

Substitution of rechargeable NiCd batteries

**A background document to evaluate the possibilities of finding
alternatives to NiCd batteries**

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4. Background material from MOLTECH explaining different positive electrode technologies, Ni-foam vs. Ni-sinter substrates.
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Introduction en français

A peu près 2/3 de la consommation mondiale de cadmium (de l'ordre de 16 000 à 18 000 tonnes) est destinée à la production de piles de NiCd (Nickel Cadmium). Environ 3/4 de cette quantité sert à la production de petites piles modèle NiCd utilisé dans les caméscopes, appareils électroménagers, outil à moteurs, éclairage de secours etc. La quantité restant, 1/4, est prévue pour la production de grandes piles industrielles utilisées au premier lieu dans des systèmes de secours de puissance stationnaire ou véhicules.

Vu l'important croissance rapide du marché radio téléphonique et du marché d'ordinateur portable, l'industrie des petites batteries est actuellement en développement sans cesse. Le nouvel chimie de batterie, Nickel-Metal Hybride, (NiMH), et Lithium Ion, (Li-ion), ont été introduit respectivement en 1991 et en 1993. L'augmentation de la demande de piles, de 1 billion en 1990 à 2.5 billions en 2000, a été fournie par des piles de nouvel chimie de batteries. La future génération d'application d'Internet mobile va renforcer cette croissance de la production de batteries rechargeables.

Malgré le fait qu'il y a une grande demande de batteries, l'augmentation des facilités de production a mené, pour certaines tailles de piles, une surproduction et une baisse de prix rapide. Si on considère seulement les piles le plus standardisés, c'est à dire ceux qui sont produit en grande quantité, les prix de Wh pour des piles de NiCd, NiMH et Li-ion se sont devenus plutôt similaires pendant l'année passée. L'origine de ce phénomène est la restructuration globale de l'industrie de batterie produisant des piles de taille de consommateurs.

En Japon, les batteries rechargeables sont aujourd'hui considérées comme des composantes stratégiques parmi leurs plus grandes groupes industrielles : Matsushita, Sanyo, Sony, Toshiba, qui produisent une grande quantité de l'équipement portable mondial tel que caméscope, la téléphonie sans fil- et portable, ordinateur portable etc. Cette politique, renforcé par des programmes de recherche nationaux soutenant le développement des nouvelles batteries supportées par le Ministère de Commerce et d'Industrie, MITI, a engendré une dominance japonaise totale dans la production des piles de consommateurs rechargeables de NiCd, NiMH et Li-ion.

La compétition entre les producteurs japonais de piles a provoqué une chute de prix pour tous les modèles de batteries, en particulier des nouveaux modèles de batterie, NiMH et Li-ion.

En comptant le nombre, les piles NiCd reste toujours le modèle dominant globalement, néanmoins lorsque le prix des nouvelles batteries sera réduit une majeure substitution est probablement à prévoir.

L'essentiel au début du développement de NiMH et Li-ion était de créer des batteries de grande capacité destinée à des téléphones mobiles et des ordinateurs portables. Dans ce domaine l'usage de NiCd est aujourd'hui marginal.

En considérant le volume des modèles NiMH et Li-ion ont chacun la double capacité par rapport à NiCd. Li-ion qui est plus légère que NiMH a en plus l'avantage de sa légèreté, 30%, par rapport à NiMH.

En considérant la capacité, ces piles sont inadéquates pour l'application des machines-outils.

Dans ce domaine NiCd est toujours la technologie dominante. Le développement de la performance grand puissance pour des piles de NiMH autant que Li-ion est pourtant déjà initié. NiMH sera la première. Déjà en 1997 le producteur des batteries américaine Moltech (précédent Energizer), en collaboration avec le fabricant japonais de machines-outils Makita, a commencé de commercialiser des machines-outils sans fil avec piles de NiMH. Une autre application de grande puissance se trouve dans des batteries destinées au véhicule électrique d'hybride, HEV. À la fin de 1997 Toyota a lancé le HEV "Prius" en utilisant relativement petite D-piles de NiMH pour l'accélération et rupture régénératrice. Les producteurs Sanyo et Toshiba ont également commencé de commercialiser des batteries de NiMH grande puissance.

Des pronostics japonais estiment que la production de piles de grande puissance de NiCd et NiMH sera comparable en 2006. Le marché de grande puissance sans fil augmente et donc une baisse plus accentuée n'est pas prévue avant 2006.

La réaction de piles de NiMH est plus simple que celle des piles de NiCd. La capacité de stockage de l'énergie de MH-électrodes est très supérieure de celle de Cd-électrodes. Quant au Ni-électrode celle-ci est équivalente dans les deux systèmes.

Ces circonstances sont favorables pour des améliorations de performance de NiMH piles, en comparant avec NiCd qui fait partie du groupe de piles de grande puissance. Makita a aujourd'hui des solutions de NiMH pour tous leurs produits de machines-outils sans fil.

Des batteries de machines-outils représentent aujourd'hui des applications les plus avancées de piles rechargeables. En outre le développement général de piles est actuellement caractérisé par un progrès remarquable. Les piles de NiMH ne sont pas uniquement introduites dans des marchés traditionnellement dominés par l'application de NiCd; éclairage de secours, système de UPS, jouets, appareils électroménagers et véhicules électriques, mais en plus dans des autres chimies de piles qui ont été commercialisées. Li-ion et Li-polymer ont été utilisés pour construire des prototypes de piles avec une performance améliorée.

Dans cette perspective la prohibition proposée, concernant la commercialisation de NiCd ou de produits qui contiennent des piles de NiCd dès 2008, établissait une situation favorable pour la transition des alternatives qui seraient déjà disponibles au marché à ce moment-là.

Une date plus récente pour des produits de grand volume utilisant piles de NiCd, comme décrit dans cette étude, serait probablement plus efficace. Uniquement des cas exceptionnels, comme pour des systèmes d'alimentation de secours de l'hôpital et de l'application aéro-électronique, des situations qui légalement exigent un processus des vérifications pour des nouveaux produits, une durée plus longue est nécessaire.

Conclusion en français

L'industrie de batteries rechargeable est pour le moment sous l'effet d'une transformation rapide. Traditionnellement cette industrie est composée par des producteurs de batteries d'acide de plomb et de NiCd européens et américaines. Au cours des années la concurrence a provoqué des fusionnements d'industries de batteries, des industries national auparavant indépendants sont maintenant regroupés en quelques industries globales.

Pendant la dernière décade trois nouvelles batteries, NiMH, Li-ion et Li-polymer ont, néanmoins été commercialisé par des entreprises japonais au marché de batteries portables de consommateurs. Le marché a progressé de 800 millions piles de NiCd en 1989 à plus de 2500 millions piles de NiCd, NiMH et Li en 1999. Cette expansion a été provoquée par des applications portables, principalement téléphones et ordinateurs portables, une tendance qui va continuer.

Les entreprises japonaises produisant des batteries sont devenues totalement dominantes pendant cette expansion, ils fournissent aujourd'hui la majorité de la nouvelle technologie de batterie. En outre, ils dominent aussi la production correspondant de NiCd. Le volume de production de NiCd a resté relativement stable depuis 1995, l'expansion du marché de batteries concerne principalement la nouvelle technologie de batterie comme la demande s'applique à des batteries de grande capacité.

La compétition des batteries de grande capacité a sans cesse réduit le prix de NiCd. La baisse a relativement été plus rapide entre les nouvelles technologies de batterie. Le prix le plus bas par Wh pour le moment est celui de piles de NiMH. Cette une tendance qui continue.

La technologie de NiMH a pendant les dernières cinq années aussi adapté avec succès à des batteries de grande puissance pour des véhicules électrique d'hybride. À la fin de 1997 Toyota a introduit le véhicules électrique d'hybride "Prius", chacun avec des piles de 240 NiMH, taille D en séries, ce qui est une application très avancée. Ayant produit plus de 30 000 automobiles pour le marché domestique au Japon, "Prius" sera introduit cette année au marché américaine et européenne. Une application de batteries de NiHM dans les véhicules à grande échelle favoriserait une réduction de prix. La compétition de Li-ion, application de grande capacité, substituerait NiCd a faveur de NiMh dans des applications typiques de NiCd.

Des prix plus bas de NiMH, en ayant une performance au même niveau où meilleure que NiCd dans des domaines de machine-outil et systèmes de d'éclairage, des applications où NiCd domine et la plus par de la production totale est destinée, vont accélérer la substitution.

L'avant garde dans ce domaine est Moltech, USA et Toshiba Batteries au Japon. La durée de transition sera, pourtant, dépendant des soucis de l'environnement des consommateurs et des actions de règlements comme prélèvements et/ ou prohibition concernant l'utilisation de cadmium. Des changements législatifs sont observés avec l'attention par les producteurs de batteries qui sont en train de commercialiser des piles de NiMH sur le marché de NiCd. D'une part le premier producteur sur le marché aura l'avantage d'être présent pendant la transition, d'autre part le lancement d'un produit un peu

modifié sur une grande échelle est très cher. Si le marché s'adapte lentement on risque de mettre en danger l'existence de l'avant garde.

L'extraction totale de cadmium est plus grand que l'approvisionnement à la production de batteries. Comme cadmium est un sous-produit de l'extraction de zinc, le coût n'a presque aucune importance.

Même si le coût du alliage d'hybride en métal aussi plonge, en particulière si des batteries de NiMH sera appliqué dans des véhicules, c'est pas clair quand le gain de capacité sera environ 30% par l'utilisation d' électrode de métal-hybride peut motiver le coût d'alliage en comparant le faible coût de cadmium.

Des soucis de l'environnement exprimé par les consommateurs de batteries est à cet égard une force d'échange qui influence les producteurs de batteries.

Des mesures pour augmenter la conscience des aspects environnementaux vont accélérer la transition d'application dans le domaine de machines-outils et d'éclairage de secours.

Puisque ces produits correspondent à la plus grande quantité restant d'approvisionnement de cadmium il y aura moins de motivation de résister une substitution de NiCd dans des autres applications.

Summary

Approximately 2/3 of the world consumption of cadmium (ranging between 16.000-18.000 tons during the last 30 years) is used for the production of NiCd (Nickel Cadmium) batteries. Of this about 3/4 are used in smaller-sized, sealed, consumer type NiCd cells for camcorders, household appliances, power tools, emergency lightning, etc. The remaining 1/4 is used for the production of large industrial cells mainly used in stationary and vehicular power backup systems.

With the advent of the rapidly increasing mobile phone and laptop computer markets the consumer size battery industry is undergoing substantial changes. The new battery chemistries, Nickel-Metal Hydride (NiMH) and Lithium ion (Li-ion) were introduced 1991 and 1993, respectively. The increased demand for cells, up from 1 billion 1990 to 2.5 billion year 2000, has mainly been covered by cells from the new battery chemistries. Future mobile internet applications will further support this increase of rechargeable battery production.

