL–AAA	10.5	67	1000	67	207
4/5 AA	14.5	43	1220	64	206
4/5 AA	14.5	43	1720	67	212
4/5 AA	14.5	43	2040	77	251
AA	14.5	50	1180	54	172
AA	14.5	50	1350	**62**	**196**
AA	14.5	50	1580	73	230
L–AA	14.5	65	1850	65	207
A	17	50	2200	**69**	**233**
L–A	17	67	3800	84	300
Fat – A	18.2	67	4500	90	**310**

Different suppliers may apply different technologies for their "standard cells", resulting in quite a variation in performance. A careful selection of the best cell for a distinct application is therefore of essential importance. Even a similar, dedicated, battery type of a different brand does not automatically show the same performance. It is therefore not always sufficient to rely only on the specification data for the proper selection of batteries for a specific application. More important are the actual conditions at which the batteries are aiming to operate, as will be outlined in more detail below.

Charge

It is obvious that the available discharge capacity of a battery is determined by the amount of charge that has been effectively stored during previously charging. The most common charging method for NiMH batteries is constant current charging. The current must, however, be limited in order to avoid an excessive rise of temperature and/or internal gas pressure (see Fig. 5). This means that severe overcharging has to be terminated by a reliable end–of–charge detection. The most commonly applied method is based on the voltage drop (–ΔV) induced by the temperature increase during overcharging [14]. Fig. 11 shows the impact of the charging current on the overall battery voltage at ambient temperature. According to kinetic considerations, the battery voltage is indeed expected to increase with increasing currents not only in the "Ni region" at low depth–of–charge (DOC), but also in the "oxygen region" at high DOC. The transition between these two regions is somewhat dependent on the charging current in that it is shifting towards lower DOC when the current is increased, making the competition
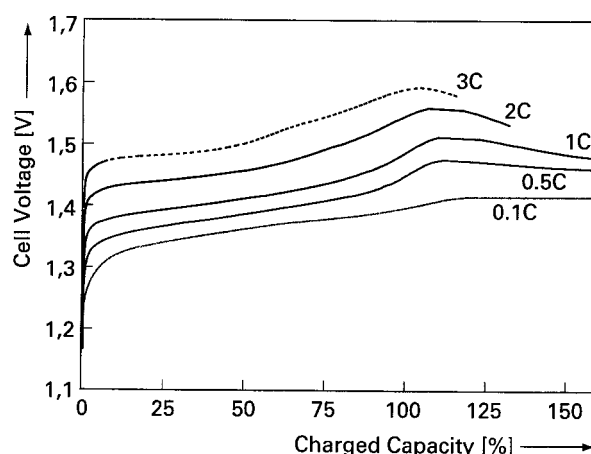

Figure 11. Cell voltage vs. time during the charging of NiMH batteries at 25°C applying various charge rates.

between the Ni and O2 reaction more severe. Furthermore, it should be noted that the –ΔV effect is much more pronounced at higher currents, resulting from a higher heat production. This is in agreement with the relationship given in Eq. (5).

Figure 12 shows the effective capacity built–up of an empty cell during charging with a 2C–rate at 25°C. A linear dependence between the effectively stored electrical energy (capacity) and depth–of–charge is found up to 85 % DOC, indicating that the charge efficiency remains close to 100 % in this region. Subsequently, the charge efficiency drops drastically, as the considerable deviation from the straight (dashed) line indicates, resulting from the occurrence of the competing oxygen reaction. Consequently, a lot of extra time is necessary to fully charge the battery, i.e. to charge the upper 15 % of the nominal storage capacity.

