Metal hydride electrodes stability of LaNi₅-related compounds

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Metal Hydride Electrodes Stability of LaNi_5 -related Compounds

Proefschrift

ter verkrijging van de graad van doctor in de
technische wetenschappen aan de Technische
Hogeschool Eindhoven, op gezag van de rector
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een commissie aangewezen door het college
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door

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geboren te Eindhoven

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prof. E. Barendrecht en prof. dr. A. R. Miedema

*aan Marie-José
Linda en Tom*

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1. SCOPE OF THIS THESIS

Batteries are the power source for many products and the number of applications will certainly increase as the performance of batteries is improved. There exist *primary* (non-rechargeable) and *secondary* (rechargeable) batteries. The two most well-known secondary batteries are the lead-acid and the nickel-cadmium cell. Important features required for a new rechargeable battery are: higher energy density, higher power density, longer durability, maintenance-free operation, lower costs and non-polluting. Evidently, many of these features are determined by the physico-chemical properties of the battery, such as the storage capacity of the electrodes, the stability of the electrode/electrolyte system and the charge/discharge mechanism of the electrode reactions.

As a result of the discovery of intermetallic compounds which are capable of absorbing and desorbing hydrogen at pressures around 1 atm and near room temperature a new type of rechargeable battery electrodes has become realizable: the metal hydride electrode. During the charging of such an electrode, hydrogen is formed by the electrochemical reduction of water and is subsequently absorbed by the intermetallic compound. During discharging, the stored hydrogen is released and oxidized. The considerations which have led to the concept of a metal hydride electrode are given in chap. 2.

LaNi_5 and LaNi_4Cu have been most-promising materials for application in rechargeable battery electrodes because of the rapid and reversible storage of large quantities of hydrogen in these intermetallic compounds. However, the storage capacity of both LaNi_5 and LaNi_4Cu electrodes declines drastically during repeated charge/discharge cycling. This deterioration process has been investigated by means of X-ray diffraction analysis, gas adsorption (BET) measurements and electron microscopy. Based upon our findings we hypothesized that hydride electrodes, made of an intermetallic compound which shows less lattice expansion than LaNi_5 on hydriding, should be more stable than LaNi_5 electrodes (chap. 3).

More than twenty different intermetallic compounds, in which lanthanum and nickel had been partially replaced by similar elements, have been prepared to examine this hypothesis. The volume expansion of these LaNi_5 -related compounds on hydrogen gas absorption, as determined from X-ray diffraction measurements, and the stability of the corresponding electrodes are indeed correlated. The stability of these multicomponent electrodes was evaluated from capacity loss measurements in half-cells in series of approximately six hundred charge/discharge cycles. Several multicomponent electrodes exhibited an excellent stability. The effect of the specific surface area and of the charge/discharge cycle regime on the stability has also been investigated. Chapter 4

is concluded with a description of a possible mechanism for the degradation of metal hydride electrodes.

The combination of the metal hydride electrode and the rechargeable nickel electrode provides a nickel-hydride battery. Based upon the behaviour of both electrodes, a sealed nickel-hydride cell is expected to have several advantages, e.g. the capability of being charged and discharged at high rates and during many cycles. Also, prolonged overcharging and overdischarging should be feasible without detrimental effects. Several sealed nickel-hydride cells which comprise a hydride electrode made of one of the stable intermetallic compounds have been constructed. The properties of these first sealed nickel-hydride batteries are discussed in chap. 5.

2. METAL HYDRIDE ELECTRODES

2.1. Rechargeable batteries

2.1.1. Introduction

In 1800 Alessandro Volta¹⁾ reported a device for converting chemical energy into electricity. This device, which is now known as the Volta pile, was the first chemical power source or *galvanic battery*. In Volta's cells, zinc was oxidized at the negative electrode and hydrogen gas was evolved at the positive, silver or copper, electrode. In 1860, more than half a century after Volta's discovery, Gaston Planté²⁾ demonstrated the first rechargeable battery: the lead-acid cell. This cell consisted of two spirally wound lead sheets separated by flannel strips and inserted into sulphuric acid. Planté formed his electrodes by repeated charging with primary cells and discharging. At the turn of the century alkaline accumulators were invented. In 1899 Waldemar Jungner presented his ideas concerning the advantages of alkaline systems in a patent³⁾. In this patent Ag_2O_2 , $\text{Mn}(\text{OH})_2$ and CuO are mentioned as positive electrode materials and Cu and $\text{Fe}(\text{OH})_2$ as negative active materials. Also in 1899, T. de Michalovski patented his findings on the nickel-zinc cell⁴⁾. The first patent on nickel-cadmium and nickel-iron accumulators was granted to Jungner in 1901⁵⁾. These rechargeable cells were also patented by Thomas Edison; the nickel-iron cell in 1901⁶⁾ and the nickel-cadmium cell in 1902⁷⁾.

Since these early discoveries many combinations of redox couples have been investigated for application in galvanic cells and many electrochemical systems are still being studied⁸⁻¹⁸⁾. The purpose of this section is not to present a comprehensive review. Instead, some well-known rechargeable electrodes are discussed primarily to illustrate our major considerations in the choice of a new battery system. Here, the emphasis will be on the relation between physico-chemical properties and performance. Aspects of cost and producibility are not discussed.

2.1.2. Principle and terminology

A galvanic cell is a device that converts chemical energy directly into electrical energy. Such a cell consists of two electrodes, spatially separated from each other but in ionic contact via an electrolyte. This is illustrated in fig. 1. Whereas one of the electrodes is rather easily oxidized, releasing electrons (the negative electrode), the other one is preferentially reduced, accepting electrons (the positive electrode). When the electrons flow through an external load from the negative to the positive electrode, the cell is discharged and electrical energy is generated. A cell is rechargeable if all reactions can be made to proceed in the opposite direction by imposing an external potential difference.

Fig. 1. Schematic display of a galvanic cell with an alkaline electrolyte: 1. active negative electrode material, i.e. reductant; 2. active positive electrode material, i.e. oxidant; 3. electrolyte, e.g. aqueous KOH solution; 4. current collectors; 5. separator; 6. external load.

The theoretical energy density of a galvanic cell ($\text{Wh} \cdot \text{kg}^{-1}$ or $\text{Wh} \cdot \text{dm}^{-3}$) is equal to the storage capacity of the two electrodes multiplied by the cell voltage. The storage capacity of an electrode, i.e. its coulombic storage density, means the amount of charge that can be stored and released via an electrochemical (Faradaic) reaction by a unit weight or unit volume of active material. Values for some well-known cells are given in table I. As is shown in this table, the actual

TABLE I

Characteristics of some well-known primary (P) and secondary (S) cells.

cell type	electrochemical system	Emf (V)	energy density ($\text{Wh} \cdot \text{kg}^{-1}$)	
			theoretical	actual *)
Leclanché, P	$\text{Zn}/\text{NH}_4\text{Cl}, \text{ZnCl}_2/\text{MnO}_2$	1.7	263	65–75
lead–acid, S	$\text{Pb}/\text{H}_2\text{SO}_4/\text{PbO}_2$	2.05	171	30–40
mercury–zinc, P	$\text{Zn}/\text{KOH}/\text{HgO}$	1.34	255	70–80
nickel–cadmium, S	$\text{Cd}/\text{KOH}/\text{NiOOH}$	1.30	210	40–50
nickel–iron, S	$\text{Fe}/\text{KOH}/\text{NiOOH}$	1.37	267	35–45
nickel–zinc, S	$\text{Zn}/\text{KOH}/\text{NiOOH}$	1.73	348	65–75

*) data from ref. 12

energy density of primary (non-rechargeable) and secondary (rechargeable) cells is approximately 30 and 20% of the theoretical value, respectively. This huge reduction is a consequence of the weight of excess active material, electrolyte and additional components and of the voltage loss due to current flow. It therefore depends on the construction of the cell and the magnitude of the current drain.

The power density of galvanic cells ($\text{W} \cdot \text{kg}^{-1}$ or $\text{W} \cdot \text{dm}^{-3}$) is determined by the ability of the cell to be discharged at high rates and by the degree of utilization of active material at these rates. The power density varies strongly with the electrochemical system (rate of electrode reactions) and the cell construction (transport phenomena).

The decisive parameter for many applications is the durability, which may be expressed as service life, i.e. number of years, or as cycle life, i.e. number of charge/discharge cycles. The durability is strongly influenced by both the stability of the electrode/electrolyte combination and the charge/discharge mechanism.

2.1.3. Thermodynamic and kinetic stability

Each electrolyte is characterized by a certain potential region, in which it is thermodynamically stable. If the potential of an electrode lies outside this region, the solution will be decomposed. Aqueous solutions are stable within a potential range of 1.23 V, the potential difference between the reversible oxygen and hydrogen electrodes. Generally, non-aqueous electrolyte solutions have a wider existence range, but their ionic conductance is much lower. The relative positions of a number of battery electrodes in aqueous electrolytes are shown in fig. 2.

Fig. 2. The electrode potentials of a number of electrodes with respect to the potential of the hydrogen electrode in the same solution; data from ref. 11.

The only thermodynamically stable cell shown in this figure is the Weston cell, i.e. $\text{Cd(Hg)} | \text{CdSO}_4 (\text{sat.}) | \text{HgSO}_4 (\text{sat.}) | \text{Hg}$. The open circuit potential of this standard cell is 1.01864 V at 20 °C and both electrode potentials lie within the existence range of water.

Most galvanic cells are thermodynamically unstable and their reactants will therefore be consumed without generating electrical energy. This process is called self-discharge. The rates of these side reactions determine whether a cell may be considered kinetically stable or not. The zinc electrode potential is 0.4 to 0.5 V more negative than that of the hydrogen electrode. However, hydrogen gas evolution can be suppressed by the use of amalgamated zinc. Both electrodes of the lead-acid cell exceed the boundaries of the stability region severely and can thus react with the aqueous solution. Due to the large overpotentials required for the hydrogen and oxygen evolution reactions the self-discharge of new lead-acid cells is practically negligible. On the other hand, during cycling antimony, usually added to the positive electrode grid, dissolves and is deposited at the active mass of both electrodes. This facilitates the evolution of hydrogen and oxygen considerably¹⁴). Several other impurities, e.g. Co, Fe, Cu, Ag, also catalyze the water decomposition reactions. Moreover, lead dioxide may react with the current-collecting grid (= lead), forming divalent lead compounds. As a result, the stored capacity of the positive electrode decreases and its grid degrades. This leads to shedding of the active material. In a similar way, the separator in a silver-zinc cell becomes oxidized by the high electrode potential of the $\text{AgO/Ag}_2\text{O}$ couple (+ 1.43 V).

Another example illustrating the importance of thermodynamic stability is the difference between the widely used cadmium electrode and the less suitable iron electrode. The equilibrium potential of the cadmium electrode is + 0.02 V versus the reversible hydrogen electrode and that of the iron electrode - 0.05 V. Although the quantitative difference is small, this potential difference has a significant consequence: in the non-working state the iron electrode corrodes and the cadmium electrode is corrosion-resistant. Nevertheless, to a lesser extent hydrogen evolution also occurs at the cadmium electrode, particularly during charging at high rates and after ageing of the electrode.

The position of the NiOOH electrode potential at the potential axis, just exceeding the upper boundary of the stability region, results in oxygen evolution during charging and in rapid self-discharge of fully charged electrodes.

Thus, the lack of thermodynamic stability of galvanic cells causes a decrease of the coulombic efficiency of the electrodes and degradation of cell components such as the current collector and the separator. In general, the rates of the side reactions are not necessarily the same at both electrodes and thus the reactants in the electrodes are unequally consumed. This will hinder further cycling of re-

chargeable cells. Furthermore, maintenance of the cell is required by the loss of electrolyte and the evolved gases must be able to escape. This prohibits hermetic sealing of the cells.

2.1.4. Charge/discharge mechanism

A large group of electrodes in aqueous solutions is charged and discharged according to a dissolution-precipitation mechanism. This group comprises the following electrodes: Pb/PbSO₄, PbO₂/PbSO₄, Zn/ZnO, Fe/Fe(OH)₂, Cd/Cd(OH)₂, Ag/Ag₂O and Ag₂O/AgO. The dissolution-precipitation mechanism involves the intermediate formation of a dissolved species, i.e. metal ion or metal ion complex, which precipitates from the solution to form a new solid phase. For instance, the discharge process of the lead dioxide electrode may be described by the equations ^{11,14}:

and in a similar way the charge process of a cadmium electrode in alkaline solution ^{11,12}:

The electrolyte not only serves as an ionic conductor, but also participates in the electrode reactions, as is shown by these equations. The conductivity of the solution may therefore depend on the state of charge of the electrodes, as for example in lead-acid cells. Furthermore, the accessibility of the internal surface may be rate-determining.

Because of the low concentration of the dissolved metal ion species ($C_{\text{eq}} = 10^{-4}$ – 10^{-5} mole.l⁻¹) high surface areas and small diffusion paths are required in order to obtain reasonable charge/discharge rates. However, inherent in the dissolution-precipitation mechanism is the change that takes place in the porous structure of the electrodes during cycling as a result of redistribution of the active material. A notorious example is the shape change of the zinc electrode ¹⁵). Generally, the major morphological changes involve:

- *nucleation and growth* of the new solid phase at the surface of the active material, already present;
- *passivation*, which consists of shielding the active material by a thin layer of dense fine-grained discharged material, e.g. the sulphation of lead and lead dioxide electrodes;
- *recrystallization*, especially after long waiting periods, which leads to the formation of larger grains and/or more stable modifications, e.g. memory effect of nickel-cadmium cells;

— *dendrite formation*, due to mass transport limitation, which may cause failure by internal short-circuiting.

Thus, the magnitude of the active surface area and its accessibility are decreased during cycling. The detrimental effects of the morphological changes increase strongly with the charge and discharge rates and with the depth of discharge. The cycle life decreases exponentially with increasing depth of discharge¹²). Therefore, the optimal degree of active material utilization lies between 25 and 45% at medium rates, i.e. during discharge periods of 5 to 20 hours. At higher current densities, e.g. discharging in less than one hour, the utilization of active material is progressively reduced. Electrodes without soluble intermediates, such as the nickel (hydroxide) electrode, do not suffer such limitations.

The solid state transitions that take place in the nickel electrode can be summarized by the Bode diagram¹⁶):

Well-crystallized $\beta\text{-Ni(OH)}_2$ has a layered structure with an interlayer distance of 4.605 Å. Each layer consists of a hexagonal planar arrangement of Ni(II) ions with an octahedral coordination of oxygen, three oxygen atoms lying above the nickel plane and three lying below. The α - and β -nickel hydroxides, used in batteries, also have a lamellar structure, but the crystal lattice is highly disordered. This low crystallinity is considered to be essential for the electroactivity. Moreover, the intersheet distance of the α -modification is expanded by the intercalation of water molecules, $d = 8\text{--}8.5$ Å, which additionally improves the kinetics of the redox reaction.

$\beta\text{-NiOOH}$ has practically the same layered structure, $d = 4.85$ Å, as $\beta\text{-Ni(OH)}_2$ and can be formed from the latter by direct reaction on removing one proton and one electron, according to eq. (3a). $\gamma\text{-NiOOH}$ represents a whole family of compounds exhibiting a large intersheet distance, $d \geq 7$ Å, with the oxidation state of nickel ranging from +3.3 to +3.75. Both water molecules and alkali ions are intercalated between the NiO_2 layers.

If overcharging is avoided, the nickel electrode can be cycled between $\beta\text{-Ni(OH)}_2$ and $\beta\text{-NiOOH}$ (eq. 3a). During prolonged overcharging and at high charge rates $\beta\text{-NiOOH}$ is converted into $\gamma\text{-NiOOH}$ (eq. 3c), which possesses a larger storage capacity. Ageing of $\beta\text{-NiOOH}$ also favours the formation of the more stable γ -modification. Because of the expanded intersheet distance of both $\alpha\text{-Ni(OH)}_2$ and $\gamma\text{-NiOOH}$, these substances can be directly interconverted, even at higher rates than the $\beta^{\text{II}}/\beta^{\text{III}}$ transition. Due to the poor conductivity of divalent nickel hydroxide, κ is about $10^{-6} \Omega^{-1}\text{cm}^{-1}$, the discharge

process stops at an average oxidation state of +2.3. The complete active mass may be discharged to this level without affecting the cycle life. This enables an overdischarge mechanism, comprising very negative overpotentials (sec. 2.1.5). The α - to β -Ni(OH)₂ transformation involves an increasing crystallinity upon ageing (eq. 3d).

The rates of the charge and discharge reactions are considered to be controlled by transport of protons and, possibly, of hydroxyl ions in the solid phase. The proton diffusion coefficients are reported to be $3.1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ during charging, i.e. $D_{\text{H}^+}(\beta^{\text{III}})$, and $4.6 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ during discharging, i.e. $D_{\text{H}^+}(\beta^{\text{II}})^{17}$. Therefore, diffusion of the intercalated protons only becomes rate-limiting at high discharge currents. Depending on the structure, the electrode may be discharged in less than half an hour.

The structural stability makes the solid state transition mechanism much more favourable than the more common dissolution-precipitation mechanism. This is demonstrated both by the remarkable cycling durability of several thousand cycles and the high rate charging and discharging capability of the nickel electrode.

2.1.5. Reactions in sealed cells

The aim underlying the development of sealed cells is to obtain batteries that will operate in any position and without requiring maintenance. The build-up of hazardous gas pressures, due to oxygen and hydrogen evolution (sec. 2.1.3), and the loss of electrolyte must therefore be prevented.

In nickel-cadmium cells this was achieved by adding uncharged negative electrode material, i.e. Cd(OH)₂ to both electrodes, as is illustrated in fig. 3. At the

Fig. 3. Schematic diagram of a sealed nickel-cadmium cell, showing the electrode dimensions and the oxygen cycles during overcharging and overdischarging.

end of charging oxygen is evolved at the positive electrode before the negative electrode is completely charged, because of the excess of active material in this electrode. Subsequently, the oxygen formed is reduced at the negative electrode. In this oxygen recombination process the transport of oxygen is rate-determining. Therefore, the cell contains as little electrolyte as possible, wetted electrodes are used instead of flooded ones, and the O_2 -permeability of the wetted separator plays a major role. If the oxygen cycle functions well, the state of charge of both electrodes does not change during overcharging and the total input of electrical energy is dissipated as heat. In a similar way, the oxygen evolved at the positive electrode as a result of side reactions is consumed at the negative electrode.