In spite of the large demand for batteries, increased production facilities have lead to overproduction of certain cell sizes and rapidly reduced cell prices. If only the most standardised cells, which are also produced in large quantities are considered, then the price per Wh (Watt hour) for NiCd, NiMH and Li-ion cells have become rather similar within the last year. This phenomenon has its origin in a major restructuring of the global battery industry producing these types of consumer size cells.

In Japan, rechargeable batteries have come to be considered as strategic components among its large industrial groups Matsushita, Sanyo, Sony and Toshiba, which produce a

large portion of the world's portable equipment such as camcorder, cordless- and mobile phones, laptop computers, etc. This policy, with the backing of R&D programs for developing new batteries supported by the Japanese Ministry of Trade and Industry (MITI) has led to a total Japanese domination in the production of rechargeable consumer size NiCd, NiMH and Li-ion cells.

Competition among the Japanese cell producers has continued to reduce the price of all these batteries but is most dramatic for the new battery types, NiMH and Li-ion.

If counted by cell numbers NiCd is still the dominant type of battery, world-wide but as the price of the new batteries comes down, an increased substitution by other types is likely.

The focus of the initial NiMH and Li-ion development was high capacity batteries for mobile phones and lap-top computers. Within this market the use of NiCd is today marginal.

On a volume basis both NiMH and Li-ion have approximately twice the capacity of NiCd. Furthermore, Li-ion being lighter than NiMH, has a weight advantage of about 30% over NiMH.

The focus on high capacity, however, makes these cells unsuitable for the use in power tool applications where NiCd still is the dominating technology.

Development of high power performance of both NiMH and Li-ion cells is, however, already made. NiMH was first. Already in 1997 the American battery producer Moltech(previous Energizer), together with Japanese power tool manufacturer Makita started to market cordless power tools with NiMH cells. Another high power application is batteries for HEV (hybrid electric vehicles) At the end of 1997 Toyota launched the HEV "Prius" using relative small consumer size NiMH D- cells for acceleration and regenerative breaking. Sanyo and Toshiba have started to market NiMH high power batteries, too.

Japanese forecasts estimate that the NiCd and NiMH power tool cell production will be of comparable sizes by 2006. The cordless power tool market is however also increasing and a more general decline in the NiCd production is not foreseen until after 2006.

The overall cell reaction of NiMH is more simple than that of the NiCd battery type. The electrical storage capacity of the MH-electrode significantly exceeds that of the Cd-electrode whereas the Ni-electrode is essentially the same in both systems.

This will make possible performance improvements of NiMH cells beyond those of NiCd a within the group of high power batteries. Makita has today NiMH solutions for all of their cordless power tool products.

Power tools batteries represent the most demanding applications of rechargeable cells. The present general battery development is exhibiting rapid progress, too. Not only have NiMH cells started to be marketed in other typical NiCd applications such as emergency lightning, UPS systems, toys, home appliances and electrical vehicles, but other competing battery types such as Li-ion and Li-polymer have also been utilised to make prototype cells presenting even further improved performances.

With this perspective the proposed ban on the sales of NiCd or products containing NiCd cells from 2008, would seem to offer a very wide margin for the transition to alternatives. For many products this would already have been done by then.

An earlier date for the large volume products currently using NiCd cells, as described in this study would probably be more effective. Only in a few exceptional cases, such as for example emergency power systems for hospital and avionics applications, which legally may demand a verification process for new products to be used, a longer time period will be needed.

Development of new rechargeable batteries

Rechargeable batteries have for most part of last century and thus through most of the modern industrial history meant lead acid batteries and NiCd batteries. Lead acid batteries from mid 19th century and NiCd batteries from the very beginning of the 20th century. Both battery technologies have constantly been developed and improved upon through the 20th century. Sealed smaller consumer sized cells were developed in the mid 20th century by General Electric.

The traditional battery industries tend to be fairly conservative establishments with a long history resting on an impressive amount of empirical knowledge. The fundamental understanding of the underlying rather complex atomistic processes in the electrode reactions has been slower to develop. It was not until the last decade's general advancements in material science that the situation was significantly improved upon.

This, in combination with an increased demand for improved batteries from the growing electronic industry, lead to a drastic change on the scene. Three new battery types were commercially introduced in large scale production during the last decade by the rapidly growing Japanese battery industries, namely the NiMH, Li-ion and last year Li-polymer batteries.

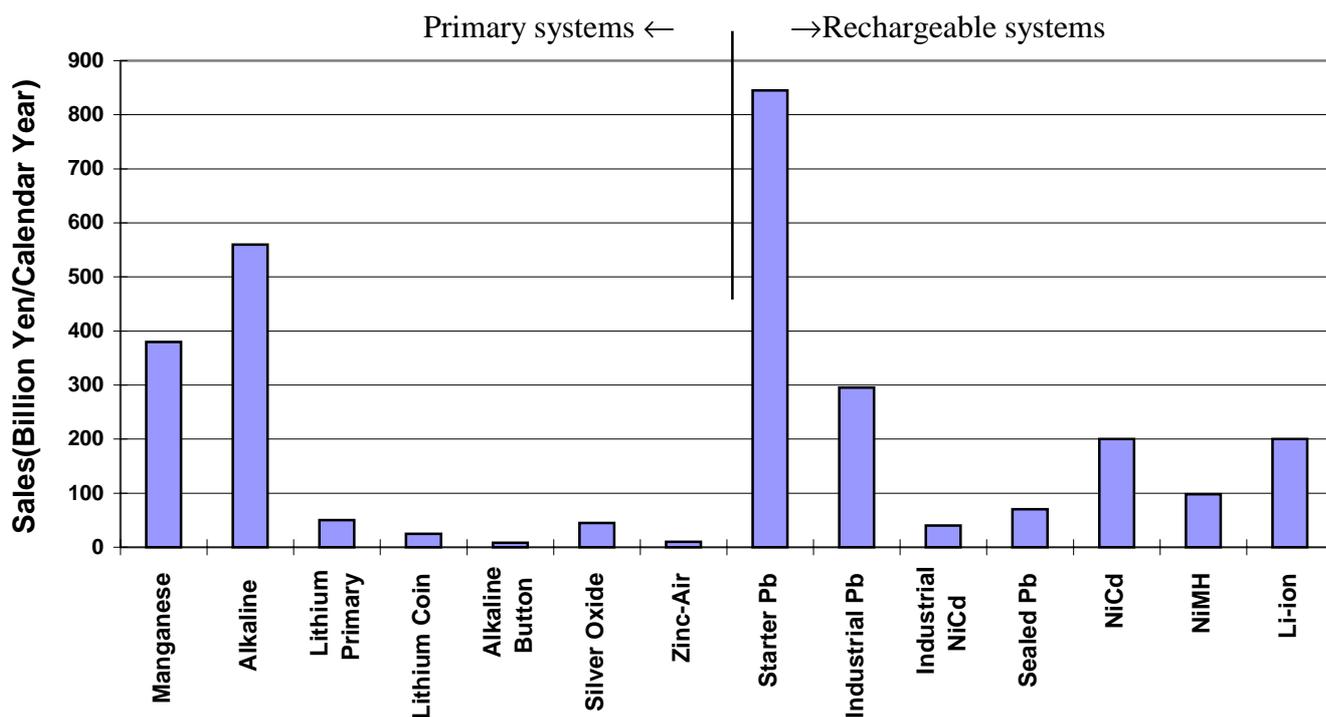


Fig. 1 . Global Battery Market for each cell type in 1997 (Nomura Research Institute) (1US\$≈105 Yen)

Rechargeable lead acid batteries dominate the global battery market with starter batteries for vehicles as the single largest application followed by industrial lead acid batteries mainly for power backup systems but also in traction applications. After this come the non-rechargeable battery systems. Manganese is referring to the older version with a zinc can as the negative electrode and a graphite rod immersed in a moist paste of

salmiac, manganese oxide and zinc chloride as positive electrode. They are also called zinc-carbon batteries. Alkaline is an upgraded version with a caustic electrolyte. These primary cells are what ordinary consumers are mainly exposed to. Primary cells are sold in almost any shop and after having been used and discharged the cells should be disposed of in a controlled manner. Even if recharging in some cases is possible, this is not recommendable because if the charging process is not carefully controlled and there is a high risk of explosion.

Next in the battery market are the rechargeable sealed consumer or portable size lead acid, NiCd, NiMH and Li-ion batteries, which are the main concern for the comparison made in this study. On this scale the industrial size NiCd battery market is rather marginal.

The lead-acid battery, being the starter battery for almost all vehicles, makes it by far the largest market for rechargeable batteries both by value and volume. Large production volumes and relative low material costs make lead acid batteries significantly cheaper. The other battery technologies are only able to compete by having a better performance in more demanding applications.

The importance of the NiCd battery, as will be further discussed below, has been reduced by the development of the new battery technologies, which all have superior storage capacities and are replacing NiCd batteries in an increasing number of applications. The NiCd technology is also under pressure from the cheaper but less robust lead acid technology, as intelligent systems for supervising charge/discharge are more sparing for the cells, making cheaper lead acid battery solutions possible to use for more demanding applications where NiCd was previously used.

At the OECD workshop on "sources of cadmium in the environment" held in 1995 in Stockholm about 11.000 tons of cadmium were reported to be used in the global NiCd production. About 3/4 or 8.500 tons were used in portable or consumer size cells (sealed NiCd). Only 1/4 or 2.500 of the cadmium for batteries is used for making larger industrial size NiCd cells. Recovery of cadmium from spent NiCd cells is almost solely made from the industrial size NiCd as effective recollection systems for the consumer size cells are still lacking.

For these NiCd cells a study on re-collection and recovery carried out (1986) under contract for the EEC and published by the Metra Consulting group forecasts the need for a recycling capacity of more than 1.000 tons of cadmium metal in the 1990's just for the Western European markets. The available recycling by the two companies SAFT (Sweden) and SNAM (France) was at most 350 tons of cadmium metal.

M. Scoullou presented similar number at the International EUPHEMET's (EU Policy for Heavy Metals), workshop in Athens in 17-18 April 2000. He reported the total mine production of cadmium to be around 20.000 tons and that the world consumption of refined cadmium to be somewhat floating, slightly increasing but for most of the last 30 years to be within 16.000-18.000 tons. For 1998 he estimated the world wide volume of recovered cadmium from spent NiCd to be 2.000 ton, which agrees well with the amount of cadmium used in industrial batteries.

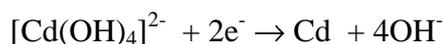
The total electrode reactions (sum of 1 and 2) can thus be described as two solid state intercalation reactions where the amount of electrolyte is constant during the reactions.