Determining the actual charge efficiency at any moment delivers a nice tool to judge batteries of different types under various charging conditions [15].
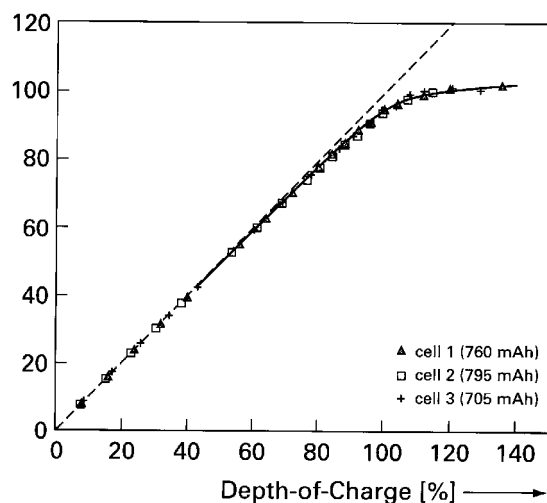

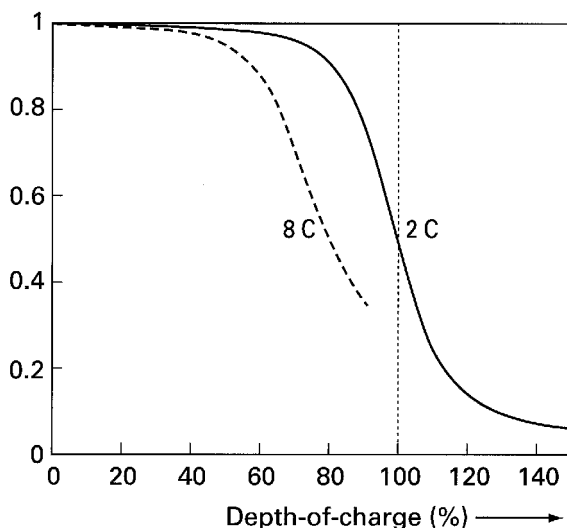*Figure 12. Capacity build–up vs. depth–of–charge of a battery during 2C–rate charging at 25°C.*

Figure 13. Actual charge efficiency at different charge rates at 25°C.

The actual charge efficiency is depicted in Fig. 13 during the charging of the same cell at different rates. This figure indeed clearly reveals the stronger competition of the oxygen reaction at high charge rates and the impact on charge efficiency. The solid curve obtained at a 2C–rate indicates that the charge efficiency drops very sharply close to 100 % DOC. Evidently, this situation is highly preferred. However, the actual charge efficiency does not drop to zero later on, which explains why the capacity still increases during prolonged overcharging (some modification changes of the Ni electrode very likely also contribute to this further capacity increase [1,2]). The integrated area below the curve represents, in fact, the electrical charge effectively stored in the form of electrochemical energy, while the integrated area above this curve reveals the ineffective amount of charge that has been converted into the oxygen side reaction. The dashed curve, obtained at an 8C–rate, is significantly shifted towards lower DOC, revealing that high current charging is only effective up to 50 % DOC for this battery. Switching to a lower current in this DOC region would, consequently, result in a much more efficient charging algorithm.

Cells of various suppliers may behave differently, due to variations in applied technologies. An example with respect to charging efficiency obtained at 45°C is shown in Fig. 14. Batteries of vendor A (solid line) clearly show a much more favorable efficiency than that of vendor B (dashed line). Although the applied current is not extremely high, the oxygen evolution reaction already starts to occur in the very early stages of charging for the vendor B battery. Obviously, this is always undesirable.

Increasing the charge temperature obviously favors the kinetics of both the oxygen reaction and Ni reaction [1]. This can be recognized by the reduced voltage levels in Fig. 15. More remarkably, Fig. 15 shows
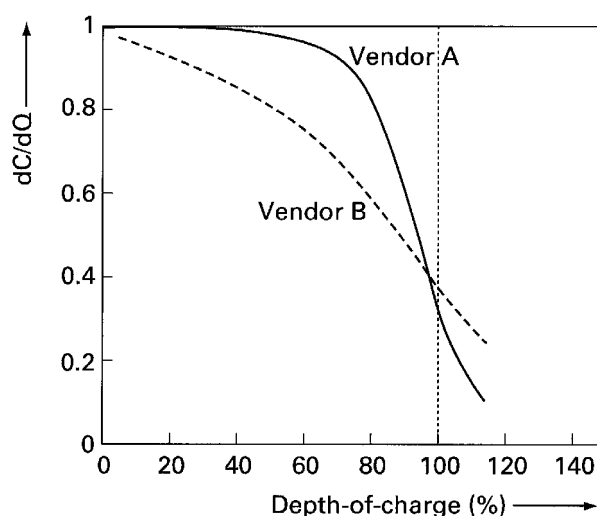