Owing to manufacturing variations, not all cells have exactly the same storage capacity. In a battery, comprising several cells connected in series, the weakest cell may therefore be overdischarged by the current which is imposed by the other cells. Without suitable precautions such an occurrence is accompanied by the decomposition of the electrolyte, while the cell voltage is reversed. However, the addition of $Cd(OH)_2$ to the nickel electrode prevents the cathodic evolution of hydrogen gas. Instead, metallic cadmium is formed and this reacts with oxygen, now evolved at the cadmium electrode. (This electrode thus reaches its maximum depth of discharge!) Again the cell is protected by an oxygen recombination cycle.

Despite the excess of $Cd(OH)_2$ in both electrodes and the thermodynamic stability of cadmium in aqueous electrolytes, hydrogen gas is evolved¹⁸⁾ due to the poor charge acceptance of aged $Cd(OH)_2$ and during charging at high current densities. Because the oxidation of hydrogen at the nickel electrode is practically negligible, the electrode capacities become unbalanced and the cell pressure rises. Sealed cells are therefore equipped with safety valves which open at about 20 atm.

The development of entirely sealed lead-acid cells is severely hindered by the gassing of the electrodes (sec. 2.1.3). Catalytic recombination of hydrogen and oxygen in the gas space above the electrolyte is only successful if the gas evolution occurs stoichiometrically ($H_2 + \frac{1}{2} O_2$). The utilization of auxiliary electrodes is not suitable for small cells. An oxygen cycle analogous to that in sealed nickel-cadmium cells may also be established in lead-acid cells, provided that the electrolyte is immobilized¹⁴⁾. However, the cycle life of such cells is reduced by the electrolyte immobilization to only 50–100 cycles¹¹⁾.

2.1.6. Conclusions

In our battery research, we aimed at a small rechargeable cell, which could be charged and discharged at high rates and would function in any position for several years without requiring maintenance. The small-sized, sealed nickel-

cadmium cell resembles this type of cell most closely. However, for reasons given above the performance of the nickel-cadmium cell would be improved if the cadmium electrode could be replaced by a different rechargeable negative electrode, in which the following requirements are fulfilled:

- (a) charging and discharging occurs via a solid state transition mechanism, analogous to that of the nickel electrode, and
- (b) hydrogen gas, possibly evolved during overdischarging, is prevented from unbalancing the cell or giving rise to hazardous pressures.

2.2. Hydrogen in metals

2.2.1. Introduction

Hydrogen reacts with elements from most groups of the periodic system to form hydrides. Well-known compounds are LiH , MgH_2 , AlH_3 , CH_4 , NH_3 , H_2O , HCl and PdH_x . Although the distinction is not always sharp, these different binary hydrides are usually classified in three categories¹⁹⁾:

- ionic or saline hydrides, e.g. LiH , MgH_2 and HCl ;
- covalent hydrides: the prototype is CH_4 , but AlH_3 also belongs to this class;
- metallic hydrides: this group comprises the hydrides formed by transition metals.

Our study is concerned with metallic hydrides. In particular, we are interested in metals which are capable of absorbing and desorbing hydrogen reversibly in the pressure range around 1 atm and near room temperature.

At 20 °C palladium, the most thoroughly investigated hydride-forming element, absorbs hydrogen at an equilibrium pressure of 6×10^{-3} atm to form the hydride $\text{PdH}_{0.6}$. A review of the palladium-hydrogen system up to 1966 can be found in the book by Lewis²⁰⁾. The hydrides of vanadium and niobium, VH_2 and NbH_2 , decompose partially to VH and NbH , respectively, near or somewhat above room temperature at 1 atm. The hydrides of the metals of group IIIA and IVA, e.g. YH_2 , LaH_2 , TiH_2 and ZrH_2 , are extremely stable and therefore decompose only at very high temperatures. On the other hand, Cr, Mn, Co, Ni and Mo only form hydrides at very high pressures. For example, CrH is stable at 25 °C and 700 atm. Recently, extensive reviews of the binary hydrides of transition metals have been published²¹⁾. Clearly, the number of suitable binary metal-hydrogen systems is severely limited by the requirement of reversibility at ambient temperatures and pressures.

The discovery of the hydriding properties of intermetallic compounds such as LaNi_5 ^{22,23)} and TiFe ²⁴⁾ has provided many new metallic hydrides. Generally, intermetallic compounds of transition metals form ternary hydrides if at least one of their constituents forms a stable binary hydride. LaNi_5 is the exponent

of a family of AB_5 compounds, each number consisting of one or more lanthanide elements (A) and 3d transition metal elements (B). Most of these AB_5 compounds are capable of storing reversibly large quantities of hydrogen^{25,26}).

A characteristic property of many hydrides is their relatively large hydrogen content²⁷). In table II both the volumetric density and the weight fraction of

TABLE II

Comparison of the hydrogen content of various hydrogen compounds.

N_H represents the number of hydrogen atoms per unit volume and

C_H gives the weight percentage of hydrogen in the various materials.

(after ref. 27)

material	$N_H \times 10^{-22} \text{ (cm}^{-3}\text{)}$	$C_H \text{ (wt \%)}$
H ₂ gas, 150 atm	0.7	100
liquid H ₂ , 20 K	4	100
liquid CH ₄	6	25
TiH ₂	9	4
LaH ₃	6.5	2.1
MgH ₂	6.5	7.6
TiFeH ₂	6	1.9
LaNi ₅ H ₆	5.5	1.4

hydrogen in representative metal hydrides are compared with those in liquid hydrogen and methane. The hydrogen density in these metal hydrides exceeds that in liquid hydrogen by a factor of 1.5 to 2. The weight fraction of hydrogen in metal hydrides is always considerably lower than in liquid hydrogen because of the weight of the metallic host.

2.2.2. Absorption and desorption phenomena

The absorption and desorption of hydrogen by metals is most conveniently represented by pressure-composition isotherms. A schematic diagram of such isotherms is given in fig. 4, which comprises the following features.

A small amount of hydrogen gas dissolves in the original metallic host without forming a second phase:

The absorbed hydrogen atoms occupy interstitial sites in the metal lattice and their concentration depends strongly on the hydrogen pressure. This hydrogen-poor solid solution is denoted by the α -phase. The next stage involves the absorption of hydrogen after the solid solution is saturated:

Fig. 4. Schematic phase diagram of a metal-hydrogen system, comprising the pressure-composition isotherms at various temperatures; $T_x > T_{x-1}$.

Now, a new solid phase, referred to as the β -phase, nucleates and grows. This is accompanied by a discontinuous change in the lattice parameters. Ideally, during the α/β -phase transition the equilibrium pressure remains constant according to Gibbs' phase rule: $F = C - P + 2$. Two components C (H_2 and M) and three phases P (two solid and one gaseous) are present, so the number of degrees of freedom F is one. Thus, at a given temperature the pressure is fixed. This constant pressure level is often called the plateau pressure. Even if the host metal consists of an intermetallic compound, in this context, it is considered to be only one component because of the immobility of its constituents at low temperatures. The concentration region between the saturated solid solution α_s and the newly formed β -phase β_0 can be regarded as a miscibility gap between two well-defined phases.

After the α -phase has been completely converted into the β -phase, further increase of the hydrogen concentration in the metal is accompanied by an increasing equilibrium pressure. Similar to the hydrogen dissolution in the 'empty' host, i.e. the α -phase, hydrogen dissolves in the hydrided β -phase.

At higher temperatures the influence of the entropy counteracts the tendency to form two separate phases. As a consequence, the miscibility gap becomes smaller with rising temperature and ultimately disappears at the critical temperature T_c .

Fig. 5. Phase diagram for the palladium-hydrogen system; from ref. 28.

As an example of a very precisely determined phase diagram, the isotherms for the palladium-hydrogen system²⁸⁾ are shown in fig. 5. The analogy between the schematic diagram of fig. 4 and that of the real system is obvious. The plateau pressures increase with increasing temperature according to the relation of Van 't Hoff:

$$\ln p_{H_2} = -\frac{\Delta H_{\alpha/\beta}^\circ}{RT} - \frac{\Delta S_{\alpha/\beta}^\circ}{R}, \quad (6)$$

where R is the gas constant and ΔH° and ΔS° are the enthalpy and entropy change per mole H_2 , respectively. Applying this equation to the data of fig. 5 results in $\Delta H_{\alpha/\beta}^\circ = -41.0 \pm 0.4$ kJ (mole H_2)⁻¹ and $\Delta S_{\alpha/\beta}^\circ = -97.5 \pm 0.8$ J (K-mole H_2)⁻¹ for the palladium-hydrogen system in the temperature range from 20 to 300 °C. The position of the critical point has also been determined with high precision: $T_c = 291 \pm 2$ °C, $x_c = 0.250 \pm 0.005$ H/Pd and $p_c = 19.7 \pm 0.2$ atm.

Several hydrogen-absorbing materials, e.g. TiFe and LaCo₅, form more than one ordered hydride phase. In the metal-hydrogen phase diagram the second hydride phase shows up as an additional plateau in the pressure-composition isotherms. Fig. 6 displays the isotherms for the TiFe-H₂ system²⁴⁾, which illustrate this phenomenon. Furthermore, it is seen that both hydrides, i.e. TiFeH and TiFeH₂, have dissociation pressures of more than 1 atm at 0 °C. The critical temperature of the TiFeH-TiFeH₂ two-phase region is approximately 60 °C. This explains the disappearing second plateau in the isotherms with increasing temperature.

Fig. 6. Desorption isotherms for the TiFe-H₂ system at various temperatures; from ref. 24.

The isotherms presented in both fig. 5 and fig. 6 have been determined during the desorption of hydrogen. For most materials the absorption process takes place at higher plateau pressures than those at which hydrogen is released. This hysteresis is not caused by a lack of equilibrium. Instead, most investigators have related this effect to the volume expansion during hydriding. The hysteresis in the absorption/desorption isotherms for TiFe-H₂ is rather large. For example, at 40 °C the first hydride phase TiFeH is formed at the equilibrium pressure of 15 atm, while the desorption pressure is only 7.5 atm. In practical applications, rapid hydrogen uptake is obtained by an applied pressure of 30 atm at 20 °C.

The absorption and desorption isotherms for LaNi₅-H₂ at 20, 40 and 80 °C are shown in fig. 7. At 20 °C LaNi₅ absorbs six hydrogen atoms at a plateau pressure of 2 atm, while the hydride formed decomposes at a constant pressure of 1.6 atm. The absorption/desorption hysteresis of the LaNi₅-H₂ system is characterized by a nearly constant $\Delta p/p$ -ratio for different temperatures. However, the pressure difference is only 3 atm at 80 °C. Moreover, even at temperatures as high as 80 °C, large amounts of hydrogen can be stored reversibly in

Fig. 7. Absorption and desorption isotherms for $\text{LaNi}_5\text{-H}_2$ at 20, 40 and 80 °C; from ref. 26.

LaNi_5 at equilibrium pressures below 20 atm. The reaction rates at room temperature for both absorption and desorption are very high for pulverized LaNi_5 . Van Vucht et al.²³⁾ measured the rate of hydrogen desorption in 1 atm of hydrogen gas at different temperatures. At 25 °C the complete desorption took only 15 min, while the underpressure was less than 1 atm.

The values of the enthalpy and entropy change for the α/β -transition of $\text{LaNi}_5\text{-H}_2$, derived from the pressure-composition isotherms according to eq. (6), are $-31 \text{ kJ (mole H}_2\text{)}^{-1}$ and $-109 \text{ J (K}\cdot\text{mole H}_2\text{)}^{-1}$, respectively. Almost the same values have been determined from calorimetric measurements²⁹⁾:

$$\begin{aligned}\Delta H_{\alpha/\beta}^\circ(298.15 \text{ K}) &= -30.40 \pm 0.35 \text{ kJ (mole H}_2\text{)}^{-1} \quad \text{and} \\ \Delta S_{\alpha/\beta}^\circ(298.15 \text{ K}) &= -111.5 \pm 0.5 \text{ J (K}\cdot\text{mole H}_2\text{)}^{-1}.\end{aligned}$$

2.2.3. Stability of metal hydrides

The purpose of this subsection is not to discuss the resistance of metal hydrides to corrosion, but rather to present some statements concerning the affinity of intermetallic compounds for hydrogen.

As already mentioned in sec. 2.2.1, transition metal compounds that form stable hydrides contain at least one metal that forms stable binary hydrides. Evidently, the stability is related to the free enthalpy change. For the various hydride-forming materials, the values of $\Delta H_{\alpha/\beta}^\circ$ can be widely different. On the

other hand, the entropy effect is found to be fairly independent of the host metal. The reason is that the entropy change during hydrogen absorption is dominated by the loss of the entropy of hydrogen gas; the standard value $S_{H_2}^\circ = 130 \text{ J (K} \cdot \text{mole H}_2\text{)}^{-1}$ at 1 atm and room temperature. The other entropy effects are relatively small compared with this term. This makes it possible to express the affinity of metals for hydrogen in terms of $\Delta H_{\alpha/\beta}^\circ$ alone. If we assume $\Delta S_{\alpha/\beta}^\circ = -110 \text{ J (K} \cdot \text{mole H}_2\text{)}^{-1}$ and define a stable hydride as one for which the plateau pressure lies below 1 atm at 300 K, a stable hydride is characterized by a formation enthalpy more negative than $-33 \text{ kJ (mole H}_2\text{)}^{-1}$. Small variations in $\Delta H_{\alpha/\beta}^\circ$ cause large shifts in the plateau pressures.

Miedema et al. formulated an empirical relation for estimating the hydride formation enthalpy of intermetallic AB_n compounds ($n \geq 1$)^{26,27)}

$$\Delta H(AB_nH_{x+y}) = \Delta H(AH_x) + \Delta H(B_nH_y) - (1 - F) \cdot \Delta H(AB_n). \quad (7)$$

The values of x, y and F vary smoothly with the composition of the intermetallic compound, i.e. with the value of n . These values are tabulated²⁷⁾. Equation (7) indicates that the stability of the ternary hydride AB_nH_{x+y} increases with decreasing stability of the intermetallic compound AB_n . This is known as the rule of reversed stability. With the help of eq. (7) the plateau pressure of an intermetallic compound can be adjusted by an appropriate choice of its constituents. For instance, at 40 °C the desorption pressure for LaNi_5H_6 is 3 atm and for $\text{LaNi}_4\text{CuH}_{5.6}$ it is 1.5 atm³⁰⁾. The plateau pressure of $\text{LaNi}_4\text{M-H}_2$ decreases progressively as M represents successively Pd, Ni, Ag, Cu, Co, Fe, Cr, Al or Mn. Similarly, an increase of the plateau pressure has been found if La in LaNi_5 is (partially) replaced by Nd, Gd, Y or Er.

2.2.4. Conclusions

The number of metal-hydrogen systems has been markedly increased by the discovery of the hydriding properties of intermetallic compounds. Large amounts of hydrogen can be reversibly stored at pressures around 1 atm near room temperature. The volumetric hydrogen density often exceeds the hydrogen content in liquid hydrogen.

Moreover, the insight gained into intermetallic compound-hydrogen systems enables us to match the properties to the specific requirements. Many applications have been suggested^{21,26,31,32)}. Among these is the utilization of metal hydrides in rechargeable batteries³³⁻³⁶⁾.

2.3. Metal hydride electrodes

2.3.1. Concept

At the end of sec. 2.1, we formulated the need for a negative battery electrode which can be charged and discharged via a solid state transition mechanism and

is capable of coping with evolved hydrogen gas. In the previous section, it was concluded that many intermetallic compounds with interesting hydriding properties are available. The synthesis of these two conclusions leads to the concept of a rechargeable battery electrode based upon the electrochemical storage of hydrogen in intermetallic compounds. Such an electrode will be denoted as a metal hydride electrode.

Charging of a metal hydride electrode consists of the electrochemical reduction of water at the metal surface, resulting in the formation of adsorbed hydrogen atoms. Subsequently, these hydrogen atoms diffuse into the bulk of the host metal to form a metal hydride. Discharging of such an electrode consists of dehydriding, followed by oxidation of the released hydrogen atoms. Inherent in metal hydrides both the host and the hydride are good electronic conductors. Thus charging and discharging proceeds according to

— a charge transfer reaction

— dissolution and diffusion in the solid state

— and recrystallization of the condensed phase

The complete electrode reaction can be described by

As is shown by these equations, the electrochemical storage capacity is proportional to the hydrogen content of the metal hydride and the electrode potential is close to that of the reversible hydrogen electrode. Decomposition of the aqueous electrolyte is no longer an unwanted side reaction but is an essential step in the charging process. Moreover, evolved hydrogen gas can be expected to be absorbed or oxidized by the hydride electrode.

2.3.2. *Electrochemical pressure-composition isotherms*

The hydrogen absorption and desorption characteristics of metals are represented by pressure-composition isotherms. Analogous plots for battery electrodes are charge/discharge curves. These plots show the variations of the electrode potential E as a function of the state of charge Q .

The equilibrium potential of the hydride electrode, i.e. of the redox couple of eq. (9), is related to the equilibrium pressure for the absorption and desorption of hydrogen gas. With the help of the electrochemical cell in fig. 8, this relation

Fig. 8. Electrochemical cell, containing a metal hydride electrode (right) and a reversible hydrogen electrode (left).

is readily derived. The hypothetical cell of fig. 8 comprises a metal hydride electrode and a reversible hydrogen electrode, both immersed in the same aqueous electrolyte with $a_{H^+} = a'$. The cell voltage ΔE thus equals the required equilibrium potential E_r with regard to the reversible hydrogen electrode potential RHE. The cell reaction can be written as

At equilibrium, one obtains:

$$-xF\Delta E = \mu_{MH_x} - \mu_M - \frac{1}{2}x\mu_{H_2}^0, \quad (11)$$

where F is the Faraday constant and μ_i is the chemical potential of component i . Recognizing that the right-hand side of eq. (11) equals the free enthalpy change of the hydriding reaction at 1 atm and using $\Delta E = E_r$ vs. RHE, we obtain

$$E_r = \frac{-RT}{2F} \ln p_{H_2} \text{ vs. RHE}, \quad (12a)$$

or at $T = 25^\circ\text{C}$:

$$E_r = -0.0296 \log p_{H_2} \text{ vs. RHE}. \quad (12b)$$

Thus, at a hydrogen equilibrium pressure of 1 atm the metal hydride electrode potential is the same as that of the RHE, and its value changes by approximately 30 mV for a ten-fold hydrogen pressure variation.