The present commercial hydrogen-storage alloy used in batteries is based on the LaNi_5 alloy family, developed by Philips Research Laboratory in Eindhoven. The typical commercial alloy composition is $\text{MmNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{Al}_{0.3}$. Mm stands for mischmetal, a mixture of rare earth metals mainly La, Ce, Nd and Pr all having similar chemical properties. They co-exist in the ore and are for cost reasons not separated when the metals are extracted. The composition varies depending on the source of the ore. Blending of mischmetal from different sources can occur to obtain the specified hydrogen storage properties, but usually the ratios of the other metals are varied to make this adjustment.

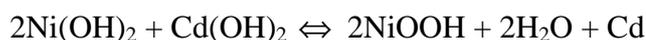
Philips Research Laboratories made two fundamental discoveries enabling the success of the NiMH batteries. First they found this specific family of hydrogen storage compounds. Secondly, they discovered how to slow down the rapid corrosion of the alloy in the alkaline battery electrolyte. The work has given Philips royalties from all the major battery producers but as will be discussed below, no significant European NiMH battery production has been started..

NiCd

The chemistry of the nickel electrode is the same as that in the NiMH cell. The cadmium electrode on the other hand is based on a dissolution/precipitation mechanism involving the intermediate formation of a dissolved specie, i.e. a metal ion complex, which precipitates to form a new solid phase as for example during charge:



The total reaction compared to the NiMH cell is:



The electrolyte not only serves as an ionic conductor, but also participates in the electrode reaction. The amount of electrolyte in the cell becomes dependent on the state of charge of the electrodes and this has to be considered in the design of electrodes and electrode porosity especially in sealed cells with a starved electrolyte.

Sealed cells have to be designed so that gas can diffuse between the electrodes to ensure proper recombination reactions (see below). This means that it is not possible to completely fill the cell with electrolyte. The amount of electrolyte has to be “starved” to ensure the passage of gases through the separator.

Furthermore, preferential crystal growth mechanisms in the dissolution/precipitation reactions may cause dendrites (so called “cadmium needles”) which cause internal shortcuts when they penetrate the separator in the cell. Preferential grain growth effects upon partial discharge cycling can also cause grain coarsening leading to the so called “memory effect” of NiCd batteries.

This phenomena arises when the cell is only partially charged/discharged over several cycles. The “unused” cadmium will undergo grain coarsening leading to a low active surface area of that part of the cadmium in the electrode. Thus the electrode will contain two fractions of cadmium. One fine grained with a high active surface area and one coarser with less. When the full capacity of the cell eventually is needed, a voltage drop will occur during the draining of the cell when the high surface cadmium is consumed. Some electronic appliances will interpret this as if the battery has run out and will switch off.

The performance of the cells can, however, be recovered if they are carefully cycled over a full charge/discharge cycle. For the non expert this is not recommended as the risk for destroying the cell pack by cell reversal is eminent. More sophisticated rechargers are, however, commercially available, which will automatically run through a reconditioning procedure when needed.

The basic NiCd chemistry is thus more complex than that of the NiMH cell and many years of development and continuous improvements lie behind the modern NiCd battery. Much of this is empirical “company know-how” and is suspiciously kept secret. This advantage for the established battery industry will partly lose its value as new battery technologies take over. The rapid success of the NiMH technology is much due to its simple chemistry that made its adaptation into a battery technology rather straightforward. Had the NiMH battery preceded the NiCd battery it is doubtful if the latter would have become anything else than a laboratory curiosity.

It is also worth mentioning that different NiCd cells have been developed for different applications putting different emphasis on for example high temperature or low temperature use. Cells have been modified so that either high power performance, or high capacity have been given priority. So far most of the NiMH development has been focused on high capacity but in recent years other types have been developed. Most of these modifications are made by altering the mechanical design, which will be further discussed below.

Mechanical design of sealed NiMH and NiCd cells

The electrodes in NiMH (and also in NiCd) consumer type cells are made as thin sheets (typically < 1 mm) of active electrode material on a conducting metallic substrate.

In cylindrical cells, as seen in Fig. 3, the electrodes are sandwiched together with a porous separator and coiled into a cylindrical complex, which is normally inserted into a standard size battery can. The negative electrode is electrically connected to the can. The positive electrode connects to the lid, which is electrically insulated from the can.

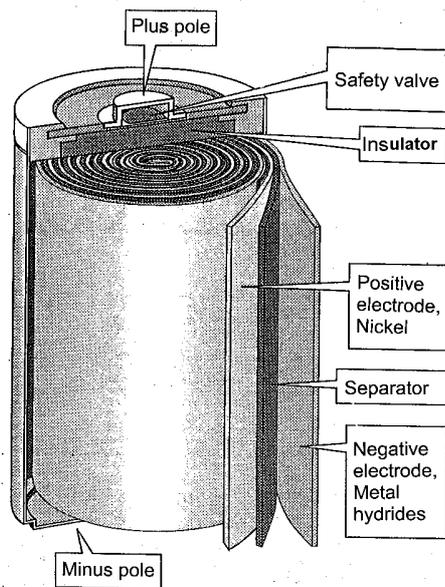


Fig. 3. NiMH and NiCd cylindrical cell.

Correspondingly, stacking alternating electrodes with an interjacent separator into a prismatic can, make prismatic cells. Positive and negative electrode plates are connected in parallel to each battery pole.

One advantage with cylindrical cells is that they can more easily be designed to withstand internal pressure build-ups. Prismatic cells on the other hand can be more effectively packed into slim battery solutions.

Here one could mention the specialised nickel - hydrogen battery that was a predecessor to the NiMH battery. The nickel - hydrogen battery has a long history especially in aerospace application due to its extremely good durability and cycle life performance. This battery is somewhat bulky, as the hydrogen is not stored in the solid state in the electrode, but as pressured hydrogen gas.

Overcharge, overdischarge reactions and charge termination in sealed NiMH cells are slightly different from sealed NiCd cells

In both chemistries it is possible to make sealed cells which are essentially maintenance-free and can be overcharged without creating excessive internal pressures. This is done by making the storage capacity of the positive nickel hydroxide electrode smaller than the negative electrode capacity. These are called positive electrode limited cells.

At the end of the charging phase there are no more accessible hydrogen atoms to be removed from the positive electrode. Instead hydrogen will be taken from the electrolyte leading to a production of oxygen molecules at the nickel oxide electrode. (c.f. Fig. 4)

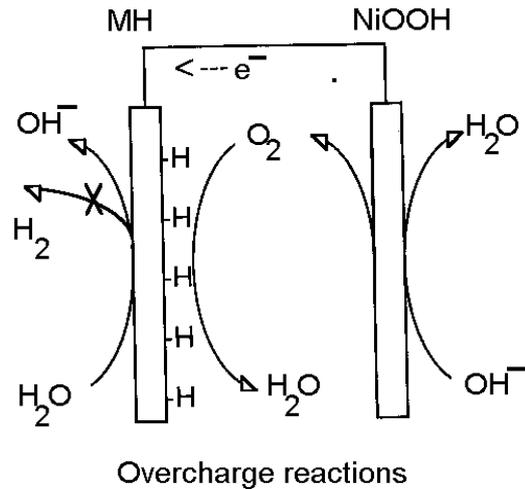


Fig. 4. Overcharge reactions in NiMH cells.

Sealed cells are designed with a certain amount of porosity in the separator that is not filled with electrolyte (starved electrolyte). This will allow for gas passage, so that the oxygen produced at the positive electrode can diffuse through the separator and be recombined at the negative electrode.

As long as the process works, the cell can be continuously overcharged without damage.

This also facilitates the handling of cells connected in series into a battery pack. By a period of overcharging the charge state of all cells can be homogenised and fully charged.

The reaction heat from the recombination will, however, heat up the battery, which if it becomes excessive will cause it to fail. Also, if the overcharge current is so high that it produces more oxygen than the recombination kinetics can recombine, the oxygen pressure will increase in the cell, until the safety valve vents to release the internal pressure build-up. This will lead to failure by electrolyte consumption and separator dry out. The amount of electrolyte in the cell is very limited in order not to fill all the porosity, which means that also small losses of electrolyte lead to a significant reduced performance of the cell. Generally the most common mode of failure for both NiCd and NiMH sealed cells is related to separator dry-out. This dry-out can be a consequence of cell abuse leading to excessive internal pressure build-ups and venting through the safety valve. The normal ageing of the cells is, however, also related to a dry-out caused by a slow phase change and swelling of the Ni-electrode, which incorporates electrolyte in its structure and dries out the separator. This ageing process is dependent on temperature and cycling but also to a large part of the type of Ni-electrode used in the cell, as will be further discussed below.

The charging of the cells is controlled by monitoring the temperature of the cells, in order to stop or reduce the charge current when the cell temperature starts to increase by overcharging.

This temperature control can be done indirectly using the cell itself as thermometer by monitoring the charging voltage. The cells are charged with a constant current and as they heat up, the overpotential is reduced leading to a dip in the charging voltage (V). This

decrease is noted by the charger, which goes over into a low current mode. The method is usually referred to as $-\delta V$ charging, which is also commonly used when charging NiCd cells.

The metal hydride electrode is, however, more effective with regard to charge acceptance, leading to a less marked reduction in overpotential upon heating, necessitating a more sensitive charger to detect the voltage drop. NiMH cell producers usually recommend that the temperature is monitored directly by, for example, a thermo-couple applied to the can of the cell. The charging of the metal hydride electrode is further an exothermic process and as its charge acceptance is reduced at elevated temperatures more careful considerations have to be made to reduce and control temperature and temperature gradients when charging a NiMH battery pack. If these precautions are taken, as will be described below, NiMH battery packs can be “fast charged”, too. If NiMH cells are charged in a “fast charger” designed for NiCd cells it is likely, that the “fully charged state” of the cell will pass undetected resulting in an a rapid failure of the cells.

To protect the cells and to improve the battery performance, more sophisticated change algorithms and cell control procedures have recently been developed in μ -processor controlled charging systems.

In contrast to other battery chemistries, the NiMH battery has, in principle, an advantage of being able to withstand a certain amount of overdischarging. When the cell is discharged and the nickel electrode is fully converted to Ni(OH)_2 it can not intercalate further hydrogen and the additional hydrogen will be emitted as hydrogen gas (H_2) from the positive Ni-electrode. As depicted in Fig. 5 this can then be recombined again at the metal hydride electrode, helped by the match of more negative electrode active mass than positive. At high current discharging the recombination kinetics is, however, too slow to be able to cope with the emitted gaseous hydrogen.