Figure 14. Actual charge efficiency of batteries from different suppliers at a 2C–rate charging at 45°C.

that the difference between the Ni– and oxygen voltage level is significantly reduced at higher temperatures to become almost absent at temperatures above 45°C. This must be attributed to the fact that the kinetics of the oxygen reaction are even more enhanced than those of the Ni reaction [9], implying that at higher temperatures oxygen evolution already starts at a lower DOC. The transfer from the main storage reactions to the overcharging reactions will be more gradual then and will be smeared out over a longer period of charging time. In the ultimate case (e.g. at 60°C) it is even impossible to 'fully charge' aqueous battery systems due to this competition.

The charging behavior of NiCd and NiMH batteries, particularly as far as fast charging is concerned, shows quite some differences. In contrast to NiCd batteries, NiMH batteries are less tolerant to overcharging and require a much more accurate
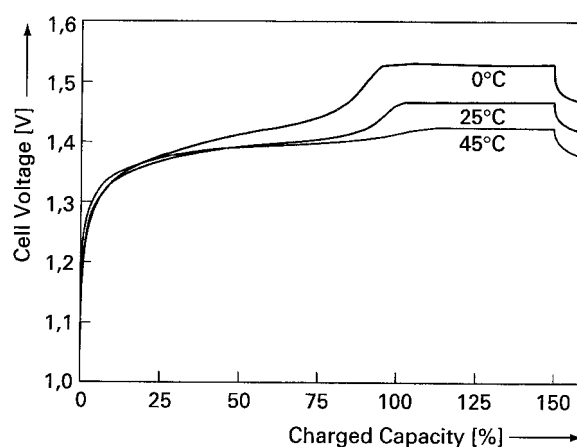

Figure 15. Cell voltage vs. time for NiMH batteries during charging (0.2C–rate) at various temperatures.

charging control. This is related to the difference in chemistry of the two negative electrodes. The Cd electrode reaction is endothermic, whereas the MH electrode reaction displays an exothermic behavior. Hence, the battery temperature remains relatively constant for NiCd batteries as long as the oxygen reactions are negligible whereas NiMH batteries already start to heat up in an earlier stage of the charging process. Apart from the thermodynamic contribution (see Eq. (5)), kinetic differences may additionally contribute to the different temperature behavior.

Discharge

The capacity of a NiMH battery depends strongly on the conditions. Very important are the rate of discharge and the ambient temperature. Parameters like cutoff voltage, cycle life and general cell condition have a minor effect. In general, the NiMH does not show the very high rate performance of the NiCd batteries. This can, on the one hand, be explained by the higher absolute values of the discharge currents used for the NiMH system (C–rates are a measure relative with respect to storage capacity, which is significantly higher for NiMH) and, on the other hand, by the difference in technology. The influence of the discharge rate is shown in Fig. 16. As for every battery system, energy is lost in two ways during battery use. In the first place there is a 'virtual loss' in discharge capacity, which is fairly limited up to currents of 1 A. The term virtual means that the capacity is not really lost but is inaccessible at high currents. Secondly, further energy is lost by the drop of the discharge voltage with increasing currents, which may becomes very pronounced at high currents (Fig. 16).