Furthermore, eq. (9) indicates that each absorbed hydrogen atom corresponds to the storage of one electron. Consequently, the state of charge Q varies linearly with the H/M ratio x . For LaNi_5 , the relation $Q = 62.x \text{ mAh}\cdot\text{g}^{-1}$ holds, as will be explained in sec. 3.2.2.

As an example, fig. 9 shows a charge and a discharge isotherm for LaNi_5 at 16°C in 6 M KOH. We determined these 'equilibrium' curves by imposing

Fig. 9. Charge (→) and discharge (←) isotherm for a LaNi_5 electrode at 16 °C in 6 M KOH.

100 ms current pulses and measuring E_t at the end of a relaxation period of 800 ms. The amount of charge passed during each pulse corresponded to only 8.33×10^{-6} H/ LaNi_5 . Comparison of figs 7 and 9 demonstrates the analogy and shows that LaNi_5 is also capable of storing and releasing hydrogen electrochemically. The corresponding theoretical storage capacity of a LaNi_5 electrode amounts to $372 \text{ mAh}\cdot\text{g}^{-1}$, which is almost the same as the value for the cadmium electrode, i.e. $366 \text{ mAh}\cdot\text{g}^{-1}$.

2.3.3. Conclusions

The utilization of intermetallic compounds as active materials in battery electrodes provides a new type of rechargeable electrode: the hydride electrode. Such an electrode operates at potentials close to that of the reversible hydrogen electrode. The charge and discharge process involves the reversible storage of large amounts of hydrogen in the metallic host. All reactions proceed in the condensed phase; no soluble intermediates are involved.

Several intermetallic compounds have been studied for use in metal hydride electrodes, e.g. TiNi ³³), TiFe ³⁴) and LaNi_5 ³⁵). In our view, LaNi_5 and related AB_5 compounds are the most auspicious materials for electrochemical applications. These intermetallic compounds combine a large reversible storage capacity at plateau pressures of approximately 1 atm at 20 °C with high reaction rates and small absorption/desorption hysteresis. Moreover, LaNi_5 is easily modified by partial substitution to provide similar compounds with more favourable properties.

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3. LaNi₅ AND LaNi₄Cu ELECTRODES

3.1. Introduction

The application of metal hydride electrodes in electrochemical cells involves the use of hydrogen as fuel, which is stored in the hydrogen-absorbing electrode. At the surface of such an electrode, hydrogen is formed by the electrochemical reduction of water, or stored hydrogen is oxidized

Thus, both aspects, hydrogen storage (bulk) and electrocatalytic properties (surface), play an important role in the choice of appropriate electrode materials. Moreover, chemical stability of the hydride-forming compound in aqueous electrolytes is an essential feature in attaining practical, rechargeable electrodes.

The possibility of rapid and reversible storage of large amounts of hydrogen gas in LaNi₅ at a plateau-pressure of about 2 atm at room temperature makes this intermetallic compound an attractive material¹⁻⁴). Several investigators have also reported on the capability of LaNi₅ to store and release hydrogen electrochemically⁵⁻⁸).

Ewe et al.⁶) found that the electrochemically determined storage capacity of LaNi₅ is about half that calculated from the limiting composition LaNi₅H₆ and attributed this observation to a different method of preparation or pretreatment. In our view, this might be due to hot-pressing (350 °C) of the electrode pellets. Moreover, they concluded that the compound LaNi₅ is resistant to corrosion in 6 M KOH.

Boter⁶) constructed rechargeable cells, the negative electrode of which consisted of LaNi₅ or one of the pseudo-binary derivatives of this compound. An electrode made from LaNi₄Cu proved to be especially suitable because of its lower plateau pressure, i.e. $p_{H_2} < 1$ atm at room temperature, and its capability of high-rate charging and discharging.

The temperature dependence of the storage capacity of LaNi₅-based electrodes in unsealed cells was studied by Bronoël et al.⁹). The electrochemically measured capacity values decreased with increased temperature as a result of a growing amount of hydrogen lost by spontaneous hydrogen gas desorption. At 20 °C the storage capacity of LaNi₅ was found to be 320 mAh·g⁻¹, which is 85% of the theoretical value. In order to reduce hydrogen gas desorption in open cells, Percheron-Guegan¹⁰) et al. also used substituted LaNi₅ compounds. They stated that electrodes made from these materials could undergo a great number of charge/discharge cycles without change of their performance (300 mAh·g⁻¹ at temperatures between -10 and 50 °C).

Van Rijswijk⁸⁾ concluded that the choice of intermetallics is severely limited by the required stability in contact with aqueous electrolytes. Only compounds in which the major component is thermodynamically stable against oxidation, i.e. nickel and the noble metals, are suitable as metal hydride electrodes.

The maximum storage capacity of the LaNi₅ electrodes, studied by Markin et al.¹¹⁻¹³⁾ for application in satellite batteries, amounted to 240 mAh·g⁻¹. They also observed a loss of capacity during charge/discharge cycling in 6 M KOH, which they attributed entirely to the presence of oxygen in the cell. On the other hand, Holleck et al.¹⁴⁾ reported a continuous decrease of the storage capacity of LaNi₅ due to the presence of water vapour. This instability of the storage material in the cell environment limits the cycle-life of a battery.

Despite all these conflicting results regarding the stability of hydriding materials in aqueous media, Bittner and Badcock¹⁵⁾ concluded in their recent review article that LaNi₅ appears to be the most promising material for electrochemical utilization studied to date.

We investigated LaNi₅ and LaNi₄Cu electrodes with special emphasis on their behaviour during repeated cycling. The electrochemical performance of these electrodes is discussed in sec. 3.2. The observed capacity loss is analysed with the help of X-ray diffraction, surface area measurements and electron microscopy, presented in secs 3.3, 3.4 and 3.5, respectively. In sec. 3.6 the first conclusions are summarized.

3.2. Galvanostatic charge/discharge cycling

3.2.1. *Sample preparation and measuring equipment*

All intermetallic compounds used were prepared by melting a mixture of the composing elements in an arc furnace under an argon atmosphere (20 torr). To obtain better homogenization the samples were turned over and remelted several times. More details of the preparation procedure have been described by Van Mal⁴⁾. All compounds were examined by X-ray powder diffraction in order to identify the structural parameters and to verify that no second phase was present.

Metal powder was obtained either by crushing and grinding mechanically or by repeated hydrogen gas absorption/desorption cycles. The specific surface area of this powder was determined by krypton gas adsorption measurements (BET), described in sec. 3.4. After pulverization only the fraction that passed through a 40 µm sieve was used as active electrode material. Both the cast and the powder of intermetallic compounds were handled in ambient atmosphere without special precautions.

The electrodes were made by mixing active particles with fine copper powder (Merck p.a. electrolytic Cu) and cold-pressing this mixture to a porous pellet.

The pellets were 8.0 mm in diameter (geometrical area 0.50 cm^2) and about 0.5 mm thick; their total weight was approximately 150 mg, so the void volume was about 30%. Varying the weight ratio active material/supporting copper powder between 1:9 and 1:2 and the applied pressure between 0.4 and $4.0 \times 10^8 \text{ Pa}$ did not influence the electrode performance significantly. Only the heavily loaded samples were deformed from flat to hemispherical after many charge/discharge cycles. Most pellets contained about 30 mg active material and were pressed at a pressure of $4.0 \times 10^8 \text{ Pa}$.

For the electrochemical measurements a pellet was attached to a copper rod ($\varnothing = 8.0 \text{ mm}$) by a shrink-sleeve and placed in a glass cell, as illustrated in fig. 10.

Fig. 10. Schematic display of the electrochemical cell; w.e., r.e. and c.e. stand for working, reference and counter electrode.

The cell comprised two compartments separated by porous glass ceramic and both were purged with nitrogen. The cell was surrounded by a water jacket to control the temperature mostly at 25°C . As counter and reference electrode we used, respectively, a platinum plate (ca. 6 cm^2) and a $\text{Hg}/\text{HgO}/6 \text{ M KOH}$ electrode. All electrode potentials are given with respect to this reference electrode whose formal potential is 930 mV more positive than the reversible hydrogen electrode. The electrolyte was a 6 M KOH solution (Merck, p.a. KOH pellets; deionized water). In order to start with a completely wetted internal surface the electrode was vacuum-impregnated with electrolyte before cycling.

Fig. 11 shows a block diagram of the automated galvanostatic charge/discharge cycling apparatus to which the glass cell was connected. The microcomputer controlled the charge- and discharge-current, the charging period and the final discharge potential and calculated the storage capacity via the measured discharging period. In another mode the discharging period could be adjusted. The 4 cells galvanostat/voltmeter unit, designed and built in our laboratory,

Fig. 11. Block diagram of the automated galvanostatic charge/discharge cycling apparatus.

imposed the currents on four cells and measured the potential variations for controlling and recording purposes. With two of these units we were able to execute simultaneously eight independent experiments. The accuracy of the galvanostats was better than 0.1% for currents between $4\mu\text{A}$ and 65 mA . All measuring data were both directly printed and stored on magnetic disks for printing and plotting afterwards.

3.2.2. Results

3.2.2.1. A single galvanostatic charge/discharge cycle

The electrochemical absorption and release of hydrogen by the compound AB_5 can be represented by the redox equation

This equation shows that each absorbed hydrogen atom corresponds to the storage of one electron. This results in a simple relation which allows us to calculate the theoretical capacity per unit weight

$$C_{\text{th}} = \frac{xF}{3.6 M_{\text{AB}_5}} \text{mAh} \cdot \text{g}^{-1}, \quad (15)$$

where F and M_{AB_5} are the Faraday constant and the molecular weight of the AB_5 compound, respectively, and x stands for the number of hydrogen atoms per AB_5 unit as defined by eq. (14). The maximum value of x being 6, as determined

by hydrogen gas desorption measurements¹⁶), the storage capacity of LaNi_5 is calculated to be $372 \text{ mAh}\cdot\text{g}^{-1}$.

The main purpose of a galvanostatic charge/discharge cycle is to establish the experimental capacity value. Moreover, the potential variations during a cycle provide important information on the processes occurring. A single cycle consists of four successive periods:

- charging with a constant cathodic current; moving to the right-hand side of eq. (14),
- resting for a short period,
- discharging with a constant anodic current; returning to the left-hand side of eq. (14), and finally
- resting.

In battery terminology the rates of charge and discharge are usually expressed in terms of C , where C is the numerical value of the electrode capacity in mAh . This value may be related to the theoretical capacity, C_{th} , eq. (15), or to a *rated* capacity as for instance C_R , which is defined as the capacity measured when the electrode is completely discharged in five hours¹⁷). A yC rate, i.e. a yC current, i_{yC} , equals the value of the current which forces the electrode to be charged or discharged completely within y^{-1} hours, assuming no kinetic limitation.

Fig. 12 depicts a complete third cycle of a typical LaNi_5 electrode, charged during one hour and discharged, both at a $1.25 C$ rate (about 14 mA). Starting at the rest potential, -852 mV , the potential decreased rapidly to about -1015 mV . At this level the potential stayed virtually constant for about 35 min. , and then gradually changed to a more negative, constant value, -1030 mV . This potential will be referred to as the hydrogen evolution potential, E_{he} . Ideally, after 48 min. charging with a $1.25 C$ current the electrode must be completely loaded

Fig. 12. The potential variation during the third galvanostatic charge/discharge cycle of a typical LaNi_5 electrode. Both charging and discharging were carried out at $1.25 C$ rate.

and hydrogen gas evolution should start. However, especially in the case of a *new* electrode there is no sharp transition from one reaction to the other. After charging was completed, the current was interrupted for 30 s to measure the open circuit potential of the charged electrode; $E_c = -960$ mV.

Subsequently, discharging started and lasted for 44.5 min; 93% of the theoretical capacity was recovered at this high rate. The potential difference between the charging and discharging curves, uncompensated for the ohmic resistance ($= \Sigma \eta_{c/d} + 2IR_u$), amounted to approximately 130 mV. The electrolyte resistance, R_u , was measured by the interruption method at a fully charged electrode evolving hydrogen gas. The R_u value between a *new* storage electrode and a well positioned reference electrode was less than 0.1Ω . During repeated charging/discharging R_u increased to 0.2Ω , due to changes in the porous structure. When the reference electrode was placed at a relatively large distance from the working electrode (about 2-3 cm), the R_u value reached only 0.8Ω as a result of the high conductivity of a 6 M KOH solution. Discharging was terminated at the moment the potential exceeded a certain previously chosen potential level, called the final discharge potential, E_{fd} . In this experiment E_{fd} was chosen to be -600 mV, but because of the steep rise of the potential near the end of discharge any potential more positive than -800 mV would be adequate, provided that the copper matrix did not oxidize ($E(\text{Cu}/\text{Cu}_2\text{O}) = -460$ mV). The steep rise did not result from a fast-growing hydrogen concentration gradient in the solid phase, but was caused by a general hydrogen depletion. When the current was stopped, the hydrogen concentration levelled off, producing a strong decrease in electrode potential. It is in fact the hydrogen concentration at the interface, together with the pH, that determines the potential. The value measured after a 15 min. relaxation period will be denoted as the discharged electrode potential: $E_d = -833$ mV.

Finally, it should be noted that the whole process took place in the immediate region of the reversible hydrogen electrode potential. For rechargeable negative electrodes in aqueous electrolytes this region is the most favourable potential range.

3.2.2.2. Repeated galvanostatic charge/discharge cycles

a. *LaNi₅* ELECTRODE

The previous section presented data on the electrode capacity and potentials. An even more important property of a rechargeable battery electrode is its *endurance*. We therefore measured the changes in the performance of the electrode during repeated galvanostatic charge/discharge cycling. Fig. 13 depicts the decay of the storage capacity of a *LaNi₅* electrode as a function of the cycle number, n . Each dot in this graph represents the capacity of a cycle, discharged at the

Fig. 13. The capacity decline of a typical LaNi_5 electrode, discharged at 1.25 C rate (dots) and 1.25 + 0.125 C rate (asterisks), and charged for 1 hour at 1.25 C rate if $n \leq 94$ and for $\frac{1}{2}$ hour at 2.5 C rate if $n > 94$.

1.25 C rate. To complete the hydrogen desorption the electrode was additionally discharged at the relatively low 0.125 C current every thirty cycles. The cumulative capacity values are denoted by asterisks.

During the first cycles the electrode was charged at the 1.25 C rate; after the 94th cycle charging was carried out at the 2.5 C rate. This change did not affect the course of the capacity curve, $C(n)$. Both this observation and the small contribution to the total capacity of the low rate-discharge illustrates again the suitability of LaNi_5 electrodes for application in high power cells.

Plots of each of the potentials E_{he} , E_c and E_d , defined in sec. 3.2.2.1, are given in fig. 14. Besides, the electrode potentials after additional, low rate discharging, E_d' , are indicated by crosses. The cumulative capacity measurements resulted in discontinuities in both $C(n)$ and $E_d(n)$. The first cycles immediately afterwards showed a slightly reduced storage capacity caused by incomplete hydrogen desorption, as shown by the less positive E_d values. Doubling of the charge current at $n = 94$ did not influence the absorption level E_c nor the high and low rate desorption levels, E_d and E_d' . The hydrogen evolution overpotential, η_{he} , increased but not by more than 10 mV.

Another noteworthy phenomenon was the strong decline of η_{he} during the first cycles. The η_{he} -decrease of five similar LaNi_5 electrodes was 105 ± 20 mV. Simultaneously, the hydrogen content after discharge diminished rapidly, so the value of E_d varied from about -900 to -750 mV, and the amount of absorbed hydrogen increased, as is expressed by the final E_c value of about -970 mV. These observations are due to an *activation* process, which took place during the

Fig. 14. The course of the potentials E_{ho} , E_c , E_d and E_d' during continuous cycling of a LaNi_6 electrode.

first 25 cycles. The consequences of this activation are summarized in table III and are illustrated in fig. 15. This figure shows the charge and discharge curves of the cycles 1, 38 and 51, all at a 1.25 C rate. The dashed line a'' represents the additional discharge at the 0.125 C rate of the first cycle; the additional capacity was 15 $\text{mAh}\cdot\text{g}^{-1}$. The abscissa quantity is the amount of stored hydrogen expressed in terms of Q , i.e. the electrical charge passed during loading or the electrical charge needed for complete discharging. This facilitated the comparison of the corresponding charge and discharge potentials with respect to the representation in fig. 12. Clearly, the behaviour of the LaNi_6 electrode was enormously improved by the activation process, resulting in a final $\Sigma \eta_{c/d}$ value of approximately 25 mV, and a larger discrepancy between charging and hydrogen evolution. The flatness of the charge and discharge curves should also be noted.

TABLE III

The changes in performance of a typical LaNi_6 electrode during the activation process.

n (cycles)	$-E_{ho}$ (mV)	$-E_c$ (mV)	$-E_d$ (mV)	$\Sigma \eta_{c/d} + 2IR_u$ (mV)	$C_{1.25}^*)$ ($\text{mAh}\cdot\text{g}^{-1}$)
1	1077	957	883	245	337
3	1030	960	833	130	345
38	985	968	752	28	295
51	982	967	746	27	269

*) $C_{1.25}$ is the storage capacity calculated from 1.25 C rate discharge.

Fig. 15. The charge and discharge curves of a LaNi_5 electrode: a and a' : cycle 1, b and b' : cycle 38, c and c' : cycle 51, all at $1.25\ C$ rate. The dashed line a'' represents the additional discharge at $0.125\ C$ rate of the first cycle.