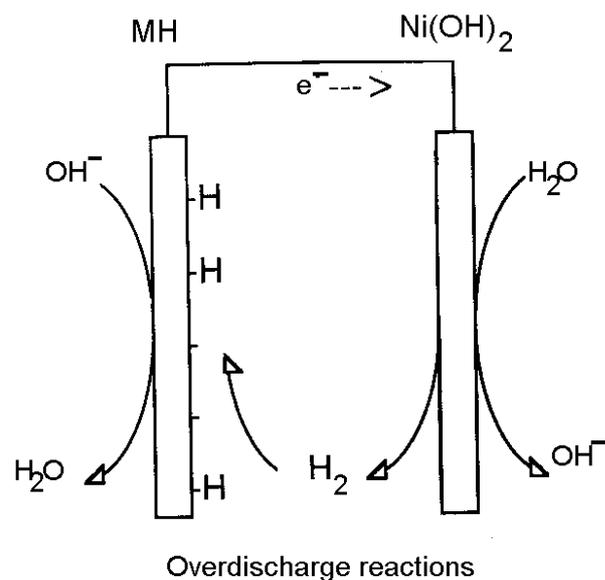


Fig. 5. Overdischarge reactions in NiMH cells.

The danger of damage by this pole reversal of some cells in the battery pack is reduced, if all cells can be fully charged to the same capacity before discharging. The practical capacity of each cell in the pack varies within some limits, usually defined by the specifications to the battery cell manufacturer. A narrow spread is desirable as it facilitates the design of the battery pack and also helps to enhance the life cycle of the battery pack. Ageing and thermal gradients across the battery pack will increase this spread in practical cell capacities and in this respect also the limited ability of the NiMH cell to withstand overdischarging will be beneficial for the life expectancy. This property will be especially valuable in EV/HEV, where several hundreds of cells are used in series.

Li-ion batteries

The principles of this cell are again similar to the NiMH cell but with lithium as energy carrier. In most commercial cell construction a lithiated cobalt oxide is used as electrode material corresponding to the nickel hydroxide in the NiMH cell. Also other material such as manganese oxide, nickel oxide or sulphur are currently being developed into new lithium battery technologies.

The chemical bond of lithium to the electrode material is stronger, leading to a significantly higher charging voltage necessary to break this bond. But on the other hand this also gives the cell a correspondingly higher cell voltage during discharge and thus the possibility of a higher-energy storage density. Dependent on the material choice and discharge state, the voltage will vary, but is typically around 3,6 V.

Lithium metal, being solid at room temperature, could in principle be used as the electrode material. Again, however, cycling can cause preferential growth in the metallic electrode, leading to internal shortcutting and as already has been observed in experimental and laboratory environments, the high energy density can lead to severe explosions and fires. To reduce the risks, lithium is intercalated in graphite or coke, which makes the analogy to the NiMH cell even closer. Instead of hydrogen intercalating a metal atom lattice, lithium atoms are intercalating a carbon lattice. This reduces the energy density but still the Li-ion technology offers the highest energy densities by weight of all the commercial rechargeable battery technologies. Compared to NiMH the advantage is presently about 30%.

Some safety issues still exist and all cells are made with intelligent circuiting preventing overcharging and overdischarging of the cells.

The electrolyte is further an organic flammable solvent, the leakage of which can cause fires, especially if the battery is unintentionally overheated.

The battery producing and consuming industry have, however, come to control these issues, which is reflected in an impressive monthly production of now over 30 million cells mainly for lap-top and mobile phone products.

Li-polymer batteries

To avoid the liquid organic electrolyte, and to further increase the energy capacity, cells with polymer or gel type electrolytes, so called lithium polymer batteries, have recently been commercialised. Initially the new lithium polymer battery is being used in the top models by the leading mobile phone producers but as battery production is continuously being improved, lowering the production cost, this cell is also predicted to be very competitive with the low-end-price batteries of today.

Here it could be mentioned that SAFT in France has presented a prototype battery intended for a hybrid electric vehicle with an impressive power density of 1500 W/kg, indicating that this technology may have great implications for the future.

Lead acid batteries

Of all the large scale produced rechargeable batteries discussed so far this has the most complex chemistry, where both electrodes are the dissolution/precipitation reactions. Even though it has been continuously developed since Planté 1859, improvements are still being made as our understanding of this battery continues to grow. By volume it is by far the largest of the rechargeable battery technologies. The complexity of the electrode reactions with competing side reactions does not make this cell as suitable for deep discharge cycling as NiCd and NiMH batteries, which means that if the total capacity of the cell is discharged the number of discharge cycles will be very limited. The advantage of the lead acid battery is the low cost and in its main application as starter battery, with a very shallow discharge, the strains on the cells are not so severe.

Historical background to the introduction of NiMH (and later Li-ion) to understand why the new batteries are better adapted to high capacity than to high power discharging

The NiMH cell has the closest resemblance to the NiCd cell both in structure, performance and at present cost of all the new battery technologies. Initially NiMH will be the major substitute of NiCd in consumer size battery products. To understand why this substitution is not proceeding at a greater pace, one has to look in more detail into the historical development of the NiMH cell construction.

Cadmium is not a very common metal. The world-wide production of about 16.000-18.000 tons is of the same order of magnitude as the silver production of 12.500 tons. Cadmium is a by-product from mainly zinc extraction. Zinc ore contains typically 0.2-0.4 per cent cadmium.

During the eighties, especially, the Japanese market for camcorders, cordless phones and other consumer appliances was growing considerably. So too was the demand for rechargeable NiCd batteries and the NiCd battery production was rising steeply. (The availability of cadmium is therefore dependent of the extraction of zinc).

The Japanese MITI (Ministry of International Trade and Industry) feared that a cadmium shortage could hamper the very successful Japanese electronic industry, producing all new electronic devices, which flooded the domestic as well as the world market.

By the mid eighties MITI funded several R&D projects together with the Japanese industry to develop new types of batteries, not relying on cadmium. Cadmium shortage and not environmental concerns was the driving force. Environmental concerns came later during the marketing of the new batteries.

The initial fear seemed, well founded, by the end of the eighties the cadmium prices peaked due to a shortage of cadmium. The price peak was, however, also caused by speculations as Japanese battery producers were stock piling cadmium from a limited market.

Meanwhile environmental concern started to prohibit the use of cadmium in other areas such as in pigment, stabilisers, corrosion protection, etc., which eased the pressure for a cadmium shortage.

This combined with an urge to make a significantly new type of battery that did not directly interfere with the profitable NiCd production, but rather to create a new market niche, lead to a development of a high energy density NiMH cell.

Table 1. Typical volumetric energy densities of the electrodes

Negative electrode		Positive electrode	
Cadmium electrode	600 mAh/cc	Sintered Ni	450mAh/cc
Metal Hydride electrode	1200 mAh/cc	Ni-foam	600 mAh/cc
		Ni-fibre	

The conventional NiCd cell uses a positive sintered Ni-electrode with a storage density of 450 mAh/cc.

The metal hydride electrode has a very high energy density of twice that of the cadmium electrode. Most of this advantage will be lost, however, when combined with the traditional sintered Ni-electrode as this anyhow takes up most of the space in the cell. Using the same nickel electrode technology in the NiCd- and NiMH cells, respectively, leads to a rather modest capacity increase of about 30% in the NiMH cell.

As the fear of a cadmium shortage subsided, the scaling up of a competing battery technology based on a rather modest increase in capacity, seemed to be a not too convincing business idea.

To further increase the NiMH cell capacity and to develop it into a new market niche, also the nickel electrode needed to be modified, in order to reach a significantly higher cell capacity. It is now that the new Ni-foam electrode was developed.

This comprises a nickel-foam made with a porosity of about 95%, which is filled with a slurry of a high density nickel hydroxide material.

Significant contribution to this development came from Sumitomo, Matsushita and Tanaka Chemicals in Japan. A corresponding development based on Ni-fibres was also made by, for example Toshiba.

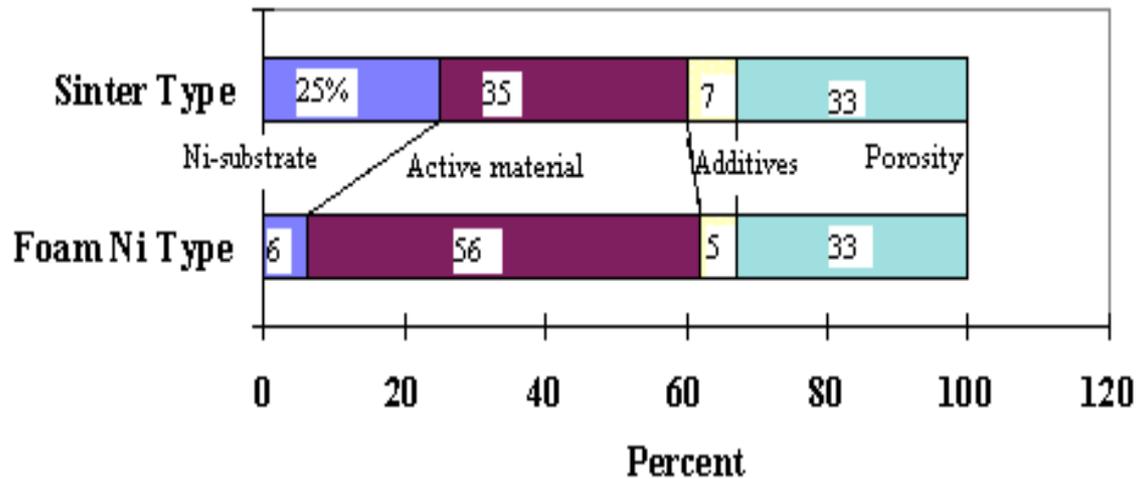


Fig. 6. The volume ratio for two different nickel electrodes (T. Iwaki)

The new foamed or fibre electrodes could contain a significant larger amount of active material, making it possible to increase the storage capacity to around 600 mAh/cc.

This, in combination with a metal hydride electrode, led to an almost doubling of the cell capacity when compared to a similar size conventional NiCd cell. The amount of conducting substrate was, however, reduced leading to difficulties in the high power region. This is the main cause for the poor high current properties of the present NiMH cells.

Thus the NiMH cell was commercially launched 1991 as a high capacity complement to the NiCd cell, primarily to be used in low power applications. Still the leading producers Sanyo and Matsushita hesitated, to ramp up the production. In some aspect the NiMH production would anyhow compete with their NiCd production. The cost of the loss of an unsold NiCd cell was somehow added to the cost of a produced NiMH cell.