These effects are further accentuated at lower temperatures, as is depicted in Fig. 17. The combination of high discharge rate and low temperature, boost the virtual capacity loss. Note the increasing effect of the cutoff voltage level at higher discharge rates, particularly at low temperatures. An arbitrary cutoff voltage level of 1
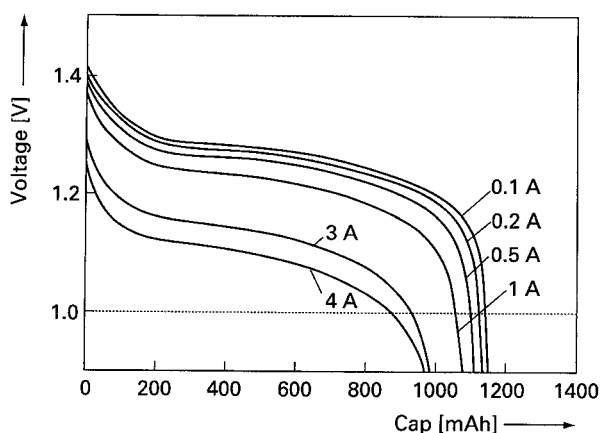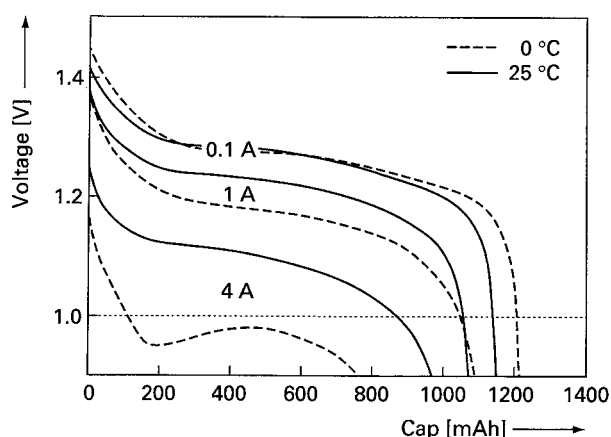

Figure 17. Influence of the discharge current and temperature on the cell voltage and cell capacity for an AA–size NiMH battery.

V is adopted in Fig. 17 and shows that it makes quite some difference for the discharged capacity whether one discharges at 25 or 0°C, especially at a high drain current of 4 A.

An overview of the discharge–ability of both NiMH and NiCd batteries is shown in Fig. 18. These data were measured some while ago in our laboratory, but the general view is still valid for improved, present–day, batteries. The high discharge capacity of NiMH batteries is shown to decrease more sharply under high–rate current conditions than for corresponding, equally–sized, NiCd batteries. The turning point, at which the discharge capacity becomes lower than that of NiCd, lies around a 4C–rate at 25°C. As expected, this is further accentuated at lower temperatures making, at present, NiCd still more favorable than NiMH batteries for high drain appliances, like power tools. The real energy losses can be even higher, due to the additional voltage losses (see Figs. 16 and 17).

The discharge voltage level is very important for the power consumption of an appliance. This level is not

Figure 16. Influence of the discharge current on the cell voltage and cell capacity for an AA–size NiMH at 25pC.
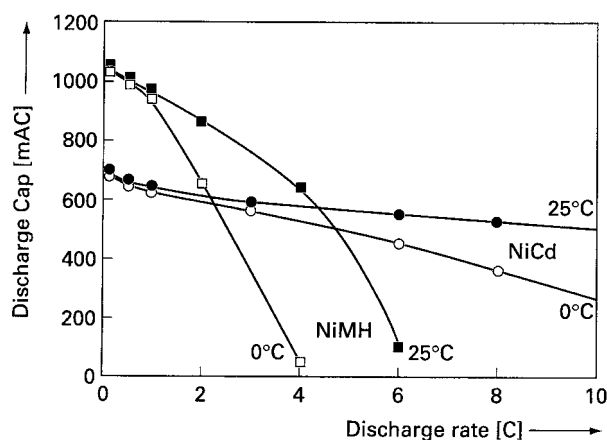

Figure 18. Comparison of capacity delivery for an AA–sized NiMH and NiCd battery as a function of discharge rate at 0°C (open symbols) and 25°C (filled symbols).

stable. Nowadays, electronics are specially designed for low power, i.e. to exploit the battery voltage as much as possible. Hence, the shape of the discharge curve of different battery types is important to enable the use of various battery systems with the same electronic circuitry. At present, the main small rechargeable batteries are NiMH and Li–ion. Most Li–ion systems are nowadays based on negative electrodes, using graphite as the intercalation material for Li ions. Sony, one of the world's major suppliers of Li–ion batteries, also employs carbon as the intercalation material in its negative electrodes. The discharge curves of both Li–ion systems and NiMH are depicted in Fig. 19. The discharge voltage has been normalized to show the very good voltage compatibility of the graphite–based, 3.8 Volt, Li–ion system and the 1.25 V–based NiMH system. Interestingly, using 3 NiMH cells in series leads to the same voltage level as a single Li–ion battery. The discharge profile of the Li–ion system with carbon shows a different shape, which makes it less compatible. Furthermore, it is worthwhile to note that the operating voltage of many present–day electronics has the tendency to decrease strongly. Obviously, it is easier to use NiMH batteries than Li–ion batteries to adjust the battery pack voltage to the required electronic voltage.