The decay of the storage capacity of a LaNi_5 electrode has already been shown in fig. 13. In order to establish the precise capacity decline during continuous charge/discharge cycling, both at $1.25\ C$ rate, several LaNi_5 electrodes were tested. The intermetallic compound was pulverized by one hundred hydrogen

Fig. 16. The capacity decline of LaNi_5 , averaged over several electrodes, all charged and discharged at $1.25\ C$ rate.

gas absorption/desorption cycles, as described in sec. 3.4. Prior to cycling, each electrode was polarized at -850 mV for 16 hours while the electrolyte was purged with nitrogen. Then the oxygen reduction current had decreased to $50 \mu\text{A}$ or less. The final discharge potential amounted to -600 mV. The sum of the $1.25 C$ and the $0.125 C$ rate capacities is considered to be the total storage capacity, C_t . The average C_t values of several LaNi_5 electrodes as a function of the cycle number, n , are represented by asterisks in fig. 16. If the C_t value of the first cycle is disregarded because of the activation process, the remaining C_t points give a very satisfactory fit to the relation

$$C_t = C_0 \exp\left(-\frac{n}{n^*}\right), \quad (16)$$

with $C_0 = 371 \text{ mAh} \cdot \text{g}^{-1}$ and $n^* = 191$ cycles. C_0 stands for the starting capacity and almost equals the theoretical value as calculated from eq. (15). The parameter n^* reflects the decay rate, and can be regarded as a stability constant. The fitting curve is also drawn in fig. 16. The cumulative capacity values of a single electrode which had been charged and discharged up to 360 times are displayed as dots. Obviously, there is a good agreement with the extrapolated curve.

b. LaNi_4Cu ELECTRODE

By the same method of average C_t values the capacity decline of LaNi_4Cu electrodes was accurately determined. There were some differences in the experimental conditions. The electrode pellet now contained 300 mg active powder,

Fig. 17. The capacity decline of LaNi_4Cu , averaged over several electrodes, all charged and discharged at $2.0 C$ rate.

encapsulated in a matrix of 600 mg copper and its geometrical area was 3.0 cm^2 . The electrodes were cycled against a rechargeable $\text{Ni}(\text{OH})_2/\text{NiOOH}$ electrode without purging of the electrolyte by nitrogen⁸⁾. Both charging and discharging of the electrodes were carried out at a 2.0 C rate, and the final discharge potential was -700 mV . The total storage capacity was determined as the cumulative value of a five-steps-discharging at different rates in the sequence: 2.0 C; 1.0 C; 0.5 C; 0.25 C and 0.125 C rate.

However, the result was again an exponential decay function but in this case with $C_0 = 343 \text{ mAh}\cdot\text{g}^{-1}$ and $n^* = 250$ cycles. Fig. 17 displays the average C_i values (asterisks), the single electrode C_i values after more than 200 cycles (dots) and the fitting curve. The maximum hydrogen content calculated from this C_0 value, 5.6 H/LaNi₅Cu, corresponds very well with hydrogen gas desorption data¹⁶⁾. The relation of eq. (16) proved to be valid for describing the capacity loss of the intermetallic compound electrodes.

3.2.3. Discussion

3.2.3.1. High cycle rate

The high rate of the electrochemical absorption and release of hydrogen by LaNi_5 and LaNi_5Cu electrodes is due to the fast hydrogen diffusion in the metal(-hydride) and the small particle size. The hydrogen diffusion coefficient D at 300 K, in LaNi_5H_6 and in $\beta\text{-TiFeH}_{1.03}$, as derived from NMR or quasi-elastic neutron scattering experiments¹⁹⁾, is 2×10^{-8} and $2 \times 10^{-12} \text{ cm}^2\cdot\text{s}^{-1}$, respectively. It has been suggested that the relatively fast hydrogen diffusion in LaNi_5H_6 is caused by a high degree of disorder in the occupation of the interstitial sites.

Van Mal⁴⁾ examined microscopically the size distribution of LaNi_5 powder after one, twenty and one hundred gas absorption/desorption cycles. He found that after twenty cycles no appreciable changes occurred and that the particle diameters were distributed around $4 \mu\text{m}$. The specific surface area of a sample after twenty cycles, as determined by the BET gas absorption method, was found to be $0.25 \text{ m}^2\cdot\text{g}^{-1}$. Assuming spherical particles of identical size (see sec. 3.4) a diameter of $3 \mu\text{m}$ is deduced.

These data enable us to estimate the time scale of the hydrogen transport process via the root-mean-square displacement equation

$$\delta = \sqrt{2Dt}. \quad (17)$$

Here δ stands for the diffusion layer thickness. For $\delta = 2 \mu\text{m}$, the LaNi_5 particle radius, the period t is calculated to be 1 s. Even during charging and discharging at a 2.5 C rate, which takes 24 min each, limitations due to hydrogen atom diffusion in the metal lattice can be disregarded. Transport limitation at the liquid side of the interface is also not expected in 6 M KOH with

$D_{K^+} = 1.96 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ and $D_{OH^-} = 5.26 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$, both values at infinite dilution at 25 °C²⁰). This explains the flatness of the charge and discharge curves and indicates that the surface kinetics are rate-determining.

The high specific surface area leads to a relatively low current density j according to

$$j = \frac{i}{m \cdot SA}, \quad (18)$$

where m and SA are the mass (g) and the specific area ($\text{cm}^2 \cdot \text{g}^{-1}$) of the active electrode material. For charging or discharging of spherical particles of diameter d at a yC rate eq. (18) can be rewritten as

$$j_{yC} = y C_{in} \frac{\rho d}{6}, \quad (19)$$

where ρ is the density of the intermetallic compound; $\rho_{LaNi_5} = 8.28 \text{ g} \cdot \text{cm}^{-3}$. This equation shows that the current density is proportional to the particle size. The current density at 4 μm LaNi_5 powder during charging at the 1 C rate amounts to only $0.2 \text{ mA} \cdot \text{cm}^{-2}$.

3.2.3.2. Activation process

The activation results in a considerable reduction of the overpotentials for charging, discharging and hydrogen evolution. For the measured hydrogen evolution overpotential, declining from approximately -160 to -55 mV , the relation between the current density j and the overpotential can be described by the Tafel equation²¹)

$$\eta = a + b \log j, \quad (20)$$

with the Tafel constants a and b defined as follows:

$$a = \frac{2.3 RT}{\alpha n_e F} \log j_0, \quad (21a)$$

$$b = - \frac{2.3 RT}{\alpha n_e F}. \quad (21b)$$

In eq. (21a) j_0 stands for the exchange current density, which is proportional to the standard heterogeneous rate constant, k° . If j_0 is constant, the -10 mV increase of the hydrogen overpotential after doubling the charge current at $n = 94$ enables us to calculate to a first approximation the apparent Tafel slope: $b = -33 \text{ mV}$. However, in three experiments the charge rate of a LaNi_5 electrode was changed from 1.25 to 2.5 C rate at the 15th cycle, resulting in an average overpotential increase of 35 mV. From this value a slope of -116 mV is calculated. The value of the derivative $d\eta/d\log j$ depends on the rate-determining step in

the reaction sequence²²). For a slow proton discharge (Volmer reaction) the characteristic value is -120 mV. If the combination of the hydrogen atoms (Tafel reaction) is rate-determining a slope of -30 mV is found. Apparently the mechanism of the hydrogen evolution reaction changes during cycling.

At a constant charge rate and with the assumption that b does not vary between the n^{th} and the k^{th} cycle, the eqs (19) to (21) can be combined to

$$\eta_n - \eta_k = b \log \frac{(k^0/d)_n}{(k^0/d)_k}. \quad (22)$$

Applying this equation to the activation process with $b = -116$ mV shows that the quotient k^0/d after activation is 8 times the starting value. The activation process is therefore due to further disintegration of the metal powder (decrease of d), even after one hundred hydrogen gas absorption/desorption cycles, and/or an improvement of the electrocatalytic properties of the electrode surface (increase of k^0).

The fact that all overpotentials, i.e. for charging, discharging and hydrogen evolution, were equally reduced by about 105 mV can also be explained in two ways. The current density was decreased by further cracking or these three reactions possessed an identical rate-determining step, which was accelerated. This common step must be the Volmer reaction

This is consistent with both the steep Tafel slope during the activation and the increasing absorbed hydrogen level. The distinction between a variation in particle size or rate constant cannot be made on the basis of this observation.

3.2.3.3. Capacity decay

Figs 16 and 17 show the drastic capacity loss of LaNi_5 and LaNi_4Cu electrodes. If we define the cycle life of a rechargeable electrode as the number of cycles during which the storage capacity has declined to 60% of the starting value, the cycle life of these electrodes is restricted to about one hundred cycles. To meet the required endurance of one thousand cycles, the stability must be improved by a factor of ten.

Van Rijswijk⁸⁾ has already pointed out that the 'demonstrated' suitability of a hydrogen-storing LaNi_5 electrode was rather surprising because lanthanum is a metal that readily reacts with water. The equilibrium potential of the reaction

is -2.07 V with respect to the reversible hydrogen electrode²³). The increase in nobility due to the formation of the intermetallic compound cannot possibly bridge 2.0 volts. As a more important effect of the formation of a compound, it

might be expected that in a regular packed structure of several kinds of atoms the selective oxidation of the least noble metal would leave a surface layer of the more noble metal, which would then determine the corrosion properties. In this way, Van Rijswijk suggested that compounds rich in cobalt, nickel or copper would be protected against corrosion by a thermodynamically stable surface layer.

Obviously, the protection is insufficient. The surface layer may possess an *open* structure, still allowing lanthanum to reach the electrode/electrolyte interface. Alternatively cracking of the metallic powder may continue, progressively yielding fresh surface. If the latter explanation holds, as partly suggested by the activation process, coating of the fine metal particles with a protective layer of for instance palladium or a passive oxide^{24,25} will not provide a solution for the severe deterioration. To characterize the degradation both the oxidation reaction and the disintegration of the intermetallic compound need further examination.

3.3. X-ray diffraction analysis

3.3.1. Results

X-ray diffraction analyses were carried out to identify the structural parameters of the pure and the hydrided intermetallic compounds and to determine the compositional changes in electrode samples after galvanostatic cycling. The X-ray diffraction diagrams were obtained on powdered specimens, using Cu(K α) radiation in combination with a graphite monochromator. The diffractometer used was a Philips PW 1130/90, equipped with a vertical goniometer PW 1050. Hydriding of the ground intermetallics was implemented by exposure to hydrogen gas of 150 atm for 24 hours. To prevent desorption during recording, the hydrided powders were coated with glue.

Fig. 18 displays the X-ray diagrams of LaNi₅, LaNi₄Cu and their hydrides. The diagrams (a) and (d) show that the intermetallic compounds consist merely of one phase which was identified as the hexagonal CaCu₅ type of structure²⁶); this crystal structure is described in space group P6/mmm. The broadened peaks of fig. 18(b) indicate the deformation of the solid phase after one hundred hydrogen gas absorption/desorption cycles at ambient temperature. Besides lattice deformation, the line broadening may partially be attributed to the small size of some crystallite fragments. However, no additional lines, due to a second phase, appeared. The X-ray diagram of LaNi₅H₆ (c) and that of LaNi₄CuH_{5.6} (e) are similar to (a) and (d), respectively, but with all peaks shifted to smaller diffraction angles, indicating the same hexagonal structure but with larger lattice parameters. Despite the glue coating some hydrogen gas had desorbed from LaNi₅H₆ and thus a small amount of LaNi₅H_{0.3} had been

Fig. 18. X-ray diffraction diagrams of pure and hydrided LaNi_5 and LaNi_4Cu : *a.* LaNi_5 , ground ($< 40 \mu\text{m}$) arc melt, *b.* LaNi_5 , pulverized by 100 hydrogen gas cycles, *c.* LaNi_5H_6 , sample (*a*) after exposure to H_2 , *d.* LaNi_4Cu , ground ($< 40 \mu\text{m}$) arc melt, *e.* $\text{LaNi}_4\text{CuH}_{0.8}$, sample (*d*) after exposure to H_2 .

formed. The arrows in fig. 18(c) mark the diffraction peaks of the latter compound. Table IV shows the crystallographic data evaluated from fig. 18 together with some additional data. It is noteworthy that the cell volumes of both compounds increase by twenty percent or more during hydriding.

In order to relate the capacity decay of LaNi_5 and LaNi_4Cu electrodes to compositional changes, we recorded X-ray diagrams as a function of the cycle number. The samples examined were obtained from the galvanostatic cycling experiments discussed in the previous section. The diagrams of a LaNi_5 electrode after 63, 176 and 359 cycles are plotted in fig. 19(a-c). The diffraction angles of pure $\text{La}(\text{OH})_3$ with the corresponding relative intensities are indicated by vertical bars (*d*). Although the LaNi_5 and the $\text{La}(\text{OH})_3$ reflections are not well resolved against the copper background, fig. 19 shows clearly an increasing amount of $\text{La}(\text{OH})_3$ with the cycle number. Moreover, at the tail of the copper reflection a shoulder appears, which is attributed to free nickel with a face-centered cubic structure.

TABLE IV
Crystallographic data of LaNi_5 , LaNi_4Cu and their hydrides.

compound	a (Å)	c (Å)	V (Å ³)	$\Delta V/V$ (%)	remarks
LaNi_5	5.003	3.971	86.06		(a)
LaNi_5	4.999	3.988	86.31		(b)
LaNi_5H_6	5.395	4.244	106.97	24.3	(c)
LaNi_5	5.017	3.982	86.80		(i)
LaNi_5H_6	5.388	4.250	106.83	23.1	(i)
LaNi_4Cu	5.034	4.002	87.82		(d)
$\text{LaNi}_4\text{CuH}_{5.6}$	5.403	4.162	105.21	19.8	(e)
LaNi_4Cu	5.032	4.004	87.80		(ii)
$\text{LaNi}_4\text{CuH}_x$	5.435	4.179	106.90	21.8	(ii)

(a)-(e) correspond to the X-ray diagrams of fig. 18; (i) data from ref. 3; (ii) data of a duplicate sample, which was placed in a special pressure holder; during the determination of the lattice parameters of the hydride ρ_{H_2} was 10 atm, which resulted in an x -value somewhat larger than 5.6.

Fig. 19. X-ray diagrams of LaNi_5 electrodes after 63 (a), 176 (b) and 359 (c) cycles. The diffraction diagram of La(OH)_3 is schematically represented by vertical bars (d); the large reflection peak at $\theta = 21.76^\circ$ is due to the copper matrix.

The X-ray diagrams of the LaNi_4Cu electrodes exhibit a much better peak-height/background ratio, as shown in fig. 20. With increasing cycle number the LaNi_4Cu peaks (unshaded) diminish and the $\text{La}(\text{OH})_3$ peaks (shaded) grow. Again nickel shoulders (dotted) appear at the tails of the copper reflection peaks. These diagrams prove explicitly that during galvanostatic charge/discharge cycling LaNi_5 and LaNi_4Cu electrodes are converted according to

and

respectively.

Fig. 20. X-ray diffraction analysis of LaNi_4Cu electrodes as a function of the cycle number: a: 0, b: 23, c: 65, d: 87, e: 148 and f: 188 cycles. Reflections due to LaNi_4Cu , $\text{La}(\text{OH})_3$ and Ni (or Ni_3Cu_2) are indicated by unshaded, shaded and dotted, respectively. The diffraction peaks of the copper matrix appear at $\theta = 21.76^\circ$ and $\theta = 25.35^\circ$.

3.3.2. *Discussion*

The large lattice expansion of twenty percent or more during hydriding together with the brittleness of these intermetallic compounds causes the pulverization into fine powder. This will be illustrated with the help of the pressure-composition isotherms depicted in fig. 21. Whenever the electrode is not com-

Fig. 21. The absorption (→) and desorption (←) isotherms of LaNi₅ at 20 °C (data from ref. 3). The inserts indicate schematically the phase distribution in each particle; unshaded and shaded represent the α - and the β -phase, respectively.

pletely charged or discharged, each intermetallic compound particle contains two phases: a hydrogen-poor α -phase and a hydrogen-rich β -phase. The outside layer always consists of the newly formed phase, which can be α or β depending on the direction of the previous process, desorption or absorption, respectively. Because of the different volumes of the α and β unit cells, enormous mechanical stresses are concentrated at the phase boundary and lead inevitably to disintegration of the particles into smaller fragments.

Measurements of changes in the magnetic properties of LaNi₅ during hydrogen gas-cycles by Schlappbach et al.^{27,28}) showed that besides the non-magnetic LaNi₅ ferromagnetic nickel precipitates were found. In their study of the surface composition of poly- and monocrystalline LaNi₅ they also found that the lanthanum concentration at the surface is considerably higher than that in the bulk, not only after exposure to air but even after cleavage in high vacuum ($5 \cdot 10^{-10}$ torr). The free energy of intermetallic compounds is minimized if the surface concentration of the element with the smaller surface energy is increased. The surface energies of lanthanum and nickel at 300 K are 0.87 and 2.39 J·m⁻², respectively, and therefore the LaNi₅ surface layers will segregate

into lanthanum and nickel²⁹). Schlapbach et al. suggested that the continuing segregation during cycling is not due to the hydrogen gas itself. They suggested that it is due instead either to the temperature rise (increase of mobility), caused by the heat of hydriding, or to the oxygen or water impurities in the hydrogen gas, which oxidize the lanthanum at the surface.

The formation of LaNi_5H_6 from LaNi_5 by the absorption of hydrogen gas is an exothermic reaction with $\Delta H_{a/b}^\circ = -30.4 \text{ kJ} \cdot (\text{mole H}_2)^{-1}$. The heat capacity c_p° (298.15 K) of LaNi_5 and LaNi_5H_6 is 152 and $236 \text{ J K}^{-1} \text{ mole}^{-1}$, respectively³⁰). Hence, in a adiabatic system or locally in a large storage container the temperature may increase considerably (ΔT : 400 to 500 K) upon hydriding. In an electrochemical cell, the heat due to this hydride formation enthalpy will not be dissipated. In such a cell, heat is only generated due to the overpotentials during current flow. However, the heat effect of LaNi_5 electrodes is negligible as a result of the low overpotentials, even at high currents.