Toshiba on the other hand had no production of NiCd and saw the NiMH technology as a good opportunity to enter the rechargeable battery industry. By 1993 they were the leading producers of NiMH. This spurred Sanyo and Matsushita to increase their NiMH production in order not to lose market shares. Coincident with this came a rapidly increasing demand from the mobile phone sector, which so far systematically continues to exceed all prognoses. In spite of the competition from the Li-ion battery, the NiMH production is still growing. Japanese companies produce about 90% of all NiMH batteries. In 1999 an amazing 860.000.000 NiMH cells, corresponding to about 20.000 tons of batteries, were made in Japan. Most were used in mobile phones produced by Europe and America. In the year 2000 the one billion mark will be passed. During 1999 Japanese monthly production volumes increased from 55.000.000 cells to more than 80.000.000 cells, climbing towards an amazing 100.000.000 cells per month. In Japan the production of NiMH cells superseded that of their

NiCd production already in 1997 and since then their domestic NiMH-production has been constantly increasing whereas the corresponding NiCd production has decreased.

Here it should be mentioned that the Li-ion battery was even more rapid in its growth and its value is now nearly twice that of NiMH. The competition between the NiMH producers and from the Li-ion production has driven the NiMH price down to the NiCd level on a price/weight basis. As NiMH is pushed out of the high price segment of high capacity batteries for laptop and mobile phone batteries, it is starting to compete more directly with NiCd in the low price segment.

Before describing the modifications needed to adjust the NiMH cell for NiCd applications such as power-tool batteries and emergency lightning it could be of interest to look in more detail at how competition managed to reduce the price of the new battery technologies.

Price development in the small secondary cell market

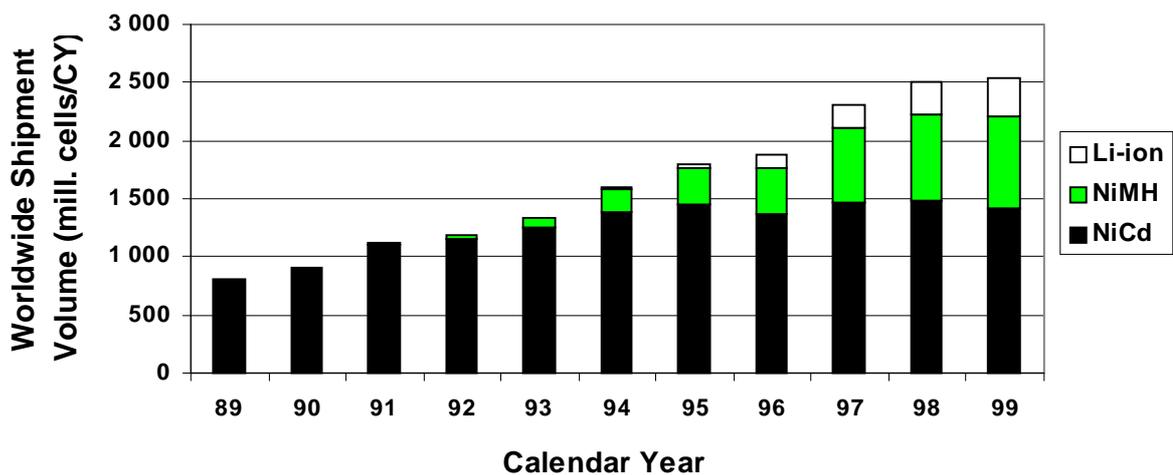


Fig. 7. Global market for small secondary cells. Market quantity.

Fig 7 depicts the development of the cell production on the global market as estimated by the Nomura Research Institute in 1999, complemented by recent Japanese Battery Association statistics. The NiCd production increased by about 10% each year until the NiMH battery began to be produced in larger volumes after which NiCd production levelled of, at slightly declining prices. It is interesting to note that the expanding volumes in the market is covered by the new technologies whereas the NiCd production remains fairly constant. At the onset of the competition from the Li-ion production in the mid-nineties, the NiMH hydride production still increased but the value levelled out. Competition came both from the Li-ion batteries and from an overproduction of NiMH cells.

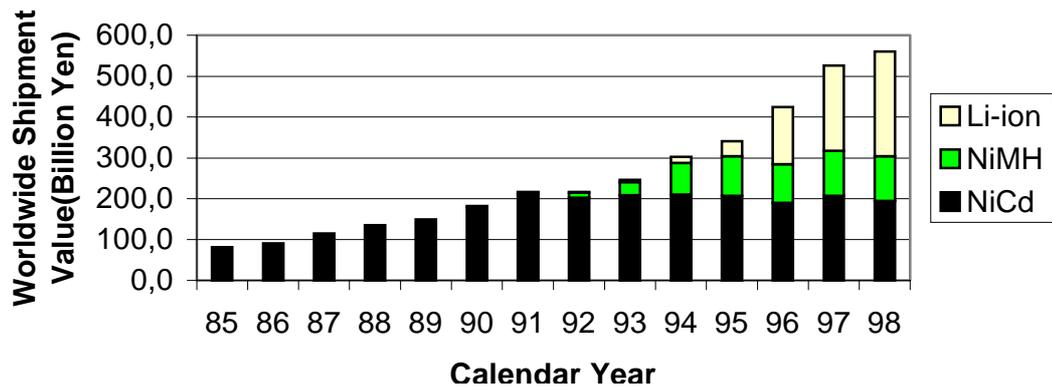


Fig. 8. Movements in the global market for small secondary cells. Market value

The global market value development is depicted in figure 8. By dividing the numbers in figure 8 with those in figure 7 an estimate of the price/cell development is obtained in figure 9.

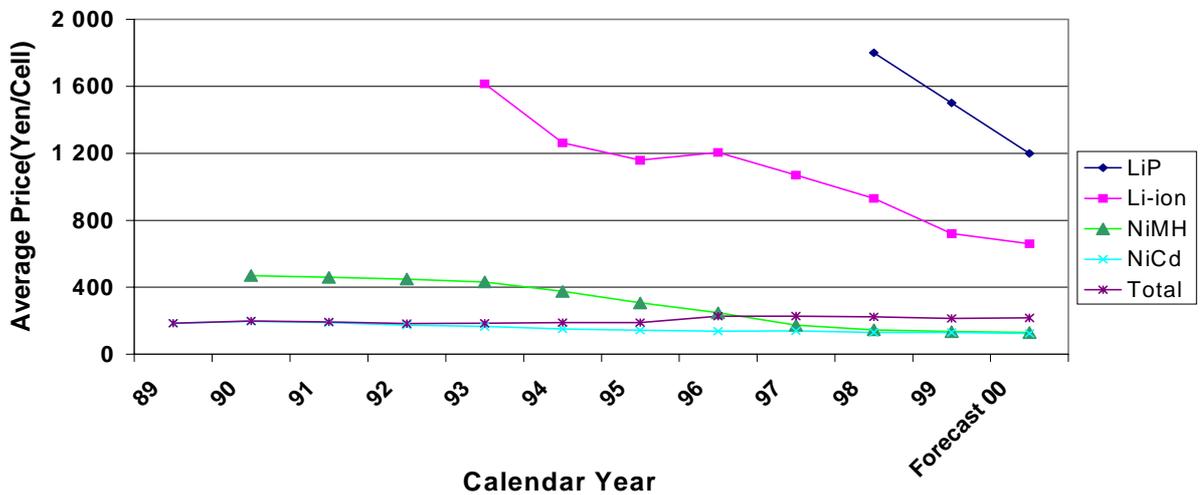


Fig. 9. Movements in the average unit sale prices of small secondary cells (global market)

It is interesting to see the rapid changes on the traditionally rather slow battery market during the last decade, resulting from the introduction of new battery technologies. Over only a short period of 5 years the NiMH price level has come down to that of NiCd. The main reason is of course competition but large-scale production has also helped to reduce the production cost of both cells and electrode materials.

It is also interesting to see that the Japanese battery industry with a very focused industrial policy and a targeted R&D has managed to become totally dominant in this market over approximately the same time span. Figure 10 depicts the Japanese shares of the new battery technologies for these consumer size batteries. One reason for this success is the Japanese effort to consider batteries as strategic components, motivating MITI to invest in battery R&D, thus enabling Japanese battery industries to develop new battery technologies. The lack of a corresponding effort outside Japan has largely turned the traditional battery industries into defenders of the previous NiCd technology, fighting to survive on a shrinking market.

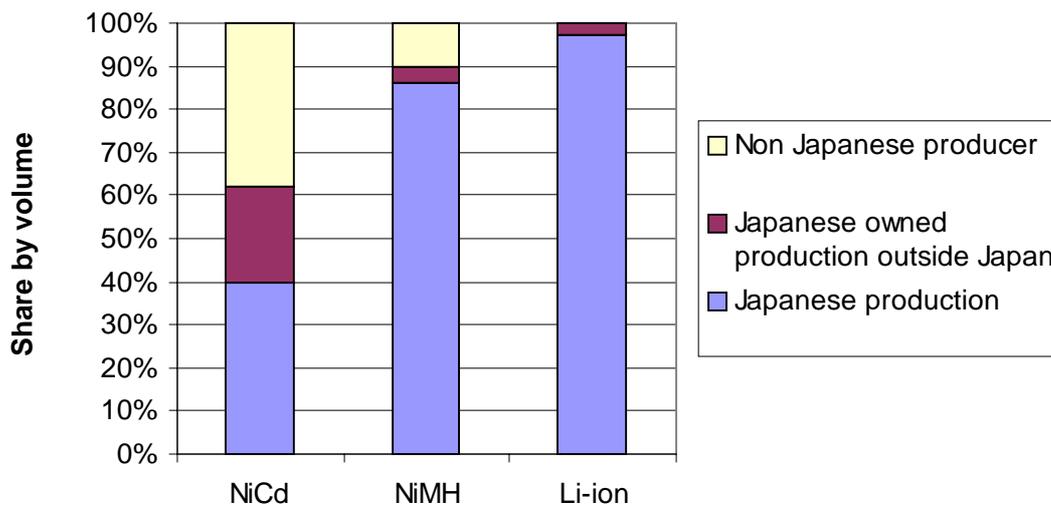


Fig. 10. The market shares of small secondary cell production in each production centre (1998, volume based).

Anyhow, the dominant Japanese position and the fact that the Japanese Battery Association compiles very reliable statistics for the domestic Japanese production, can be used to better compare the price/cell and price/Wh for the different cells.