Self–discharge

The capacity of NiMH batteries decreases in time during storage due to self–discharge. As outlined in the previous section self–discharge is caused by several mechanisms. Besides the mentioned electrochemical origins, the type of separator is, in addition, also very important. All these effects contribute to the observed differences in self–discharge rates of batteries from different suppliers. The self–discharge rate decreases exponentially in time and depends strongly on the temperature [9]. The higher the temperature the greater the rate of self–discharge. This is illustrated in Fig. 20.

In general long–term storage in either the charged or discharged state, does not have a detrimental effect on the storage capacity. The capacity losses, due to self–discharge are therefore, in principle, reversible and batteries can recover to full capacity by recharging them. Full recovery, however, may take a few cycles. Nevertheless, permanent damage during storage can arise when cells are overdischarged for a long period of time, i.e. in the 0 V region (see Fig. 7).

Cycle life and Battery life

The capacity of NiMH batteries is affected by repeatedly cycling. The cycle life is governed by the conditions under which they are charged and discharged. The end–of–life of a battery is defined as the number of charge/discharge cycles until the capacity has decreased to a certain pre–defined percentage. Besides the cycling dependence, the capacity of a battery depends also on its actual calendar life. Important parameters for cycle life and/or battery life are:
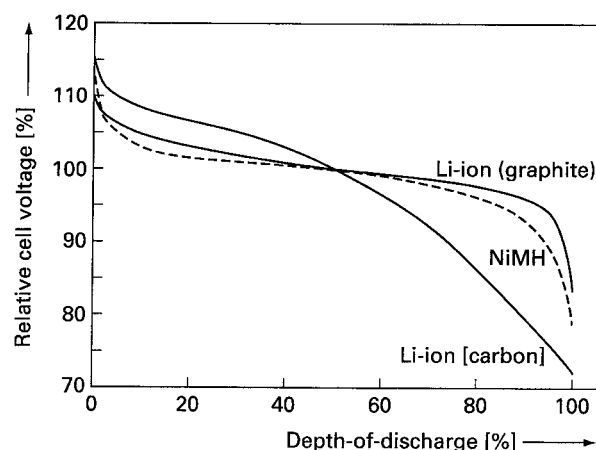
Figure 19. Comparison of the normalized discharge voltage of two types of Li–ion batteries and a typical NiMH battery at 25°C.

(i) Charge and discharge current; (ii) Temperature during charge and discharge; (iii) Depth–of–discharge (DOD); (iv) Exposure to overcharge and overdischarge; (v) Calendar life and storage conditions. Typically, under proper conditions of use, about 500 cycles can be easily achieved while the battery still delivers at least 80% of its rated capacity. An example of a charge–discharge (0.2C rate) cycle life experiment at room temperature is shown in Fig. 21.