The free energy change of the LaNi_6 oxidation according to eq. (25a) equals the ΔG° of the reaction of lanthanum with water (eq. 24) minus the ΔG° of the formation of the compound LaNi_6 . Thus, neglecting the entropy change of the LaNi_5 formation from lanthanum and nickel.

$$\Delta G^\circ(\text{LaNi}_6 \text{ oxidation}) = -n_e F E^\circ - \Delta H_f^\circ(\text{LaNi}_6). \quad (26)$$

This leads to $\Delta G^\circ(\text{LaNi}_6 \text{ oxidation}) = -472 \text{ kJ} \cdot (\text{mole LaNi}_5)^{-1}$, which is almost four times $\Delta H_f^\circ(\text{LaNi}_5) = -127 \text{ kJ} \cdot (\text{mole LaNi}_5)^{-1}$. So, in aqueous environments the driving force for the segregation of LaNi_6 is not the difference in the surface energy of the constituents but the strong affinity of LaNi_6 for water. This explains the observed discrepancy in capacity loss after electrochemically (6 M KOH) and volumetrically (pure H_2 gas) cycling.

Thus, the intermetallic compound electrodes decompose into oxidation products which are inactive for the storage of hydrogen. Because the charge transfer reactions of the corrosion process, i.e. the reduction of water and the oxidation of lanthanum, occur readily, the segregation of LaNi_5 must be the rate-determining step. It can therefore be expected that the specific surface area would play an important role in the rate of the capacity decay.

3.4. Specific surface area measurements

3.4.1. The BET method

The specific surface area of pure intermetallic compound powders and electrode pellets was determined from gas adsorption measurements, applying the BET method³¹). In 1938 Brunauer, Emmet and Teller derived an equation to describe a multilayer adsorption isotherm, which is now generally known as the BET equation

$$\frac{V}{V_m} = \frac{cp}{(p_o - p) \left[1 + (c - 1) \frac{p}{p_o} \right]}, \quad (27)$$

where p and p_o are the pressure and the saturation pressure of the adsorbate, and V and V_m are the total volume of gas adsorbed and the volume adsorbed at monolayer coverage. The parameter c is defined as

$$c = \exp \left(\frac{|E_{\text{ads}}| - |E_{\text{vap}}|}{RT} \right), \quad (28)$$

and indicates the relative preference of an adsorbate molecule for attaching itself to the adsorbent or to a layer already covered by the adsorbate. E_{ads} and E_{vap} refer to the adsorption and the vaporization free energies. Thus, the BET equation describes the volume of gas adsorbed at different values of p/p_o in terms of two parameters V_m and c . It should be noted that V_m equals the volume of gas which would be adsorbed if a monolayer was formed; it is not assumed that the monolayer is completely filled. Therefore, the surface area A may be evaluated from V_m if the area occupied per adsorbate molecule σ° is known

$$A = \frac{V_m}{V_{\text{mol}}} \cdot N_A \sigma^\circ, \quad (29)$$

where V_{mol} is the molar volume of the adsorbate at the same p and T as V_m ; N_A is Avogadro's number. To evaluate V_m , eq. (27) can be rearranged into the following linear form

$$\frac{1}{V} \cdot \frac{p}{p_o - p} = \frac{c - 1}{cV_m} \cdot \frac{p}{p_o} + \frac{1}{cV_m}. \quad (30)$$

This form suggests that a plot of $p/(V \cdot (p_o - p))$ versus p/p_o should yield a straight line with slope $m = (c - 1)/(cV_m)$ and intercept $b = (cV_m)^{-1}$. Now it is easily seen that $V_m = (m + b)^{-1}$. In the range $0.05 \leq p/p_o \leq 0.30$ the linear form of the BET equation fits the experimental data very well for a variety of gases and adsorbents. This feature has made the BET method a standard technique for surface area determination.

Many of our samples were electrode pellets, consisting of approximately 120 mg copper powder and only 30 mg active material. To determine the specific surface area of the active material with an accuracy of at least $0.2 \text{ m}^2 \cdot \text{g}^{-1}$, the deviation from the average of the measured areas should not exceed $6 \cdot 10^{-8} \text{ m}^2$. The determination of such small areas with the required accuracy was achieved by means of a special experimental approach. We used krypton as adsorbate and a turbo-molecular high vacuum pump for thoroughly removing adsorbed contaminants from both the apparatus and the samples. The BET apparatus was

designed and built in our laboratory. After exposure of the interior to the ambient environment the apparatus was degassed by heating at 100 °C and pumping until a pressure of 10^{-10} torr was reached. Prior to the adsorption measurement each sample was degassed by heating at 200 °C and pumping for 14 hours. The pressure was then about 5×10^{-7} torr.

Krypton differs from the more commonly used adsorbate, nitrogen, in two ways. The cross-sectional area σ° of an adsorbed krypton atom is slightly larger than that of a nitrogen molecule. The σ° values recommended for krypton and nitrogen at 77 K are 20.2 Å² and 16.2 Å², respectively³²). However, the much lower value of the saturation pressure of krypton at the boiling point of nitrogen (= 77 K), $p_o = 2.1$ torr, is more important. If the adsorbate is added with successive increments of $\Delta(p/p_o)$, about the same amount of gas will be adsorbed (actually: 16.2/20.2), but krypton adsorption takes place in a much lower pressure range. A larger volume of krypton gas is thus needed to accomplish the same increment $\Delta(p/p_o)$. Because the gas volume per $\Delta(p/p_o)$ step is inversely proportional to the saturation pressure, the sensitivity is improved by a factor of 300. Besides krypton behaves more like an ideal gas than nitrogen at the liquid nitrogen temperature.

The surface area of all samples was evaluated from at least two isotherms. The average difference between the duplicate measurements on electrode pellets was found to be 0.01 m² or 2.6%.

Fig. 22. The BET isotherm at 77 K of a LaNi₂ electrode after 103 charge/discharge cycles. The sample consisted of 102.6 mg copper powder and 28.5 mg remaining LaNi₂, plus oxidation products; • and × are data points of duplicate measurements.

Concluding this section, a practical example of the method will be given. The two isotherms of a LaNi_5 pellet after 103 charge/discharge cycles, plotted in fig. 22, coincide. Obviously, the linear form of the BET equation fits well. The results, evaluated from the data of fig. 22 and summarized in table V, show the excellent agreement between the two measurements. The surface area of the pellet, A , is 0.7586 m^2 . From the electrochemical experiments it is known that after 103 charge/discharge cycles only 58% of the LaNi_5 is still present and 42% of the initial material has been converted to oxidation products. The specific area of the remaining LaNi_5 plus the formed oxidation products, $SA_{\text{electrode}}$, expressed in $\text{m}^2 \cdot \text{g}^{-1}$ LaNi_5 starting material, is calculated from A according to

$$SA_{\text{electrode}} = \frac{A}{m_{\text{LaNi}_5}} - \left(\frac{m_{\text{Cu}}}{m_{\text{LaNi}_5}} \right) \cdot SA_{\text{Cu}}, \quad (31)$$

where m_{LaNi_5} is the mass of LaNi_5 assuming no oxidation took place; m_{Cu} and SA_{Cu} are the mass and the specific surface area of the copper powder in the pellet.

The SA_{Cu} of a pressed, dry pellet amounts to $0.216 \text{ m}^2 \cdot \text{g}^{-1}$. After 37 cycles, carried out by potentiodynamic scanning in the potential range of a real electrode, we measured a specific surface area of $0.292 \text{ m}^2 \cdot \text{g}^{-1}$. The electrode potential of a LaNi_5 electrode acted as the 'function generator' for the potentiostat, which controlled the copper pellet potential. The increase is due to oxidation of the copper surface, wetted by 6 M KOH. Because the electrode potential was always negative with respect to the $\text{Cu}/\text{Cu}_2\text{O}$ reversible potential (-460 mV), this oxidation was caused by oxygen after the electrode was removed from the cell, despite thorough rinsing in water and methanol immediately and further storing in a desiccator for 24 hours. Therefore, we assumed the value of $0.292 \text{ m}^2 \cdot \text{g}^{-1}$ to be independent of the number of cycles. The $SA_{\text{electrode}}$ value of the sample in fig. 22 is $26.8 \text{ m}^2 \cdot \text{g}^{-1}$.

TABLE V
Results evaluated from the data points of fig. 22.

parameter	•-points	×-points	average
$b \text{ (ml STP)}^{-1}$	0.0263	0.0314	
$m \text{ (ml STP)}^{-1}$	7.1191	7.1315	
$V_m \text{ (ml STP)}$	0.1400	0.1396	0.1398
$A \text{ (m}^2\text{)}$	0.7595	0.7577	0.7586

3.4.2. Results and discussion

In sec. 3.2.3 it was suggested that the activation process of the powder and the capacity loss are related to further disintegration. We therefore measured the specific surface area of LaNi_5 powder after repeated hydrogen gas absorption and desorption, and of LaNi_5 and LaNi_4Cu electrodes as a function of the number of galvanostatic charge/discharge cycles.

Pulverization by continuous gas cycling was carried out in an automated, volumetric absorption/desorption apparatus between 20 and 10^{-3} atm at ambient temperature. To prevent oxidation or poisoning of the powder surface by oxygen or water vapour^{14,33}), special precautions were taken. The inlet hydrogen gas ($\text{H}_2 \geq 99.99\%$; $\text{O}_2 < 10$ ppm; $\text{H}_2\text{O} < 10$ ppm) was additionally purified by molecular sieves (*oxysorb*), which reduced the oxygen and water content to less than 0.1 and 0.5 ppm, respectively. Desorption took place in two steps via a low-pressure, buffer vessel. This vessel was also preceded by *oxysorb* adsorbents. The apparatus was constructed of stainless steel and proved to be 100% leak-tight as checked by the helium test. The cycle time was 45 min; absorption took 20, desorption 25 min.

Fig. 23 shows the specific surface area of LaNi_5 powder as a function of the number of gas cycles. Several samples were taken from different arc melts; all gave similar results. Cracking mainly occurred during the first fifty cycles, leading to a specific surface area of $0.22 \text{ m}^2 \cdot \text{g}^{-1}$, which is in agreement with the findings of Van Mal⁴). The SA value after one thousand absorption/desorption cycles increased to only $0.28 \text{ m}^2 \cdot \text{g}^{-1}$. The latter sample was measured again after one year of storage in a desiccator and within 2% the same value was found!

Fig. 23. The specific surface area of LaNi_5 powder from several arc melts as a function of the number of hydrogen gas absorption/desorption cycles.

Assuming the powder consists of spherical particles, all with diameter d , we can easily evaluate this typical length from the specific surface area

$$d = \frac{6}{\rho \cdot SA} \quad (32)$$

The final size of LaNi_5 particles, corresponding to $SA = 0.28 \text{ m}^2 \cdot \text{g}^{-1}$, is $2.6 \mu\text{m}$. The 'diameter' of the crystallites in these arc melt samples varied from 100 to $200 \mu\text{m}$, as determined microscopically. Thus, not only the crystallites are separated from each other, but also transcrystalline fractures occur as a result of cycling.

The specific surface area of LaNi_4Cu after several gas-cycles was found to be $0.24 \text{ m}^2 \cdot \text{g}^{-1}$. We also determined the specific surface area, obtained after grinding LaNi_5 powder by mechanical means and passing it through a $40 \mu\text{m}$ sieve. The result was remarkable: $0.25 \text{ m}^2 \cdot \text{g}^{-1}$. Apparently, there is a characteristic limiting value for the specific surface area of this type of intermetallic compound under mechanical stress.

The determination of the specific surface area of a LaNi_5 electrode after repeated electrochemical cycling was described in the previous sec. (3.4.1). Fig. 24(a)

Fig. 24. The specific surface area of LaNi_5 (○) and LaNi_4Cu (●) electrodes, expressed in $\text{m}^2 \cdot \text{g}^{-1}$ (g refers to initial active material). The charge/discharge rates of the LaNi_5 and the LaNi_4Cu electrodes were 1.25 and 2.0 C, respectively. (a) and (b) display the dependence on the cycle number and on the fraction of oxidation products, respectively.

displays the data for LaNi_5 and LaNi_4Cu electrodes as a function of the cycle-number. The specific surface area of the remaining active material plus the oxidation products is very large compared to the final value of the gas-cycled powder and increases approximately in proportion to the cycle number. It is therefore probable that these high values are largely due to the oxidation products. However, during the activation process cracking of the active material might have contributed to the surface area enlargement. Therefore, we have to consider the specific surface area of the electrode to be due to two terms

$$SA_{\text{electrode}} = SA_{\text{active}} \cdot \frac{C}{C_0} + SA_{\text{oxidprod}} \cdot \left(1 - \frac{C}{C_0}\right), \quad (33)$$

If C and C_0 represent the actual and the initial storage capacity, then the factors C/C_0 and $(1 - C/C_0)$ express the fraction of the remaining active material and that of the oxidation products, respectively, both per unit mass initial active material. Atomic emission spectroscopy has shown that the amounts of lanthanum and nickel in the electrode pellet do not change during cycling. The parameter SA_{oxidprod} is given by

$$SA_{\text{oxidprod}} = \frac{M_{\text{La(OH)}_3}}{M_{\text{LaNi}_5}} \cdot SA_{\text{La(OH)}_3} + \frac{5M_{\text{Ni}}}{M_{\text{LaNi}_5}} \cdot SA_{\text{Ni}}, \quad (34)$$

where M_i and SA_i are the molecular weight and the specific surface area of compound i .

Considering that for large cycle numbers the first term of eq. (33) is substantially smaller than the second and assuming that the parameter SA_{oxidprod} is constant, a plot of $SA_{\text{electrode}}$ versus $(1 - C/C_0)$ should result in a straight line which, when extrapolated passes through the origin. The value of SA_{oxidprod} can be evaluated from the slope of this line. From the difference between the (larger) measured values and the extrapolated line, information can be obtained concerning changes in the specific surface area of the active material.

In fig. 24(b) the specific surface area values of LaNi_5 and LaNi_4Cu electrodes are plotted as a function of $(1 - C/C_0)$. It should be noted that the abscissa is not a time axis, but $(1 - C/C_0)$ merely represents the fraction of oxidation products formed. It is therefore surprising that the value of the LaNi_4Cu slope is about half that of the LaNi_5 slope: 45 and 85 $\text{m}^2 \cdot \text{g}^{-1}$, respectively. The specific surface area of La(OH)_3 is possibly influenced by the initial active material density in the pellet; LaNi_5 : 20 wt% and LaNi_4Cu : 33 wt%. The stability of the intermetallic compound electrodes cannot therefore be directly deduced from the specific surface area increase.

The information on changes in the specific surface area of the active material, as obtained from fig. 24(b), is very limited. The differences between the measured and the extrapolated values are of the same order of magnitude as the ac-

curacy of the fitted lines. It is curious that the linear relationship between SA and n describes the measured data better than that between SA and $(1 - C/C_0)$, in spite of the exponential capacity decay. Apparently, the SA values measured at high cycle numbers are too large. If the assumed constancy of SA_{oxidprod} would be incorrect, its value is expected to decrease with n because of processes such as crystal growth or conglomeration of particles. This would make the description according to eq. (33) even worse.

The results of the BET measurements do not indicate to what extent further disintegration occurs. However, after only three galvanostatic cycles, we determined specific area values of 1.4 and 1.3 $\text{m}^2 \cdot \text{g}^{-1}$ for LaNi_5 and LaNi_4Cu electrodes, respectively, which are more than five times greater than the values obtained from the gas-cycled powders. This suggests that additional cracking takes place in the electrolyte.

3.5. Electron microscopy; results and discussion

The changes in the morphology of the intermetallic compound and the formation of new phases were studied by both transmission and scanning electron microscopy (TEM and SEM). The TEM and SEM micrographs were made with a Philips PSEM 500 and a Philips EM 301, respectively.

Fig. 25 depicts several TEM photographs of material from cleaved LaNi_4Cu electrode pellets after galvanostatic cycling. Two kinds of particle are found: jagged pieces, which disintegrated from approximately 10–15 μm to 1–2 μm 'diameter' during the first fifty cycles, and needles which only appeared after twenty cycles or more. These needles are monocrystals, slightly bent and with a hexagonal structure (the c -axis coincides with the needle axis), as determined by electron diffraction. We therefore concluded that these needles consist of $\text{La}(\text{OH})_3$ precipitated from the solution in the immediate vicinity of the intermetallic compound. The needle dimensions did not change considerably with the cycle number. Characteristic values are: length between 0.1 and 0.4 μm , width between 0.01 and 0.02 μm and thickness about half the width. The specific surface area of $\text{La}(\text{OH})_3$, calculated from these values, varies from 60 to 140 $\text{m}^2 \cdot \text{g}^{-1}$. This order of magnitude is consistent with the high surface area values determined from the BET measurements.

Figs 26 and 27 are compilations of SEM photographs, which give an illustrative overview of the degradation of LaNi_5 electrodes. The corresponding photographs are made of the same spot at the cleaved pellet surface, but the magnification of each photograph in fig. 27 is four times that of its counterpart in fig. 26. Fig. 26(a) depicts LaNi_5 powder pulverized by one hundred hydrogen gas absorption/desorption cycles and embedded in copper particles. LaNi_5 is present as conglomerates of small fragments, which are generated by transcrystalline

Fig. 25. TEM photographs of material from cleaved LaNi_4Cu electrode pellets after galvanostatic cycling: *a*: 3 cycles, *b*: 300 cycles, *c*: 43 cycles, *d*: 23 cycles, *e*: 63 cycles, *f*: 300 cycles. The bar represents $1.0\ \mu\text{m}$.

cracks. Such conglomerates are revealed as the large jagged pieces in TEM photographs. The size of the fragments decreased upon further cracking from approximately $7\ \mu\text{m}$ in the starting material to $2.5\text{--}3\ \mu\text{m}$. The latter value was found between the 25th and the 63th galvanostatic cycle.