Table 2. Price per capacity of each small secondary cell type sold as bare cells (Domestic Japanese production, 1998)

	Size	mAh	Yen	Yen/Wh	Share	Ave. Yen/Wh.
NiCd	<i>Sub-C</i>	1700	130	64	42%	74
	<i>4/5A</i>	1200	110	76	16%	
	<i>AA</i>	700	70	83	21%	
	<i>Others</i>			85	21%	
NiMH	<i>4/3FA</i>	4500	240	44	8%	112
	<i>AA</i>	1300	125	80	15%	
	<i>AAA</i>	550	85	129	9%	
	<i>4/3AAA</i>	700	100	119	17%	
	<i>5/3AAA</i>	900	165	153	14%	
	<i>F6</i>	650	130	167	10%	
	<i>Others</i>			100	28%	
Li-ion	<i>18650</i>	1500	480	89	37%	146
	<i>17670</i>	1250	320	71	13%	
	<i>34488</i>	1000	700	194	11%	
	<i>30486</i>	600	720	333	13%	
	<i>Others</i>			150	26%	

Table 2 lists the price/cell for the different cell types produced in Japan during 1998. Based on the average capacity of each standard size cell type the price/Wh can be calculated. The average Yen/Wh costs for NiCd, NiMH and Li-ion are 74, 112 and 146, respectively. The rather large difference in NiCd and NiMH cost originates, however, as seen in the table, from a large production of small special sized *AAA* cells for the mobile phone market. The lowest price/Wh is actually reached with the *4/3 FA* NiMH cell. If the same size *AA* cells are compared, NiMH was slightly cheaper than NiCd per Wh. Also the more standard Li-ion battery sizes 18650 and 17670 reach down to these price levels per Wh.

Since 1998 the intense competition has further reduced the prices. The Li-ion 18650 cell capacity has now increased to 1800 mAh but the price has for some customers fallen to 300 Yen, which means that the price per energy unit is down to below 50 Yen/Wh. This has further reduced the *4/3 FA* NiMH cell price to 180 Yen corresponding to 33 Yen/Wh. (M. Wada, Toshiba Batt., Personal comm.)

These low prices are now approaching the material costs for the parts needed for assembling the cells and the battery producers are complaining that they have to discount the cells below their production price. It is difficult to forecast what the future development will be but in the short-term there is likely to be a further concentration of large scale cell producers in Japan.

Varta, as an example, is closing its own cylindrical cell production to buy Toshiba cells, which are built into battery packs under their own brand. The few remaining cell producers are fighting to further reduce production costs.

Table 3. Material cost, comparison of NiMH vs. NiCd (1US\$≈105)

Ni MH			Ni-Cd		
Positive electrode			Positive electrode		
	Yen Unit Price	Cost per Wh in Yen		Yen Unit Price	Cost per Wh in Yen
Positive Ni-foam substrate	2300/m ²	7.96	Sintered Ni-positive punched steel substrate	500/m ²	1.73
Nickel Hydroxide	1000/kg	2.90	Ni-powder	1400/kg	1.68
			Nickel nitrate	400/kg	4.02
Cobalt additive	4400/kg	0.66	Cobalt nitrate	900/kg	0.58
Others		0.20	Others		1.06

Negative electrode			Negative electrode		
Negative substrate	500/m ²	2.16	Punched steel substrate	500/m ²	2.16
MH-alloy	1750/kg	6.99	Cadmium oxide	600/kg	2.26
			Conducting additives	1400/kg	1.32
Others		0.44	Others		0.44
Construction parts, can lid, separator, etc.		8.16	Construction parts, can lid, separator, etc.		8.16
Total		29.47	Total		23.40

In table 3 Toshiba Battery is presenting an estimate of the material cost of two comparable NiMH and NiCd cells. The current effort is to reduce the NiMH material costs by developing cheaper positive electrode substrates to eliminate the fairly expensive Ni-foam and to continue to persuade the metal hydride alloy producers to further reduce their prices.

The latter has so far been successfully, facilitated by the continuously increasing production volumes (c.f. Fig.11). The recent hybrid electric vehicle (HEV) development as exemplified by the Toyota “Prius” and Honda “Insight” as discussed below, will further promote a reduction of the alloy cost. The car industry has a long history of being able to reduce the cost of its sub-contractors.

The alloy price target for Toyota is now 1000 Yen/kg. When this is realised, concomitant with the cheaper positive electrode substrate currently being developed, the material cost of the NiMH cell will be reduced below that of NiCd.

As also seen in table 3 the material cost difference today is not very large, roughly only 20%. With the present rather unusual competition on the market it is, however,

interesting to note that the NiCd cells can be sold with a higher profit margin. This fact will not stimulate the cell producers to abandon their NiCd production.

The decreasing NiMH costs concomitant with increasing production volumes (c.f. figure 11 for the year 1999 statistics from JBA) have now also made the NiMH AA cell price/Wh lower than for NiCd, also when sold over the counter in Japan (Yamashita, Osaka National Research Institute, Japan, Personal comm.). Of the total Japanese NiMH production for 1999 close to 95% were exported to battery users abroad, namely to the mobile phone producers Ericsson and Nokia. Of the corresponding Li-ion production 40% were exported abroad.

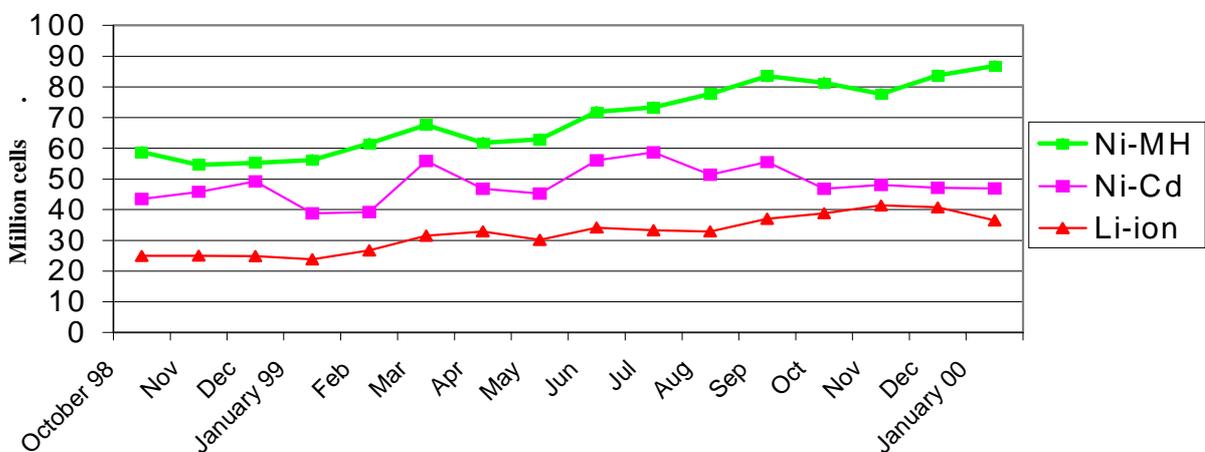


Fig. 11. Monthly secondary battery shipment from the Japanese manufacturers, according to Japan Battery Association statistics.

To conclude, for the most common standard battery sizes the cost/Wh for NiMH is now lower than for NiCd. When the NiMH battery was introduced in 1991 this was not believed to be possible.

Now when NiMH battery types, i.e. for high power applications or for emergency lightning, are developed a similar situation will occur. Initially the production cost of new types will be expensive, but increasing volumes and competition will bring down the price. When the NiMH battery was introduced, the mobile phone and laptop producers could cope with this, as the increased battery performance was essential for the customer. As will be discussed below, the improved battery performance of the NiMH power tool cell will be less marked. Customer response to the environmental benefits will therefore be more important for a successful commercialisation.

Development of high power NiMH cells

This has to a certain extent already been done by for example the leading power-tool battery producers Matsushita and Sanyo, when they developed NiMH batteries for hybrid electric vehicles (HEV).

HEV-battery cells must be of a high and even quality as usually several hundreds cells are connected in series, and as with a chain, the weakest link determines the durability. Good high power performance is needed, both for discharging to accelerate the vehicle as well as charging to recover the regenerative braking energy. Matsushita has been delivering D-size NiMH cells to the Toyota Prius HEV since 1997. Each car uses 240 cells in series in an extreme high power application severely testing for the quality and uniformity of the cells. The monthly production of Prius is close to 2000 vehicles, leading to a production volume of about 400.000 cells. Last October also Sanyo presented a D-size cell for hybrid vehicles which had a power density of 900 W/kg. (see appendix 1). The prismatic NiMH cells for the new Prius II to be introduced on the European and USA market later this year has a reported power density of 1100 W/kg.

According to Atlas-Copco, a professional cordless tool manufacturer, the typical power drain in professional power tools is 400-500 W/kg with peak powers up to 900 W/kg. This means that the possibility for large-scale production of batteries with power-tool performance already actually exists.

Matsushita and Sanyo are, however, already the largest NiCd power tool battery producers, making it less likely that they will start to produce suitable battery sizes (i.e. sub-C size) that will compete directly with their own NiCd.

The main development necessary for obtaining a NiMH high power cell is to revert back to a better conducting nickel electrode containing a larger fraction of conducting metal. As discussed above in Fig. 6, this is done at the expense of the amount of active electrode material in the cell and the capacity advantage of such a NiMH cell will be only about 30% compared to NiCd.

In contrast to when NiMH was first introduced, it has now been shown that the battery cost can be significantly reduced in large-scale production. The hydrogen storage alloy price has also become significantly lower. This will facilitate the introduction of NiMH power-tool batteries although the capacity advantage is more marginal than when the first version of the NiMH cells was specially developed for high capacity application.

Moltech (previous Energizer) have been marketing NiMH power-tool batteries based on their traditional sintered Ni-electrode, since 1997 together with Makita, Japan. The performance has so far been reported to supersede that of NiCd (appendix 2). Makita is the second largest power tool manufacturer after Black and Decker, but even among other power tool producers seen as taking the initiative in power tool development (appendix 3).

Moltech is producing NiCd power-tool cells for the low price end (6-12 V packs) and NiMH cells (14-24 V packs) for the professional power-tool manufacturer, where a higher cost for a better performing battery can be motivated. In this segment their NiMH production has already superseded that of NiCd.

Moltech is estimating that environmental arguments can help them to expand their market share.

It is, however, important to explain the differences between NiMH and NiCd to the end user and to instruct the end user how to modify their battery handling procedures to ensure optimal benefit of the new NiMH cells. A direct substitution into existing products is usually not possible. As mentioned above, the different batteries need different charging algorithms. They also perform differently with respect to temperature and temperature gradients, which needs to be considered when designing the battery application in order to obtain the best performance at an optimum cost.

A number of sophisticated and computer controlled chargers has also become available, which use intelligent algorithms for an optimal charging of NiCd as well as the new battery chemistries. This improves both cell performance and life expectancy but is often a too costly solution for many low priced products. A more effective way is to consider the different behaviour of the NiMH chemistry already in the design of both cells and power tool applications in a collaboration between cell manufacturer and power tool manufacturer as for example the collaboration of Makita and Moltech. From a short-term perspective and maybe understandable, the established NiCd producers are not very helpful in this matter. In addition, some of the equipment producers are putting up a rather stubborn resistance, thus denying the possibility to for NiMH to substitute NiCd.