The capacity is gradually reduced, due to an increase of the internal resistance caused by irreversible changes in the electrodes and loss of electrolyte. These phenomena may differ somewhat from one cell to another and explains the spread in the data in Fig. 21. Optimum life will, in general, be achieved at room temperature. At extreme temperatures, the detrimental effects will be stronger. Particularly, operation at high temperatures during (over)charging, may cause high internal gas pressures, resulting in cell venting. Opening of the vent means releasing gas and loss of electrolyte. Moreover, at high temperatures, deterioration of the separator and other materials will be accelerated. On the
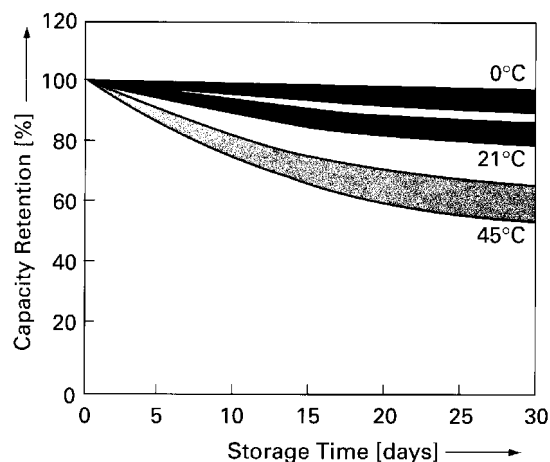
Figure 20. Self–discharge characteristics of a NiMH battery at various temperatures [16].
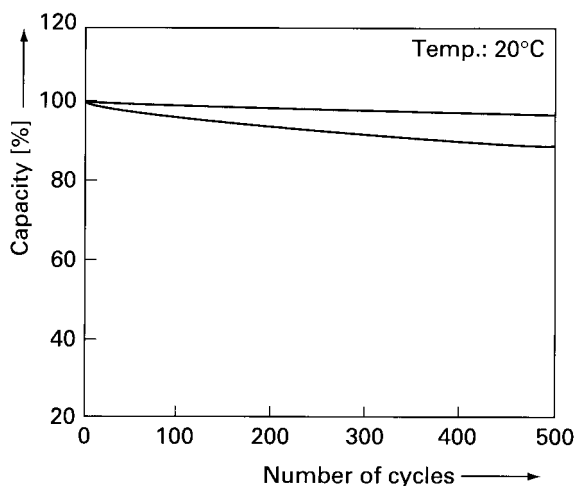
Figure 21. Cycle life of NiMH batteries at ambient temperature [13].

other hand, low temperatures will slow down the oxygen recombination reaction. Hence, overcharging may easily lead to a high gas pressure built–up.

Similar causes diminish cycle life at high charge rates and high amounts of charge input. Again, the oxygen recombination will not be able to prevent high gas pressures. Additionally, the temperature will rise to a 'damaging' level. The more effective the method to enable the prompt termination of fast charging when deleterious overcharging starts, the longer the cycle life will be.

The data in Figure 21 represent full charge/discharge cycles, i.e. cycling between 0 and 100% of the available capacity. Cycling with less than 100% will extend cycle life proportionally or even beyond. Considerably higher cycle lifes will be obtained with shallow charge/discharge cycles, assuming that severe overcharging and deep–discharging are avoided. The cumulative charged/discharged capacity will go beyond that of full capacity cycling.

Battery life is affected by the same factors as the cycle life, because they are based on the same phenomena. Summarizing: Optimum battery life will be achieved when operating and storing at room temperature and avoiding extreme (over)charge or (over)discharge conditions.

Miscellaneous

NiMH batteries are sealed and can therefore be used in any operating position. They are reliable and maintenance–free under the condition that they are not abused and are applied in accordance with the recommended procedures prescribed by the manufacturer. Furthermore, it is desirable to keep them clean and dry during storage.

When the internal gas pressure rises due to overcharge, short–circuiting, reverse charge or other

misuse, the self–resealing vent is activated to prevent any serious mechanical damage. An example of the activation of the safety vent during overcharging is depicted in Fig. 22.

Safety is generally not a big issue for NiMH batteries under normal operating conditions and will be limited to venting and temperature rise. The chemical nature of NiMH batteries forces the composition of the vented gas to be a mixture of hydrogen and oxygen. Depending on the compositional ratio of this mixture an explosive situation might occur when, in addition, the batteries are in direct connection with an ignition source. Disadvantageously, once the batteries have been
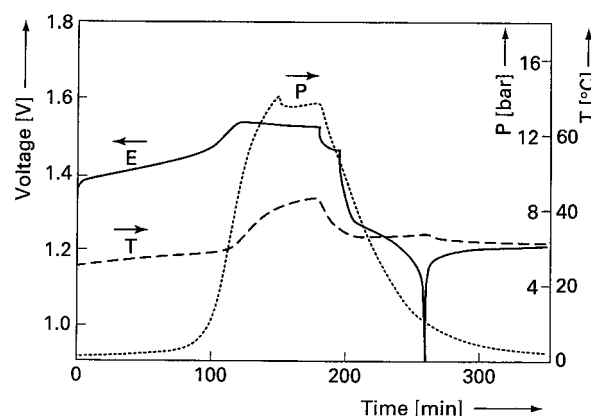

Figure 22. Typical example of the opening of the safety vent at higher pressures for a NiMH battery during prolonged overcharging.

opened and have vented gas and accompanying electrolyte, a white powder will be formed on top of the battery after a while. This is due to crystallized alkaline electrolyte (mainly KOH), which remains after water evaporation. Evidently, this holds for all aqueous battery systems. This powder is rather aggressive for metals and skin during prolonged contact.