However, additional electrochemical charging and discharging resulted in further size reduction, now caused by the decomposition of the intermetallic compound. This is indicated by the development of rounded edges of the frag-

Fig. 26. SEM photographs of LaNi_5 electrode pellets at several cycle numbers: *a-e* corresponds to 0, 12, 25, 63, 176, 359 cycles, respectively. One bar represents $10\ \mu\text{m}$.

ments and larger gaps between them; neighbouring chunks no longer fit in with each other. After 12 cycles $\text{La}(\text{OH})_3$ needles already appear and after 176 cycles small domains (ca. $0.3\ \mu\text{m}$) become vaguely recognizable. The latter may be attributed to nickel precipitates, which have also been detected by X-ray diffraction. Finally, the electrode surface is completely covered by a thick layer of porous $\text{La}(\text{OH})_3$.

Considering the irregularity and the roughness of the chunk surfaces, the characteristic length of $7\ \mu\text{m}$ after gas cycling agrees well with the $3\ \mu\text{m}$ evaluated

Fig. 27. SEM photographs of LaNi₅ electrode pellets; identical to fig. 26 but at a larger magnification: one bar represents 1.0 μm.

on the assumption of smooth, spherical particles from the BET result of $0.25 \text{ m}^2 \cdot \text{g}^{-1}$. The size reduction of these fragments as a result of additional cracking is less than a factor of 3, which accounts only partly for the decreasing overpotential during the activation process. Consequently, the heterogeneous rate constant of the charge transfer reaction has increased during the activation process.

The thickness of the electrode pellets was accurately determined by means of low-magnification SEM photographs. The thickness of LaNi₅ electrodes, con-

taining about 80 wt% copper, gradually increased with growing $\text{La}(\text{OH})_3$ concentration from 0.45 to 0.69 mm ($> 50\%$!) without the electrodes falling apart. The mechanical strength of the copper matrix ensured the maintenance of electrical contact.

3.6. Conclusions

The large amount of hydrogen stored and released electrochemically in LaNi_5 and LaNi_4Cu is practically the same as that determined from gas absorption/desorption experiments on these materials. The rechargeable electrodes made from these intermetallic compounds allow high rate charging and discharging of the full capacity at low overpotentials in the vicinity of the reversible hydrogen electrode potential.

During repeated cycling the storage capacity declines drastically as a result of the conversion of the intermetallic compounds into $\text{La}(\text{OH})_3$ and 3d transition metal precipitates. This conversion process can be described by the exponential decay function

$$C(n) = C_0 \exp\left(-\frac{n}{n^*}\right). \quad (35)$$

The n^* value for these compounds is about 200 cycles. To meet the requirements of practical rechargeable battery electrodes, it should be increased by a factor of 10.

The rate-determining step in the deterioration process is the segregation of the intermetallic compound. Because of the heterogeneous character of this reaction, its rate can be expected to change proportionally with the specific surface area. The final surface area value of hydrogen-gas-cycled LaNi_5 and LaNi_4Cu powder amounts to $0.25 \text{ m}^2 \cdot \text{g}^{-1}$. However, during the first 25 to 50 galvanostatic cycles, i.e. during the activation process, the surface area of the active material is increased by a factor of 2 to 3 as a result of further disintegration. This increase did not progressively affect the capacity degradation rate. On the contrary, for all 350 cycles the rate of the degradation process continuously decreased with the cycle number

$$v = -\frac{d}{dn} C(n) = \frac{1}{n^*} C(n). \quad (36)$$

This observation may be interpreted in terms of a gradual improvement of the surface layer protection, because this layer becomes more and more enriched by precipitates of the more noble element(s). But even after a considerable fraction of the intermetallic compound has been converted, the protection remains completely insufficient.

Another explanation for the diminishing conversion rate follows from the fact that eq. (36) is a first order rate equation. The degradation rate is proportional to the actual capacity, i.e. to the amount of remaining active material. This is a rather unexpected relationship for a heterogeneous reaction. However, it suggests that the capacity decay is related to the storage process. This means that the rate-determining step, i.e. the segregation of the intermetallic compounds, depends on the absorption and release of hydrogen by this compound. The thermodynamical, driving force for segregation is the large decrease of the Gibbs free energy due to the formation of $\text{La}(\text{OH})_3$. However, the mobility of the constituent elements at room temperature is very low. Because of the negligible heat effects of LaNi_5 electrodes, the rate of the segregation reaction is not increased by a temperature rise. Therefore the kinetics of the segregation reaction should be affected by the repeated expansion and shrinkage of the particles during cycling. The mechanical stress accompanying this 'respiration' process can be regarded as the 'driving' force for the 'peristaltic' transport of lanthanum to the surface.

As a consequence of this latter explanation, we formulated the hypothesis that a reduction of the lattice expansion during hydriding should lead to more stable metal hydride electrodes.

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4. MULTICOMPONENT ELECTRODES

4.1. Introduction

We concluded the previous chapter with a hypothesis for improving the stability of metal hydride electrodes. Hydride electrodes made of a compound the lattice constants of which increase less than those of LaNi_5 on hydriding would be more stable than LaNi_5 electrodes. Hence, in order to examine this hypothesis experimentally, intermetallic compounds which expand less on hydriding, are required.

Van Mal, Buschow and Kuijpers¹⁾ investigated the hydrogen absorption of $\text{LaNi}_{5-z}\text{Co}_z$ compounds and the corresponding changes in lattice parameters as a function of the composition parameter z . They obtained the hydrogen pressure-concentration isotherms of the $\text{LaNi}_{5-z}\text{Co}_z$ series during desorption, see fig. 28. The largest hydrogen absorption capacity is observed for LaNi_5 ($z = 0$): 6 H atoms per formula unit at a constant pressure level, the plateau pressure. Whereas the isotherms of the compound with $z = 0.5$ and $z \geq 3.5$ contain two well defined plateaus, the equilibrium pressure of compounds with intermediate z values increases continuously with the hydrogen concentration after the first hydride phase has been formed. Replacement of nickel by cobalt lowers the equilibrium pressure of the first hydride. Moreover, the maximum absorption capacity at moderate pressures ($p_{\text{H}_2} \leq 10$ atm) decreases gradually with increasing cobalt content.

Fig. 28. Pressure-concentration isotherms of various $\text{LaNi}_{5-z}\text{Co}_z\text{-H}_2$ systems obtained during desorption at 40°C ; the z values are indicated (data from ref. 1).

All the hexagonal compounds of the $\text{LaNi}_{5-x}\text{Co}_x$ system possess a limited hydrogen solubility of a few tenths of a H atom per formula unit. This hydrogen-poor phase is denoted by α . The changes in lattice dimensions of the various $\text{LaNi}_{5-x}\text{Co}_x$ compounds caused by hydrogen absorption lead to the formation of four distinguishable hydride phases, denoted by β^I , γ , H^I and H^{II} . Both the β^I and the γ -structures are orthorhombic, because of an anisotropic expansion of the originally hexagonal basal plane of the CaCu_5 -type²). The H^I and H^{II} phases are indexed hexagonally, but are probably orthorhombic with a lattice constant ratio $a/b \approx \sqrt{3}$. The occurrence of these crystallographically different phases is indicated schematically in fig. 29 as a func-

Fig. 29. Schematic representation of the changes in phase observed by X-ray diffraction in $\text{LaNi}_{5-x}\text{Co}_x$ samples after increasing the hydrogen content; ΔV represents the absolute volume increase per formula unit. The two arrows indicate a hydrogen concentration of 4 H atoms per formula unit (data from ref. 1).

tion of the hydrogen-induced lattice expansion, ΔV . This figure clearly shows that even a partial substitution of cobalt for nickel in LaNi_5 results in a considerable reduction of the expansion of the unit cell.

We therefore studied the relationship between the stability and the unit cell expansion of LaNi_5 -related compounds, modified by substitution. Electrodes made of such compounds are here referred to as multicomponent electrodes. Furthermore, the dependence of the stability on the specific surface area and on the cycle procedure was investigated.

4.2. Lattice expansion and stability

4.2.1. Electrochemical data

The capacity curve of the multicomponent electrodes was determined from repeated galvanostatic charging and discharging over many cycles. The sample preparation and measuring equipment were as described for LaNi_5 in sec. 3.2.1. However, some of the as-cast samples of the substituted intermetallic compounds needed vacuum-annealing at high temperatures, i.e. $800 < T < 1100^\circ\text{C}$, to obtain homogeneous compounds with the CaCu_5 structure.

The changes of the total storage capacity of the $\text{LaNi}_{5-z}\text{Co}_2$ and $\text{LaNi}_{5-z}\text{Co}_2\text{Al}_1$ systems with the cycle number are depicted in the figs 30 and 31, respectively. As in the previous chapter, the total storage capacity C_t is considered to be equal to the sum of a high-discharge-rate capacity and the additional $0.125 C$ rate capacity. At first all electrodes were both charged (1 hour) and discharged at $1.25 C$ rate. After approximately one hundred cycles the charging conditions were altered to $2.5 C$ rate for half an hour while the discharge rate was kept unchanged. Between the 250th and the 350th cycle the discharge rate was also increased to $2.5 C$. The doubling of the charge current did not generally affect the C_t curve. However, for some compounds slightly diminished C_t values were found, probably due to somewhat less efficient hydrogen absorption. On the other hand, the positive step in the storage capacity values measured after increasing the discharge current is attributed to a smaller loss of stored hydrogen by spontaneous desorption in an open cell.

Fig. 30. The capacity decline of various $\text{LaNi}_{5-z}\text{Co}_2$ electrodes during cycling; the z values are indicated.

Fig. 31. The capacity decline of various $\text{LaNi}_{5-z}\text{Co}_2\text{Al}_1$ electrodes during cycling; the z values are indicated.

The measured capacity curves of the compounds with the highest cobalt content, i.e. $z = 4$ or 5 , differ markedly from the others. The reason for this unexpected behaviour is not clear. On the contrary, the capacity curves of the compounds with $z \leq 3.3$ change gradually as a function of z . Both the initial capacity and the capacity decay rate decrease with increasing substitution of cobalt for nickel.

We also conducted investigations into the $\text{LaNi}_{5-z}\text{Co}_2\text{Si}_1$ system, the results of which were nearly identical to those for the $\text{LaNi}_{5-z}\text{Co}_2\text{Al}_1$ system. Furthermore, we measured the electrochemical behaviour of intermetallic compounds in which also the constituent lanthanum was partially replaced by other lanthanides and/or titanium. An essential feature of all these lanthanum-replacing elements is that each forms a stable binary hydride. An example of this type of material is $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.8}\text{Co}_{2.4}\text{Si}_1$. The variation of both the 1.25 C rate capacity and the total storage capacity of a $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.8}\text{Co}_{2.4}\text{Si}_1$ electrode is represented in fig. 32. Charging of this electrode was also carried out at the 1.25 C rate. In this figure two important characteristics of this multicomponent electrode are shown. First, the excellent stability is demonstrated by the very small capacity loss after more than six hundred and fifty cycles. The average capacity decay rate is 0.35 times the initial capacity per thousand cycles. Moreover, the small contribution of the additional 0.125 C rate capacity illustrates the high-rate chargeability and dischargeability.

A survey of the initial storage capacity and the stability of nineteen multicomponent electrodes is given in table VI. Because the capacity decay could

Fig. 32. The capacity curves of a $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.6}\text{Co}_{2.4}\text{Si}_{1.1}$ electrode; upper: total storage capacity, lower: 1.25 C rate capacity.

not generally be described by a simple linear or exponential function, the stability is expressed in terms of a capacity ratio

$$S_{400} = \frac{C_t(400)}{C_t(0)} \quad (37)$$

Here, $C_t(0)$ and $C_t(400)$ represent respectively the initial total storage capacity, determined from extrapolation to the zeroth cycle, and the remaining total storage capacity after four hundred cycles. Although this stability parameter has been chosen rather arbitrarily, it facilitates comparison of the tested materials. Several compounds were found to lose less than twenty percent of their storage capacity after four hundred cycles ($S_{400} \geq .80$), and therefore are designated as *stable* electrode materials.

Table VI also gives the number of stored hydrogen atoms per formula unit, x , the value of which was calculated from $C_t(0)$ according to eq. (15). Within a group of materials, with or without aluminium or silicon, the stability is inversely related to the number of stored hydrogen atoms. H. Peisl³⁾ has reported that the absorption of hydrogen by metals increases the unit cell volume by $2.9 \text{ \AA}^3$ per stored hydrogen atom independent of the material. This already suggests a relationship between the stability and the expansion of the lattice.

4.2.2. Crystallographic data

The crystallographic data for the substituted intermetallic compounds and their hydrides were determined by X-ray diffraction analysis. The experimental approach was the same as that used for LaNi_5 and LaNi_4Cu samples.

TABLE VI

The initial storage capacity, expressed in $C_i(0)$ and in the number of absorbed H atoms per formula unit compared with the stability of multicomponent electrodes, S_{400} .

compound		$C_i(0)$ (mAh·g ⁻¹)	x (H/AB ₆)	S_{400}
LaNi _{5-z} Co _z ;	$z = 0$	372	6	.12
	1	372	6	.25
	2	342	5.5	.30
	2.5	324	5.2	.45
	3	292	4.7	.61
	3.3	273	4.4	.64
LaNi _{5-z} Co _z Al _{1.1} ;	$z = 0$	355	5.8	.16
	1	365	5.9	.30
	2	315	5.1	.59
	2.5	313	5.1	.82
	3	289	4.7	.94
LaNi _{5-z} Co _z Si _{1.1} ;	$z = 1$	350	5.7	.33
	2	310	5.0	.65
	2.5	296	4.8	.81
	3	280	4.6	.96
La _{0.8} Nd _{0.2} Ni ₃ Co ₂		302	4.9	.48
La _{0.7} Nd _{0.3} Ni _{2.5} Co _{2.4} Al _{1.1}		293	4.8	.87
La _{0.8} Nd _{0.2} Ni _{2.5} Co _{2.4} Si _{1.1}		293	4.7	.88
La _{0.7} Nd _{0.2} Ti _{1.1} Ni _{2.5} Co _{2.6} Al _{1.5}		254	3.9	.90

Hydriding was achieved by exposure to hydrogen gas at 150 atm for at least 24 hours, and desorption during recording of the X-ray diagrams was prevented by coating the hydrided powders with glue.

The data on the expansion of the lattice constants and of the unit cell due to hydriding are summarized in tables VIIA and VIIB. The hydride phase of the compounds with $z \leq 3.3$ has been indexed hexagonally, table VIIA, whereas the structure of the hydride phases richer in cobalt is orthorhombic, table VIIB. Our results for the LaNi_{5-z}Co_z system agree very well with the data reported previously¹⁾. The anisotropic expansion of the basal plane results in the formation of the orthorhombic structure. Furthermore, with increasing cobalt content the elongation of the c -axis (Δc) decreases much faster than that of the a - or b -axis (Δa or Δb). This is attributed to the re-

TABLE VIIA

Lattice expansion due to the formation of hexagonal hydrides.

 V is the unit cell volume of the intermetallic compounds; $V_H = \Delta V/x$; the unit cell expansion in $\text{\AA}^3$ per absorbed H atom.

compound		V ($\text{\AA}^3$)	$\Delta a/a$ (%)	$\Delta c/c$ (%)	$\Delta V/V$ (%)	V_H ($\text{\AA}^3$)
$\text{LaNi}_{5-z}\text{Co}_z$;	$z = 0$	86.06	7.8	6.9	24.3	3.5
	1	87.32	7.3	6.3	22.5	3.3
	2	87.74	7.0	5.3	20.5	3.3
	2.5	87.94	6.2	2.1	15.1	2.6
	3	88.02	5.9	0.9	13.3	2.5
	3.3	88.20	6.1	0.7	13.3	2.7
$\text{LaNi}_{5-z}\text{Co}_z\text{Al}_{1.1}$;	$z = 0$	86.92	7.3	6.9	22.9	3.4
	1	87.41	7.1	5.6	21.0	3.1
	2	87.57	6.8	4.5	19.1	3.3
	2.5	88.16	6.2	3.9	17.1	3.0
	3	88.23	5.6	2.1	13.9	2.6
$\text{LaNi}_{5-z}\text{Co}_z\text{Si}_{1.1}$;	$z = 1$	87.50	6.6	4.6	19.0	2.9
	2	87.48	6.9	3.6	18.4	3.2
	2.5	87.85	6.0	1.5	14.0	2.6
	3	87.73	5.8	1.5	13.6	2.6
$\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_3\text{Co}_2$		87.11	7.2	4.6	20.1	3.6
$\text{La}_{0.7}\text{Nd}_{0.3}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Al}_1$		87.26	5.8	2.1	14.3	2.6
$\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$		87.06	6.1	1.7	14.6	2.7
$\text{La}_{0.7}\text{Nd}_{0.2}\text{Ti}_{1.1}\text{Ni}_{2.5}\text{Co}_{2.0}\text{Al}_{1.5}$		88.78	4.5	3.4	12.8	2.9

TABLE VII B

Lattice expansion due to the formation of orthorhombic hydrides.

 V is the unit cell volume of the hexagonally indexed intermetallic compound. The volume of the orthorhombic unit cell is twice as large.

compound	V ($\text{\AA}^3$)	$\Delta a/a$ (%)	$\Delta b/b$ (%)	$\Delta c/c$ (%)	$\Delta V/V$ (%)
LaCo_6	89.56	7.3	5.2	0.2	13.1
$\text{LaNiCo}_4\text{Al}_{1.1}$	89.44	5.9	6.4	1.1	13.9
LaCo_6Al_1	89.88	4.4	6.2	0.2	11.1
$\text{LaNiCo}_4\text{Si}_{1.1}$	89.09	5.8	6.4	0.4	13.0

duced number of absorbed hydrogen atoms; these hydrogen atoms preferentially occupy sites in the metal layers perpendicular to the *c*-axis²).

The volume expansion of the unit cell decreases from twenty four percent for compounds rich in nickel to about thirteen percent for compounds containing nickel and cobalt in the ratio 2:3. Further replacement of nickel by cobalt does not appreciably influence the volume expansion. Table VIIA also gives the volume expansion of the unit cell per stored hydrogen atom. For the calculation of this quantity the electrochemically-determined *x* value given in table VI was used. Although the average value of the 'hydrogen atom volume', V_H , is $2.9 \text{ \AA}^3$ (the value reported by Peisl³)) the intermetallic compounds can easily be divided into two groups: the nickel rich materials ($z = 0, 1$ or 2) with $\overline{V}_H = 3.3 \text{ \AA}^3$ and the compounds with $\overline{V}_H = 2.7 \text{ \AA}^3$.