Black & Decker recently wanted to show that NiMH could not be used in high power application by testing the Panasonic NiMH HHR 3 Ah sub-C cell against sub-C high power NiCd cells.

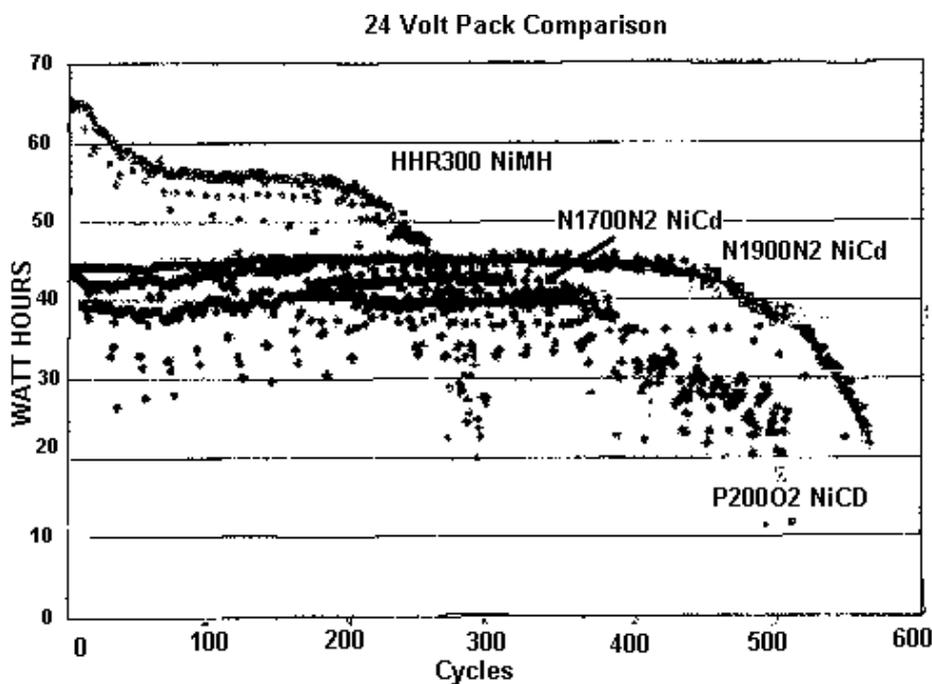


Fig. 12. Cyclic performance for NiMH cells.

The test results (Fig 12) show that the cyclic performance at high drain is very poor for the NiMH cell even if the total capacity is initially larger.

Black & Decker selected the Panasonic NiMH based on it being "the best NiMH high performance now on the market."

This is in a sense correct but high performance should in this case be understood as high capacity. The nickel electrode in the Panasonic HHR cell is based on a foamed Ni substrate and it has been optimised to give the cell a very high capacity of 3 Ah.

Electrolux, another end user but with a declaration to remove cadmium from its products, had a similar experience with this battery type.

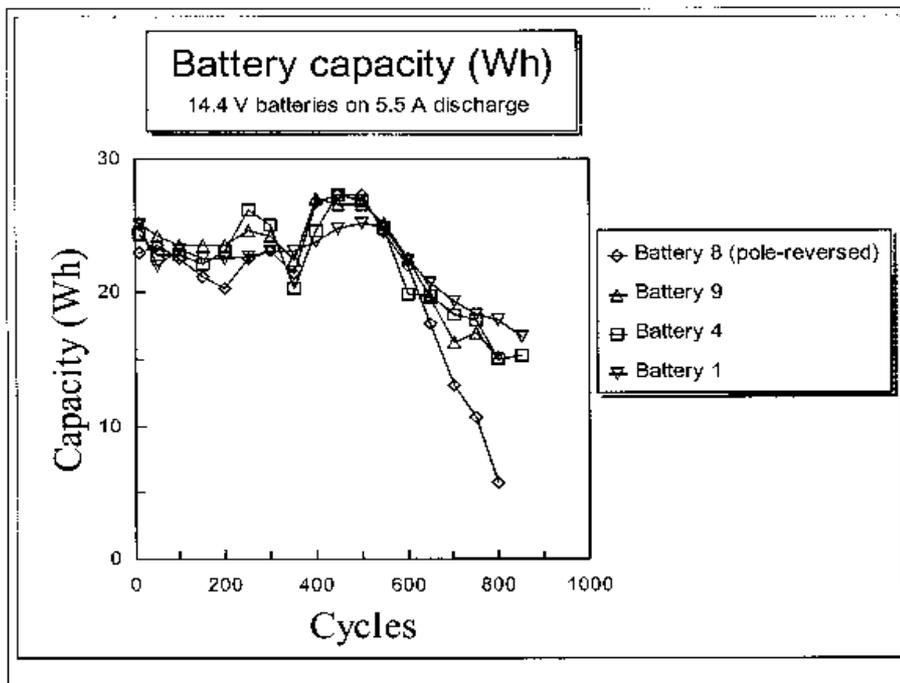
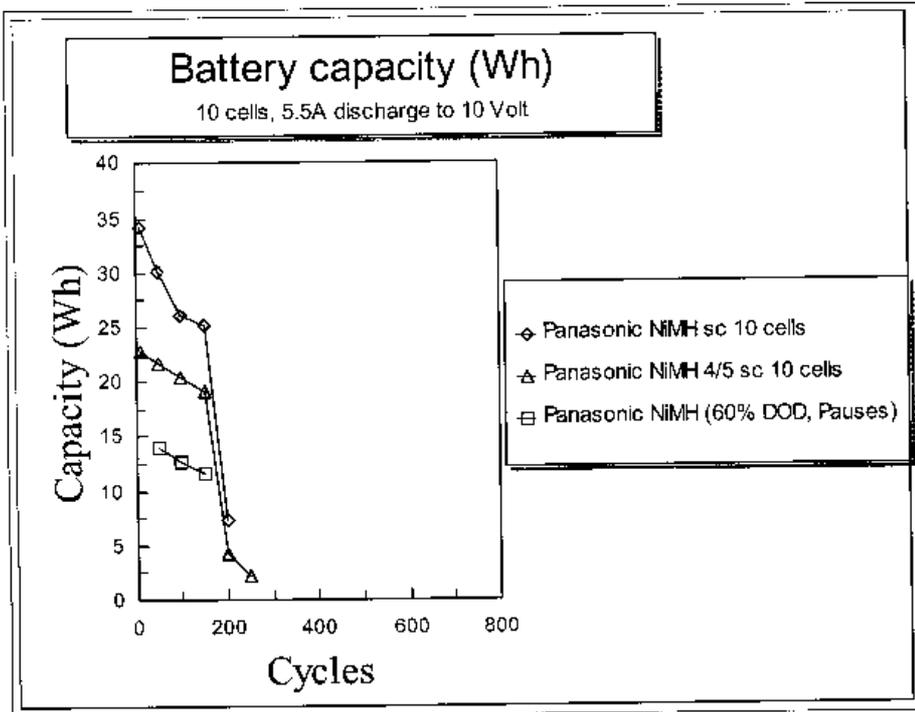


Fig. 13. Battery capacities.

In Fig. 13 Electrolux compare the Panasonic HHR and their other NiMH cells to an Energizer NiMH cell made with a sintered nickel electrode, which has been optimised to give a good high power performance but with a lower total capacity of 2.2 Ah. It is

important to understand that the optimisation of certain properties usually are done at the expense of others. In this example high capacity is traded for high power performance. It is worth to notice, however, that the total capacity of the high power NiMH cell is still significantly larger than that of a corresponding NiCd cell.

Again the Panasonic cell has a higher initial capacity but at this high rate cycling a shorter cycle life. The difference is somewhat underestimated as the Panasonic cells were measured in a 10-cell pack whereas the Energizer cells were measured in a 12-cell pack.

The difference in performance should not be understood as a general difference in quality of the cells from the different producers but as a result of a different optimisation of energy density versus power density. Again the very high capacity of the Panasonic cell is possible at the expense of the extreme high rate properties. If the Panasonic HHR cell was to be used at a lower power density it would be able to deliver an impressive amount of energy over a long period of time.

A fundamental problem with the nickel electrode compared to the metal hydride electrode is that the Ni(OH)_2 formed in the discharge state is a non conductor in contrast to the NiOOH in the charged state of the electrode.

Doping the nickel hydroxide with cobalt-oxide is one common method of improving the conductivity of the nickel electrode. A conducting CoOOH -network contributes to the conductivity of the electrode as it reaches its discharge state, thereby increasing the utilisation of the active nickel material.

At lower discharge potential also the CoOOH will, however, convert to insulating Co(OH)_2 . The combination of high discharge currents inducing large potential gradients and high temperatures will disturb the cobalt doping, redistributing the conducting network, resulting in poorer power performance and loss of life expectancy.

In this respect the sintered nickel substrate has an advantage, as it constitutes a very fine and dense dendritic structure of conducting metallic nickel, leading to very short electron migration paths in the nickel hydroxide.

In a foamed electrode with a more open microstructure the importance of cobalt doping increases. In appendix 4 Moltech has given some related informative material exemplifying how this effect influence the performance of the cells.

A foamed nickel substrate can, however, also be improved for high-power application by increasing the conductive network and reducing the distance over which the current has to be passed. Inevitable this is done, however, at the expense of the amount of active material in the electrode.

Toshiba has decided to enter the high-power NiMH area, with their own high power modification of the Ni-electrode, which they use in their ordinary NiMH cell (See appendix 5).

In their documentation they describe how the end user should take precautions to avoid problems caused by extreme temperature and temperature gradients over the battery packs in order to increase the life expectancy of the batteries. This is facilitated by the higher energy densities of the NiMH cells in respect to NiCd, as a smaller NiMH cell can

be selected for the battery pack giving more space for convective cooling within the battery pack without increasing the outer dimensions.

Toshiba has no previous NiCd production, and again this can be an incentive for scaling up their NiMH power battery production, as previously when they pioneered the scaling up of the NiMH production in Japan.

Both Moltech and Toshiba are, however, intently following the environmental discussion concerning cadmium, which is mainly being debated in Scandinavia. The evaluations of the signals coming out of this discussion is important for how the companies will decide to challenge the established NiCd industries in this fairly substantial market segment. The major NiCd power tool battery producers are, however, also preparing for a race on the NiMH power tool market once the market demands it.

Already at the beginning of last year also SAFT announced in a press release, that it will start producing NiMH for power tool applications. Impressive performance data from the new cells was also presented by F. Auriel at the Battery 2000 meeting in March 28-29, 2000. SAFT, like Toshiba, are also further developing the positive electrode by improving its conductivity. The big players are currently watching each other, waiting for future legislation and looking out for signs showing that major consumers are beginning to demand cadmium-free batteries.