A well–known 'problem' for NiCd batteries is the so–called memory effect. This phenomenon is related to a voltage drop, causing a (virtual) capacity loss and results from repetitive cycling of only partially discharged batteries. During the first subsequent full discharge cycle, the voltage of the previously uncycled material is observed to be depressed compared to the standard voltage curve. This voltage drop has been explained by changes of the physical characteristics, which results in an increase of the resistance of that part of the electrodes that remained 'uncycled' and has been kept for a long period of time in the charged state. A relatively high overvoltage is experienced when this part of the electrodes is discharged, which, consequently, results in an extra voltage drop. This problem also arises for NiMH batteries, but to a lesser extent than NiCd since no cadmium is involved. It should be emphasized that this is just a temporary capacity loss, because it is a reversible phenomenon and that the full capacity will be
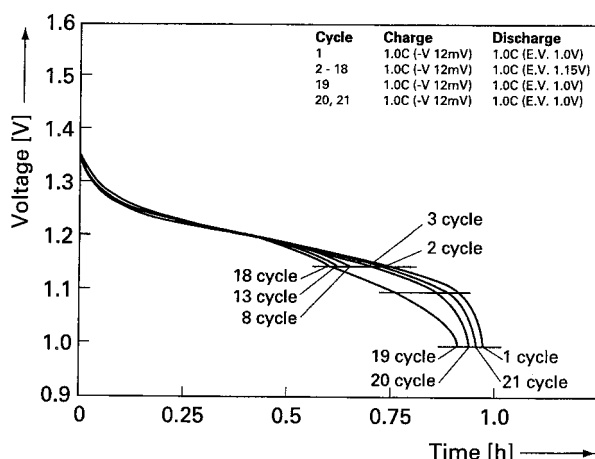
Cycle	Charge	Discharge
1	1.0C (-V 12mV)	1.0C (E.V. 1.0V)
2 - 18	1.0C (-V 12mV)	1.0C (E.V. 1.15V)
19	1.0C (-V 12mV)	1.0C (E.V. 1.0V)
20, 21	1.0C (-V 12mV)	1.0C (E.V. 1.0V)

Figure 23. Voltage drop and voltage recovery of a NiMH battery, caused by partial charge/discharge cycling [14].

restored after a few full charge/discharge cycles. Fig. 23 clearly illustrates the memory effect on the discharge voltage and the recovery to the original discharge curve. Consequently, a regular full discharge is good advice to keep the battery in good shape.

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Peter Notten

Peter Notten was born in The Netherlands in 1952 and joined the Philips Research Laboratories in 1975. While working at these laboratories on the electrochemistry of the etching of III-V semiconductors he received his PhD from the Eindhoven University of Technology in 1989. A book on this subject was published in collaboration with two co-authors. Since 1989 his research activities have been focussing on the research of hydride-forming electrode materials for application in rechargeable NiMH batteries and switchable optical mirrors. Nowadays his interest also includes modeling of various types of small rechargeable batteries. Recently, he has been appointed as part-time professor in 'electrochemical energy storage' at the Eindhoven University of Technology.

René van Beek

René van Beek was born in the Netherlands in 1945. After his education in chemistry, he joined the Philips Research Laboratories in 1967. He was concerned with several subjects in the fields of photochemistry and electrochemistry, i.e. micro-photographic systems, electroless metallisation and electrochemical machining. Later his interests changed to battery materials. After investigations on the rechargeability of the Li-metal electrode, he was involved in the invention of the multicomponent AB5-type metal-hydride materials, which made the NiMH batteries feasible. His current work is in the application of conventional and new type small rechargeable batteries.

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