This observation may be ascribed to the loss of the original volume contraction which generally accompanies the formation of intermetallic compounds. The volume contraction upon formation of AB_5 compounds is due to a redistribution of the electronic charge between the electropositive lanthanide atoms with a low electron density and the electronegative cobalt or nickel atoms with a high electron density⁴). If one calculates the volumes of the $LaNi_5$ and the $LaCo_5$ unit cell from the atomic volumes of the pure constituents 92.0 and $92.8 \text{ \AA}^3$ are found, respectively. Comparison of these values with the unit cell volume presented in the tables VIIA and VII B shows that the volume contraction upon the formation of AB_5 compounds is much larger for the nickel rich compounds than for the cobalt rich compounds. On the other hand, hydrogen absorption results in a partial reestablishment of the atomic volumes because the electron density of hydrogen is smaller than that of nickel or cobalt. A larger apparent hydrogen atom volume is therefore expected for the nickel rich intermetallic compounds. As an advantageous consequence, the storage capacity does not decline in proportion to the reduction of the volume expansion, but less rapidly.

The electrochemical and crystallographic data may only be related to one another if the corresponding hydride phases have the same composition. The composition of a hydride, i.e. the value of *x* in AB_5H_x , depends on the hydrogen equilibrium pressure. In electrochemical experiments in an open cell the maximum 'pseudo-equilibrium' hydrogen pressure is about 10 atm , as is indicated by the open circuit potential of fully charged electrodes, $E_c = -960 \text{ mV}$. The volume expansion of the intermetallic compound $La_{0.8}Nd_{0.2}Ni_{2.6}Co_{2.4}Si_{1.1}$ on hydriding was also determined during exposure to hydrogen gas at different pressures. As sample holder for recording X-ray diagrams, we used a pressure vessel which comprised a beryllium window. The sample was a porous pellet consisting of an equal amount of $La_{0.8}Nd_{0.2}Ni_{2.6}Co_{2.4}Si_{1.1}$ powder and nickel powder.

Fig. 33. The volume expansion of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ due to hydriding at 25°C ; $p_{\text{H}_2} \leq 9$ atm.

The relative volume change of this intermetallic compound at different stages of hydriding is illustrated in fig. 33. Whereas the lattice expansion of LaNi_5 , 24.3% is mainly due to the phase transition $\text{LaNi}_5\text{H}_{0.8} \leftrightarrow \text{LaNi}_5\text{H}_6$, only a volume increase of 9.5% is found for the saturated solid solution $\leftrightarrow$ hydride transition ($\alpha_s \leftrightarrow \beta_0$) of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$. After this phase transition the volume gradually increases as more hydrogen atoms dissolve in the hydride phase. The volume expansion determined from the hydride phase which was prepared by exposure to 150 atm and glue coating is the same as that of the hydride which is in equilibrium with hydrogen gas of 7 atm. Thus, the expansion data of table VII also describe the volume increase during electrochemical charging.

4.2.3. Discussion

The data on the stability of multicomponent electrodes during repeated charging and discharging and on the lattice expansion of the corresponding intermetallic compounds during hydriding have already been presented in the previous sections. In fig. 34 we have plotted the stability parameter S_{400} as a function of the relative volume increase. Two classes of intermetallic compound can be discerned: compounds of the $\text{LaNi}_{5-x}\text{Co}_x$ system and materials containing a small amount of aluminium or silicon. For both classes the stability increases proportionally to the decreasing volume expansion. The increasing anisotropy of the lattice expansion with increasing cobalt content (table VIIA) is no obstacle for the growing stability.

Fig. 34. The stability S_{400} of LaNi_5 -related hydride electrodes as a function of the lattice expansion, $\Delta V/V$. The solid and dashed lines correspond to $\text{LaNi}_{5-x}\text{Co}_z$ compounds (●) and intermetallics containing Si or Al (open symbols), respectively: $\text{LaNi}_{5-x}\text{Co}_z\text{Si}_{1.1}$ (△), $\text{LaNi}_{5-x}\text{Co}_z\text{Al}_{1.1}$ (○) and others (□).

Our hypothesis that a reduction of the lattice expansion during hydriding should lead to more stable metal hydride electrodes has thus been verified by the experimental results, presented in this section. The basis of the hypothesis was that mechanical stress caused by the repeated absorption and release of hydrogen will enhance the local mobility, i.e. the local diffusion rate, of the constituent metal atoms enabling segregation to take place even at room temperature. The magnitude of the surface area is assumed to be the same for all compounds, at least after a certain number of cycles. However, a reduction of the volume expansion may also lead to less disintegration, leaving larger particles and therefore resulting in a diminished corrosion rate.

It is remarkable that two classes of intermetallic compound have been observed. The slope of the linear relationships of fig. 34 is a measure for the sensitivity to mechanical stress due to lattice expansion. The sensitivity of the compounds containing aluminium or silicon is twice that of the $\text{LaNi}_{5-x}\text{Co}_z$ compounds. The small additions of aluminium or silicon, only two atomic percent, may impede the transport of lanthanum or neodymium to the surface by the formation of an oxide layer. This surface layer is only capable of maintaining its obstructing function if it is not damaged, i.e. cracked, by the volume changes of the particle. This interpretation is consistent with the high sensitivity to mechanical stress. Alternatively, the process of disintegration of the intermetallic compounds may be influenced by small additions of aluminium or silicon.

Clearly, the particle size of stable intermetallic compounds needs further examination.

4.3. Specific surface area; results and discussion

The stability of several multicomponent electrodes is higher than that of LaNi_5 by a factor of seven to eight. If it is assumed that the corrosion rate per unit surface area is independent of the material, the final particle size of these stable intermetallic compounds should be seven to eight times larger than that of LaNi_5 .

The specific surface area of the stable compounds $\text{La}_{0.7}\text{Nd}_{0.2}\text{Ti}_{0.1}\text{Ni}_{2.5}\text{Co}_{2.0}\text{Al}_{0.8}$ and $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ after pulverization by continuous gas cycling was determined by the BET method; see sec. 3.4. After 25 to 50 hydrogen gas absorption/desorption cycles the 'final' particle size was obtained. The corresponding value of the specific surface area was found to be $0.25 \text{ m}^2\cdot\text{g}^{-1}$, as shown in table VIII. The powder obtained by mechanical grinding had ap-

TABLE VIII

The specific surface area of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ti}_{0.1}\text{Ni}_{2.5}\text{Co}_{2.0}\text{Al}_{0.8}$ and $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ powder as a function of the number of hydrogen gas absorption/desorption cycles.

compound	<i>n</i> (cycles)	SA ($\text{m}^2\cdot\text{g}^{-1}$)
$\text{La}_{0.7}\text{Nd}_{0.2}\text{Ti}_{0.1}\text{Ni}_{2.5}\text{Co}_{2.0}\text{Al}_{0.8}$	25	0.26
	150	0.23
	300	0.23
	715	0.25
$\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$	25	0.18
	75	0.25
	98	0.21
	750	0.19
	*)	0.17

*) Pulverization was carried out by mechanical grinding.

proximately the same specific surface area. Thus, as a result of repeated hydrogen gas absorption and desorption, these stable compounds crack at the same rate and to the same extent as LaNi_5 and LaNi_4Cu .

The increase of the BET surface area of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ electrodes due to electrochemical cycling was also measured. These electrodes were made from powder, pulverized by 75 hydrogen gas cycles. Both charging and discharging were carried out at 1.25 *C* rate. At every thirtieth cycle the electrode was additionally discharged at 0.125 *C* rate. The capacity curves of one of these electrodes have already been shown in fig. 32. During galvanostatic cycling the specific surface area, SA, increased in proportion to the cycle number, *n*,

according to the relationship: $SA = 2.13 + 0.035n \text{ m}^2 \cdot \text{g}^{-1}$. As with LaNi_5 electrodes, the possible increase in surface area caused by additional cracking was overshadowed by the high specific surface area of the oxidation products.

The improvement of the reaction kinetics due to the activation process of these $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ electrodes is comparable to that of LaNi_5 electrodes. Within 40 cycles the overpotential for hydrogen evolution measured at eight electrodes, decreased by $92 \pm 6 \text{ mV}$. Application of eq. (22) with the Tafel slope $b = -118 \text{ mV}$ indicates that the quotient (k^0/d) after activation is 6 times the initial value. For LaNi_5 electrodes we found a factor of 8. However, scanning electron micrographs showed that the LaNi_5 particle size was reduced less than 3 times.

The changes in the morphology of the multicomponent electrodes during electrochemical cycling were also investigated by scanning electron microscopy. The SEM photographs of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ electrodes are shown in fig. 35. The selected micrographs, showing two magnifications of three cleaved electrode pellets, give a good illustration of the alterations due to cycling. The micrographs of an unused electrode in fig. 35(a) and (b) display a conglomerate of the disintegrated intermetallic compound embedded in a copper matrix. These photographs are indistinguishable from those for fresh LaNi_5 electrodes; for comparison see figs 26(a) and 27(a). After approximately 40 cycles hydroxide needles have been precipitated and the average fragment size has diminished from 7 to 5 μm . During further cycling the electrode morphology does not change appreciably. The micrographs of fig. 35(e) and (f) show the fragments after 666 cycles. The jagged structure with its sharp edges is still present.

Whereas during electrochemical charging and discharging the specific surface area of LaNi_5 powder increased from 0.25 to $0.70 \text{ m}^2 \cdot \text{g}^{-1}$, the specific surface area of stable intermetallic compounds only grew from 0.25 to $0.35 \text{ m}^2 \cdot \text{g}^{-1}$. This difference between LaNi_5 electrodes and stable multicomponent electrodes can not account for the observed stability improvement. The corrosion rate is therefore mainly determined by factors other than the specific surface area. The relationship between the stability and the lattice expansion on hydriding must primarily be a consequence of the enhanced segregation rate during cycling.

4.4. Interrupted galvanostatic cycling; results and discussion

All the capacity curves presented so far have been measured by continuous repetition of charge/discharge cycles as described in sec. 3.2. This procedure for examining materials results in a capacity decay rate per cycle, which gives a lifetime expressed in a number of feasible cycles, i.e. the cycle life. Besides the cycle life, the time dependence of the storage capacity is also an essential aspect of the electrode stability.

Fig. 35. SEM photographs of cleaved $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrodes after 0 (*a* and *b*), 41 (*c* and *d*) and 666 cycles (*e* and *f*). One bar represents $10\ \mu\text{m}$ in *a*, *c* and *e*, and $1\ \mu\text{m}$ in *b*, *d* and *f*.

From repeated charge/discharge cycles at $1.25\text{C}/1.25\text{C}$ rate the capacity decay rate of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrodes was found to be 0.35 times the initial capacity per thousand cycles. Cycling of the same electrode material at $2.5\text{C}/2.5\text{C}$ rate resulted in a capacity loss of 25% after one thousand cycles. Halving the cycle period from two hours to one seems to lower the decay rate. Alternatively, these data can be interpreted as a capacity decay rate of $0.30 \times 10^{-3} C_0$ per cycle, determined with an accuracy of $0.05 \times 10^{-3} C_0$ per cycle.

Hence, we tried to gain insight into the time dependence of the storage capacity by interrupting the galvanostatic cycles for long waiting periods. By imposing fixed electrode potentials during these waiting periods the electrodes were maintained in the charged or discharged state at -990 mV or -850 mV, respectively. These experiments were conducted on LaNi_5 and $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrodes, both charged and discharged at $1.25 C$ rate. The resulting capacity curves of these electrodes are shown in the figs 36(a)–(b) and 37(a)–(b); (a) and

Fig. 36. Capacity curves of LaNi_5 electrodes during interrupted cycling, compared with those during continuous cycling, both at $1.25 C/1.25 C$ rate. During the interruptions the electrodes were kept in the discharged (a) or in the charged (b) state. The periods of interruption and their duration, expressed in number of cycle-periods, are indicated. — interrupted cycling: high-rate capacity; $\times$ interrupted cycling: cumulative capacity; --- continuous cycling: high-rate capacity; continuous cycling: cumulative capacity.

Fig. 37. Capacity curves of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrodes, analogous to fig. 36.

(b) refer to the exposure to the 6 M KOH solution in the discharged and the charged state, respectively. The last cycle before each waiting period was followed by discharging at $0.125 C$ rate; the cumulative capacity values are denoted by crosses. The vertical bars and the figures below them indicate the points of interruption and the duration of the waiting periods, expressed in the number of $1.25 C/1.25 C$ rate cycles. For comparison, the high-rate capacity and the cumulative capacity curves of continuously cycled electrodes are also displayed in the figs 36(a)–(b) and 37(a)–(b).

Because of the waiting periods discontinuities are found in the capacity curves. These are ascribed to various causes. The LaNi_5 electrodes lost 3 to 6% of their storage capacity during the first waiting period. The discharge efficiency of LaNi_5 and $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrodes was reduced temporarily after maintaining these electrodes in the discharged state (figs 36(a) and 37(a)); this

was shown by the less positive values of the open circuit potential after discharge. On the other hand, the discharge kinetics were improved by the storage of these electrodes in the charged state (figs 36(b) and 37(b)). The oxidation of the stored hydrogen atoms takes place at nickel and/or cobalt sites. It is possible that the number and/or the activity of these sites were increased and decreased by the imposed potentials: -990 mV and -850 mV, respectively. If this is the case, then the change in active sites should occur even at -850 mV, notwithstanding the more positive oxidation potentials of nickel and cobalt: $E(\text{Ni}/\text{Ni}(\text{OH})_2) = -820$ mV and $E(\text{Co}/\text{Co}(\text{OH})_2) = -825$ mV.

Despite the observed discontinuities, the interrupted capacity curves of both materials very closely resemble the corresponding capacity curves determined from continuous charging and discharging. Disregarding the slight capacity loss of LaNi_5 , exposure of both charged and discharged electrodes to the electrolyte has no detrimental effect on the storage capacity. Corrosion of the intermetallic compounds only occurs during cycling. Consequently, corrosion must be related to the process of expansion and shrinkage of the intermetallic compound particles and not to the completely expanded state. During both charging and discharging a large hydrogen concentration jump, located at the phase boundary, moves through the particles. Hence, the large mechanical stress induced by the distorted lattices at the phase boundary also travels through the particles and evidently vanishes when the 'new' crystal structure has been formed.

4.5. Conclusions

The volume expansion of a series of pseudo-binary AB_5 compounds upon hydriding varies between thirteen and twenty-four percent, depending on the chosen composition of the substituted compound. Because of the different values of the 'hydrogen atom volume' the initial storage capacity declines less rapidly than in proportion to the reduction of the lattice expansion from 372 to about $280 \text{ mAh}\cdot\text{g}^{-1}$.

The enormous improvement in stability due to the reduction of the lattice expansion is not caused by reduced disintegration of the intermetallic compounds. After a certain number of electrochemical cycles the specific surface area of the intermetallic compounds only varies from 0.35 to $0.70 \text{ m}^2\cdot\text{g}^{-1}$.

The capacity loss of both LaNi_5 and multicomponent electrodes is directly related to the charging and the discharging process. The degradation of the intermetallic compounds proceeds only during cycling and provided that an oxidizing agent, e.g. water or oxygen, is present. Because of the low mobility of the constituent elements at room temperature, the rate-determining step of the corrosion reaction is the segregation of the intermetallic compounds into

lanthanides and 3d transition metals. The 3d metals form small metallic crystallites. Lanthanum and neodymium are immediately oxidized by water and subsequently precipitate as hydroxide needles. As a result, the chemical potential of lanthanum and neodymium at the solid-liquid interface is maintained at a very low value. Nevertheless, diffusion only occurs simultaneously with the process of expansion and shrinkage of the intermetallic compound particles. Heat effects are not involved. The activation energy for diffusion should therefore be diminished by the mechanical stress, which results from the lattice expansion upon hydriding. This increased mobility is located near the phase boundary. As a consequence, during charging and discharging a zone of enhanced mobility travels through the intermetallic compound particles, enabling the transport of lanthanum and neodymium to the surface. This mechanism for the degradation process is strongly supported by the linear relationship established between the stability of metal hydride electrodes and the decreasing lattice expansion. In this way, the hypothesis formulated in chap. 3 has been verified.

There is no such a travelling zone of enhanced mobility in materials in which a separate hydride phase will not be formed upon hydrogen absorption. In terms of pressure-concentration isotherms this means that the hydrogen equilibrium pressure of such a material should gradually increase with increasing hydrogen content (sloping plateau). The degradation mechanism discussed above therefore implies that electrodes made from amorphous alloys should be more stable than those made from the corresponding crystalline intermetallic compounds.

Two classes of intermetallic compounds can be discerned: compounds of the $\text{LaNi}_{5-x}\text{Co}_x$ system and materials containing a small amount of aluminium or silicon. Electrodes made from one of the materials of the latter class are exceptionally stable provided that its lattice expansion is minimal. Only thirty percent of the initial storage capacity of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.6}\text{Co}_{2.4}\text{Si}_{0.1}$ is lost after one thousand cycles. Besides the particular influence of the small volume expansion, this high stability is attributed to the formation of oxide layers containing aluminium or silicon. These surface layers function as an additional hindrance for the transport of the lanthanide elements to the solid-liquid interface.

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5. SEALED NICKEL-HYDRIDE BATTERIES

5.1. Cell concept

The combination of the rechargeable nickel electrode and one of the metal hydride electrodes provides a new galvanic cell: the nickel-hydride battery. Such a battery has several inherent advantages over the lead-acid and the nickel-cadmium sealed storage cells.