The introduction of NiMH power tool batteries will probably be as swift as when NiMH was first introduced. Meanwhile NiCd batteries are being produced on production lines where the investment has already been made thus making each postponement of the substitution profitable.

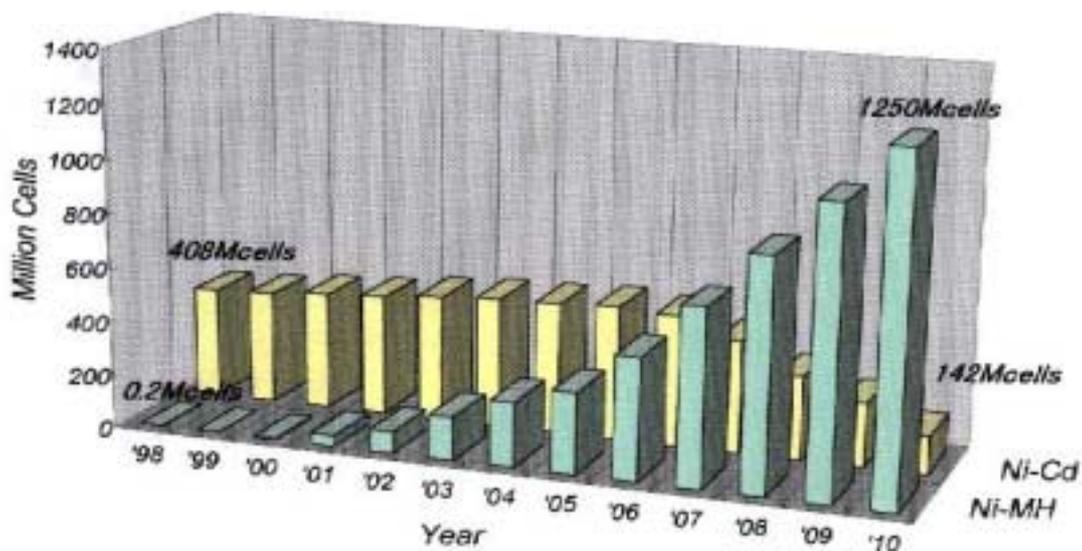


Fig. 14. Power Tool Cells Market Forecast

Fig 14 shows Toshiba Battery's estimate of the future global market for power tool batteries. The trends are similar to when NiMH was first introduced in 1991. The NiCd production shows a slight increase whereas the general expansion of the power-tool market is covered by the new cells. In about 2006 the productions of NiCd and NiMH for power

tool applications are comparable and only thereafter is a decline of NiCd production foreseen.

If an EU-ban on NiCd is introduced in 2008 at least within this production area there will be enough production capacity available well ahead of that date.

Batteries for emergency lightning and Uninterrupted Power Supply (UPS)-systems

This is the other main area where NiCd is presently used. In these applications the cells are seldom cycled, which reduces the demand on the cyclic durability. Lead acid battery based systems could therefore also be an alternative for many of these applications.

The systems are, however, often installed in places such as under the ceiling close to other power equipment, where temperatures can be significantly above ambient, and where availability of cooling by convection is limited. This will again demand a modification of the conventional high capacity NiMH cell. A better exchange of information between battery producers and end users is a solution, in order to design systems where the cells are not continuously overcharged at excessive temperatures. Many systems are already installed with chargers designed for NiCd cells making a direct substitution difficult. The chargers are also often rather simple keeping the cells under continues overcharge to circumvent self-discharge. This in combination with high temperatures is not suitable for the present NiMH batteries.

In the metal hydride electrode hydrogen is stored in the alloy with a chemical bond to the metal atom framework. This bond must not be too strong in order for hydrogen to also be released at low temperatures. Present NiMH battery specifications demand certain discharge rate properties at low temperatures. Adjusting the alloy composition adjusts the hydrogen bond strength and thus the hydrogen release pressure. A high hydrogen release pressure at low temperatures reduces the hydrogen absorption at high temperatures. NiMH batteries for high temperature application thus need a metal hydride with an adjusted chemistry.

Furthermore, at high temperatures the metal hydride will be more sensitive for oxidation by the oxygen gas produced/emitted during overcharge, which means that the charging procedure needs to be modified to eliminate excessive overcharging.

Both Moltech and Toshiba have, however, already begun to market NiMH batteries where modifications have been made, both to the cell chemistries as well as to the charging algorithm in order to comply with usage at elevated temperatures.

Industrial size NiMH batteries

Industrial sized batteries are usually understood to be larger prismatic cells used for example in power back up systems in industries, hospitals, airports, train carriages etc., but also in applications as starter batteries for aeroplanes or traction batteries for vehicles.

Industrial NiCd batteries are produced with pocket type- or sintered electrodes depending on cost and performance specifications. For the same cost consideration as above the corresponding NiMH technology has not yet been introduced. This market segment is also significantly smaller than the previous one and with only a few producers, making the incentive to substitute the established NiCd production even less.

Prototype electric vehicles with NiMH batteries having a corresponding performance have, however, been tested in various prototype projects over the world. It is usually difficult to make a fair comparison of cells from different technologies as they have been developed to meet specifications from different applications. Development of EV batteries have, however, lead to several studies comparing batteries from different technologies in the same application. In 1994 the worldwide largest battery producer Matsushita Battery who have made EV-batteries based on all types made the following comparison in a review “New Battery Technologies” edited by S. Kawauchi et al:

Table 4. Performances of EV batteries

	Energy Density Wh/kg	Power Density W/kg	Cycle Life Cycles
Lead Acid	35	150	500
NiCd	50	160	1000
NiMH	70	160	1500
Li	120	?	?

From these experiences it seems likely that the NiMH technology would be able to substitute the industrial size NiCd batteries at least from the performance perspective. The experience already invested in the development of electric vehicle NiMH batteries ought at least to facilitate and reduce the cost when developing industrial NiMH batteries for a future substitution.

Recycling of NiMH vs. NiCd

NiMH recycling is different and much simpler than NiCd recycling. The absence of cadmium and other hazardous metals makes it possible to recover spent NiMH batteries together with steel scrap. This means that no special recovery system needs to be established, as in the case of NiCd which has to be kept separate from other recovery systems due to handling precautions with cadmium. This, in combination with a valuable metal content mainly from nickel and cobalt, gives NiMH scrap already today a positive value. NiMH producers can conveniently get rid of this production scrap and faulty cells through ordinary scrap merchants and recover a positive value. At present the recycling is practically made by recycling the cells together with steel scrap for the steel industry.

It is, however, important to keep spent NiCd cells out of the scrap stream. A cadmium-contaminated scrap will not be accepted. This will be a problem endangering a profitable NiMH recycling.

Recollected NiCd cells have to be recycled in a separate process which increases handling costs. These handling and subsequent procedures for eliminating the cadmium are costly and the recycling costs can only be recovered by collecting a handling fee from the deliverer of the NiCd scrap.

Recycling of Li-ion cells

The large amount of cobalt in the positive electrode which essentially is lithiated cobalt oxide combined with a high cobalt price, have made all of the major Japanese materials companies such as Sumitomi Metal, Santoku, Furukawa Metal, Japan Metals & Chemicals etc. active within the recovery of spent Li-ion batteries.

The recollection of spent batteries is also facilitated by the Japanese system of leasing the mobile phones to the consumer. When the consumer is upgrading his mobile phone, the old one will be handed in to the shop.

A review of the different recycling technologies used was recently presented in detail in *Materia Japan* Vol. 38, No 6 (1999).

Conclusions

The rechargeable battery industry is currently undergoing rapid changes. Traditionally this industry consisted of European and American producers of lead acid and NiCd batteries. Over the years competition fused a large number of independent national battery companies into a few dominant global companies.

During the last decade three new rechargeable batteries, NiMH, Li-ion and Li-polymer have, however, been commercialised by Japanese companies on the consumer size portable-battery market. This market expanded from 800 million NiCd cells in 1989 to more than 2500 million NiCd, NiMH and Li cells in 1999. Behind this expansion lies the remarkable growth in portable appliances, mainly mobile phones and lap top computers. As we have only seen the beginning of mobile internet applications, this expansion is set to continue.

Japanese battery companies have, with this expansion, become not only totally dominating as producers of the new battery technologies but also leaders in the corresponding NiCd production. The NiCd production volume has been fairly stable since the mid-nineties and the expansion in the battery market is taking place within the new battery technologies as it is essentially driven by demand for high capacity batteries.

Competition from new high capacity batteries has continuously reduced the NiCd price. The relative price decrease has been even swifter within the new battery technologies themselves. The lowest price/Wh is presently found among the NiMH cells. This trend will continue.

During the last few years NiMH technology has also been successfully adapted to high power applications in batteries for hybrid electric vehicles. At the end of 1997 Toyota introduced the hybrid electric vehicle Prius, each with 240 NiMH D-size cells in series, which is a very demanding battery application. After having produced more than 30.000 cars for the domestic Japanese market, Prius will this year be introducing cars on both the American and European markets. A large-scale vehicle application of NiMH batteries will further help to reduce the price.. The competition from Li-ion in high capacity applications will push NiMH into typical NiCd applications.

Lower NiMH prices with a performance similar or better than NiCd in areas such as power tool and emergency lighting systems, where NiCd are dominating and where most of the NiCd cells are used, will accelerate the substitution.

The front runners are Moltech, USA and Toshiba Battery, Japan. The transition time will, however, be dependent on environmental concerns of consumers and on legislative actions such as levies and/or prohibition put on the use of cadmium. Any changes in such prerequisites are anxiously observed by the battery producers, about to launch NiMH cells on the NiCd market. On one hand it will be an advantage to be first on the market, when the transition takes place, but on the other hand the launching of an even slightly modified product on a large scale is costly. If the market is slow to develop it can even endanger the existence of the forerunners themselves.

More Cadmium is produced than is needed for battery production. As cadmium is inevitably produced as by-product of zinc extraction, it can end up with a close to zero cost.

Even if the cost of the metal hydride alloy is also decreasing, and especially if NiMH batteries will come to be used in vehicle application. The question of whether the capacity gain of about 30% from using a metal-hydride electrode can motivate the alloy cost compared to an almost zero cost for cadmium is still an open one.

Environmental concerns felt by battery consumers is in this respect an important driving factor for the battery producers. If they already are NiCd producers they are also, however, aware at the same time that the cost for a non-sold NiCd cell ought to be included in the NiMH price.

Measures to increase the consumer awareness of environment issues will accelerate the transition in the power-tool and emergency lighting applications.

As these products correspond to the largest remaining use of cadmium there will be less incentive to withstand a future further substitution of NiCd in other applications.

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