The reactions at both electrodes of the nickel-hydride cell have already been described in detail in chap. 2. In a simplified form, the charge ($\rightarrow$) and the discharge ($\leftarrow$) reaction of the nickel electrode can be represented as

and at the hydride electrode as

where M and MH_x stand for the hydride forming compound and the metal hydride. So, the overall cell reaction for charging and discharging is

For both electrodes, the charge/discharge mechanism does not involve the intermediate formation of dissolved metal ion species. Instead, charging and discharging occurs via a solid state transition mechanism, which results in a high structural stability of both electrodes. During operation of the cell, there is neither a net generation nor a net consumption of electrolyte species, such as OH^- and H_2O . This permits a simple and compact construction. The theoretical energy density of a nickel-hydride cell with $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.6}\text{Co}_{2.4}\text{Si}_{1.1}$ as negative electrode material amounts to $202 \text{ Wh}\cdot\text{kg}^{-1}$ ($\text{Emf} = 1.35 \text{ V}$; $x = 5 \text{ H/AB}_6$). This value is almost the same as that of the nickel-cadmium cell, i.e. $210 \text{ Wh}\cdot\text{kg}^{-1}$. However, due to the reasons mentioned above, the actual energy density of the nickel-hydride battery is expected to be larger than the usual 20% of the theoretical value.

As is illustrated by eq. (40), charging and discharging of a nickel-hydride battery can be viewed as a mere pumping of protons from one electrode to the other. As discussed in chap. 2, this implies that such a cell is capable of being charged and discharged at high rates and with a high degree of utilization of active material. The power density is therefore expected to be considerably larger than that of nickel-cadmium cells.

Moreover, in sealed nickel-hydride cells, both overcharging and overdischarging are allowed provided that the storage capacity of the hydride electrode

exceeds that of the nickel electrode¹). Oxygen, evolved at the nickel electrode during overcharging, will be reduced at the hydride electrode. This oxygen evolution/reduction cycle is identical to the oxygen recombination process in sealed nickel-cadmium cells, as discussed in sec. 2.1.5. But, in contrast with the situation in a nickel-cadmium cell, hydrogen gas evolved at the nickel electrode during overdischarging, has no negative effect on the cell performance either. The hydrogen formed will be absorbed by and oxidized at the hydride electrode. As a consequence, a hazardous gas pressure is not built up during overcharging or overdischarging.

Furthermore, nickel-hydride cells do not contain the poisonous heavy metals cadmium and mercury. This is particularly important for the widespread use of small batteries, where recycling would involve complicated procedures.

5.2. Electrode materials

5.2.1. Introduction

Up to now, the insufficient durability of LaNi_5 and LaNi_4Cu electrodes hindered the development of the nickel-hydride cell. Since several stable multi-component electrodes have now been found, the nickel-hydride battery appears feasible. Table VI contains seven intermetallic compounds with a stability factor S_{400} of more than 80%. The capacity loss of these electrode materials was determined from half-cell measurements. For these measurements small amounts of active material were tested in contact with a large volume of electrolyte solution, continuously purged with nitrogen to remove oxygen and with the counter electrode placed in a separate compartment (sec. 3.2).

It is therefore necessary to establish the endurance of these stable intermetallic compounds also in the even more corrosive environment of complete cells. Moreover, the examination of the behaviour of the hydride electrode during overcharging and overdischarging is only possible in sealed cells.

5.2.2. Negative electrode

Obviously, in the selection of an appropriate intermetallic compound the stability is a very important factor. However, besides stability the high rate chargeability and dischargeability may become decisive. This holds in particular when high power density batteries are required. The dependence of the capacity on the charge and discharge rate is compared for three stable multi-component electrodes in fig. 38. The total storage capacity is considered to be equal to the sum of a high-discharge-rate capacity and the additional 0.125 C

rate capacity. The total storage capacity was determined every thirtieth cycle and the resulting curves are similar to those of the figs 30 and 31. Successively, three different cycle regimes were applied:

- (i) cycling was started with both charging and discharging at 1.25 C rate,
- (ii) after about one hundred cycles the charge rate was doubled to 2.5 C, and
- (iii) at approximately the three hundredth cycle the discharge rate was also increased to 2.5 C.

In all cases, the final discharge potential remained -550 mV.

Fig. 38. The total storage capacity (dashed curves) and the high-rate capacity (solid lines) of several multicomponent electrodes as a function of the cycle number and for various rates: charge rate: 1.25 C if $n \leq 100$ and 2.5 C if $n > 100$; discharge rate: 1.25 C if $n \leq 300$ and 2.5 C if $n > 300$; (●) $\text{La}_{0.7}\text{Nd}_{0.3}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Al}_{1.1}$; (■) $\text{LaNi}_2\text{Co}_3\text{Al}_{1.1}$; (▲) $\text{La}_{0.9}\text{Ti}_{0.1}\text{Ni}_{2.5}\text{Co}_{2.0}\text{Al}_{1.5}$.

The total storage capacities, measured for the three multicomponent electrodes of fig. 38, only differ slightly, but the amounts of charge recovered at high discharge rates vary considerably for the various compounds. For $\text{La}_{0.7}\text{Nd}_{0.3}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Al}_{1.1}$ electrodes the fraction of the high-discharge-rate capacity lies between 85 and 90% and is almost independent of the applied cycle regime. On the other hand, the 1.25 C rate capacity of electrodes made from $\text{LaNi}_2\text{Co}_3\text{Al}_{1.1}$ and $\text{La}_{0.9}\text{Ti}_{0.1}\text{Ni}_{2.5}\text{Co}_2\text{Al}_{1.5}$ is about 75 and 40% of the total capacity value, respectively. Moreover, for these electrodes doubling of the discharge current to 2.5 C additionally results in substantially reduced capacities.

For the three electrodes, neither the 1.25 C rate capacities, nor the total storage capacities are affected when only the charge current is increased. Evidently, the charge kinetics of these electrodes proceed more easily, than the kinetics of the discharge reactions. This is also clearly demonstrated by the first

charge/discharge cycle. While a new electrode is capable of accepting charge at 1.25 C rate, less than 10% is generally recovered during discharge at the same rate. Possibly, the electrochemical oxidation of stored hydrogen is the rate-limiting step. This assumption is supported by the observation that self-discharge of fully charged electrodes in open cells takes place via the spontaneous escape of hydrogen gas. However, different hydrogen diffusion rates in the α - and β -phase may also play a role.

As is seen from fig. 38, the intermetallic compound $\text{La}_{0.7}\text{Nd}_{0.3}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Al}_{1.1}$ is more favourable than $\text{LaNi}_2\text{Co}_3\text{Al}_{1.1}$ and $\text{La}_{0.9}\text{Ti}_{0.1}\text{Ni}_{2.5}\text{Co}_2\text{Al}_{1.5}$ for application in high power density batteries, despite its slightly lower stability. The behaviour of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrodes is almost identical to that of $\text{La}_{0.7}\text{Nd}_{0.3}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Al}_{1.1}$, as is shown by table VI and comparison of the figs 32 and 38. Because the compound containing silicon had been characterized more extensively (chap. 4), this intermetallic compound was selected for the first experiments in sealed cells.

The potential variations of a $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrode in 6 M KOH at 25 °C are depicted as a function of the state of charge Q in fig. 39. Similar to the determination of the LaNi_6 isotherms, shown in fig. 9, we approached the equilibrium state by imposing 100 ms current pulses and measuring the induced potential transients. With the amount of charge passed during each pulse corresponding to 1.25×10^{-4} H/AB₅, the relaxation process took about 500 ms. We measured the equilibrium potential after 700 ms.

Both the charge and the discharge isotherm shows a plateau between $Q = 30$ and $Q = 210 \text{ mAh} \cdot \text{g}^{-1}$, which is a consequence of the α/β -transition. The bound-

Fig. 39. Charge (→) and discharge (←) isotherm for a $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrode at 25 °C in 6 M KOH measured vs. Hg/HgO reference electrode. The lower and the upper boundary of the two phase region, α_s and β_o , are indicated by arrows.

aries of the two-phase region, calculated from 30 and 210 $\text{mAh}\cdot\text{g}^{-2}$, are: $\alpha_s = 0.5$ and $\beta_s = 3.4 \text{ H/AB}_5$. Due to inhomogeneities in the sample, which was not annealed at high temperature, the plateau is slightly sloping ($5 \text{ mV}/(\text{H/AB}_5)$). At $x = 2.1 \text{ H/AB}_5$, i.e. $Q = 130 \text{ mAh}\cdot\text{g}^{-1}$, the desorption pressure amounts to 0.2 atm ($E = -907.6 \text{ mV}$) and the potential difference between the charge and the discharge isotherm is only 6.3 mV. When the equilibrium potential reaches -956 mV during charging in an open cell, which corresponds to 7.4 atm, further storage becomes impossible owing to the evolution of hydrogen gas. The escape of hydrogen gas is also observed during the first stage of the discharge isotherm. This explains the intersection of the charge and the discharge isotherm at $Q = 270 \text{ mAh}\cdot\text{g}^{-1}$.

The electrochemical data of fig. 39 agree very well with the X-ray diffraction results, discussed in sec. 4.2.2 and illustrated in fig. 33. Moreover, the electrochemical isotherms for $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ resemble closely the pressure-composition isotherm for the $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{-H}_2$ system of fig. 28.

5.2.3. Positive electrode

The active material of the positive electrode is nickel hydroxide, which is present as a micro-crystalline precipitate in the pores of a sintered nickel plate. The oxidation of $\text{Ni}(\text{OH})_2$ to form NiOOH corresponds to a storage capacity of $289 \text{ mA}\cdot\text{g}^{-1}$. Actually, the oxidation state of nickel changes between $+2.3$ and $+3.0$ to $+3.7$, depending on which NiOOH modification (β or γ) is formed during charging, as is discussed in sec. 2.1.4. So, the storage capacity may vary from 200 to $400 \text{ mAh}\cdot\text{g}^{-1}$, depending on method of charging.

From measurements in open cells, we determined total capacity values as high as $360 \text{ mAh}\cdot\text{g}^{-1}$ after high rate charging ($360 \text{ mA}\cdot\text{g}^{-1}$ for 1 hour). However, for these high oxidation states the rate of self-discharge is very high and the nickel electrode degrades. A typical value for the capacity of the nickel electrode is therefore $250 \text{ mAh}\cdot\text{g}^{-1}$. During charge/discharge cycles the open circuit potential of the nickel electrode varies between 1.20 and 1.50 V vs. RHE.

5.3. Electrode and cell construction

5.3.1. Electrode preparation

Two types of hydride electrode have been made: pressed plate and paste electrodes. $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ powder, pulverized by repeated hydrogen gas absorption/desorption cycles, was used as active material. The pressed plates were shaped by mixing active particles with fine copper powder in the mass ratio 1:4 and subsequently cold-pressing this mixture on a grid of expanded nickel. The applied pressure was $4 \times 10^8 \text{ Pa}$. Each plate contained about 1.5 g active mass and its dimensions were $4.0 \times 3.5 \times 0.1 \text{ cm}^3$. The structure of these plate electrodes was similar to that of the electrode pellets used in the half-cell measurements (sec. 3.2).

The preparation of a paste electrode is illustrated in fig. 40. The paste was made by adding a methyl cellulose solution to a mixture of pulverized $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ and carbonyl nickel powder ($m_{\text{act}}/m_{\text{Ni}} = 5$). The hydride electrode was completed by coating a strip of expanded nickel, which served as current collector, with the paste. The width of the paste electrodes was always 3 cm and the length was chosen between 12 and 20 cm, depending on the cell requirements. As a consequence of the experimental set-up the electrode thickness was not constant. However, the thickness remained below 0.9 mm. So, the average density of active material varied from 0.11 to 0.14 $\text{g}\cdot\text{cm}^{-2}$.

Fig. 40. Preparation of a paste metal hydride electrode from the intermetallic compound $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$.

The positive electrodes were sintered nickel electrodes. The active material $\text{Ni}(\text{OH})_2$ was precipitated in the pores of sintered nickel plates by alternately impregnating the base plates with concentrated solutions of $\text{Ni}(\text{NO}_3)_2$ and NaOH . The active mass density depended on the number of impregnation cycles. We prepared electrodes with an average density of 0.084 and 0.10 $\text{g}\cdot\text{cm}^{-2}$ after four and five cycles, respectively. The nickel electrodes with the lower density were applied in our cells. The electrode thickness was 0.8 mm and the geometric area varied with the cell design.

5.3.2. Cell design

In order to allow overcharging of a sealed nickel-hydride cell the storage capacity of the hydride electrode must exceed that of the nickel electrode. When this is the case, oxygen evolution starts at the nickel electrode at the end of charging, while the negative electrode is still storing hydrogen. As the oxygen, which is formed subsequently reacts at the hydride electrode, the state of charge of both electrodes remains constant.

Moreover, it is preferable to have the hydride electrode already partially charged prior to cycling of a new cell. This spare charge of the hydride electrode prevents the evolution of oxygen at this electrode during overdischarging. Instead, hydrogen gas is formed at the nickel electrode. A capacity-determining nickel electrode is therefore essential for the functioning of a sealed nickel-hydride cell.

However, as we have seen, the excess storage capacity of the hydride electrode will decrease during cycling owing to the corrosion of the intermetallic compound. Failure of the sealed cell is expected when the storage capacities of both electrodes become equal. If cycling is still continued, the pressure in the cell gradually increases and ultimately exceeds the level at which the safety valve opens (about 20 atm). Thus, the durability is primarily determined by the excess of active mass and the corrosion rate of the hydride electrode. The calculated cycle life of nickel-hydride cells is given in fig. 41 as a function of these parameters.

Fig. 41. Calculated cycle life of nickel-hydride cells as a function of the corrosion rate of the hydride electrode material at various ratios for the excess negative active mass ($= m(-)/m(+)-1$).

The assumptions made for the calculation, are:

- a. at $n \geq n_f$ failure occurs because the actual storage capacities of both electrodes have become equal,
- b. the storage capacity of the nickel electrode remains $250 \text{ mAh} \cdot \text{g}^{-1}$,
- c. the initial storage capacity of the hydride electrode is $290 \text{ mAh} \cdot \text{g}^{-1}$; however, 10% of this value is utilized as spare charge,
- d. only the fraction of the intermetallic compound which participates in the cycling process corrodes; this is a consequence of the results discussed in chap. 4,
- e. the hydrogen formed by the oxidation of lanthanum and neodymium will also be absorbed by the hydride electrode, which leads to a substantial increase of the apparent corrosion rate ($1.64 \times$).

The plots of fig. 41 enable us to select an appropriate intermetallic compound, for instance from table VI, and to tailor the relative size of the electrodes to the required cycle life. On the other hand, if the corrosion rate in batteries differs from that in half-cells, the correct value can be estimated from the cycle life of the battery with the aid of fig. 41.

5.3.3. Cell construction

Both prismatic and cylindrical cells have been constructed. The prismatic cells contained two pressed plate hydride electrodes and between them one sintered

Fig. 42. Assembling of a cylindrical nickel-hydride battery.

nickel electrode, which is enveloped by a separator (polyamide; 0.2 mm thick). For the cylindrical cells, a paste hydride electrode, completely enclosed in separator cloth and a nickel electrode strip were rolled together and placed in a battery can (sub C size; $\varnothing_1 = 21$ mm), as illustrated in fig. 42. A solution of 5 M KOH and 1 M LiOH was used as electrolyte. After the electrodes plus separator were thoroughly wetted by means of vacuum impregnation, the surplus electrolyte was removed.

Fig. 43. Cylindrical nickel-hydride test cell and pressure vessel.

Both the parallel-sided cell stacks and the wound electrode packages were mounted in a stainless-steel container. The void volume, i.e. the volume of the gas space, was 26 and 3 ml for the prismatic and the cylindrical cells, respectively. Each of the steel containers was equipped with a pressure gauge and a transducer, as shown in fig. 43. One of the cylindrical cells (cell *D*) was also provided with a Hg/HgO reference electrode.

5.4. Results and discussion

In this section the data obtained from four different nickel-hydride cells will be presented and discussed. The distinguishable features of these four cells are summarized in table IX.

TABLE IX
Features of the various nickel-hydride cells tested.

cell	type	C_{rated} (mAh)	$\frac{m(-)}{m(+)} - 1$ ^{a)}	spare charge	cycle regime ^{b)}	number of cycles	testing period ^{c)}
A	prismatic	300	1.85	—	1h, 1C	>2750	9.5
B	prismatic	300	0.76	—	↑	>1100	9
C	cylindrical	600	1.13	—	1h, 1C	1251	4.5
D	cylindrical	675	1.25	10%	1h, 1C; ↓	> 850	4.5

^{a)} $m(-)/m(+)$ = active mass ratio of the hydride and the nickel electrode.

^{b)} 1h, 1C: cycling over the complete rated capacity at 1.0 C rate; ↑: overcharging at 0.25 C rate; ↓: overdischarging.

^{c)} testing period expressed in months.

5.4.1. Cell A; high-rate cycling

This prismatic cell with a rated capacity of 300 mAh was mainly cycled over its complete capacity at 1.0 C rate. In order to activate the electrodes the cell was subjected to a less exacting charge/discharge regime during the first 43 cycles. In table X the cycle regime of this cell is listed in more detail. The procedure used for the activation was rather arbitrarily chosen and may be shortened considerably.

The storage capacity is plotted as a function of the cycle number in fig. 44. The most remarkable feature of this plot is the almost constant value of both the high-rate capacity and the total capacity during 2750 cycles. With the excess active mass ratio being as large as 1.85, one obtains a calculated cycle life of 3500 cycles from fig. 41, if the corrosion rate of the intermetallic compound is taken as 0.03%·cycle⁻¹ (table VI). Since the hydride electrode did not contain ten per cent spare charge even a larger cycle life is expected (about 4000 cycles). The

TABLE X
Cycle regime of cell A^{a)}.

cycle numbers	charging period, rate	discharging rate, V_{fd} ^{b)}
1- 30	1 h, 0.25 C	0.25 C, 0.9 V
31- 33	4 h, 0.25 C	0.25 C, 0.9 V
34- 43	2 h, 0.50 C	0.50 C, 0.9 V
44- 965	1 h, 1.0 C	1.0 C, 0.9 V
966-1015	8 h, 0.125 C	0.125 C, 0.9 V
1016-2750	1 h, 1.0 C	1.0 C, 0.9 V

^{a)} Additionally to the listed regime, 0.125 C rate discharges were carried out regularly to determine the total storage capacity.

^{b)} V_{fd} : final discharge voltage (= cut off voltage).

curves of fig. 41 are based upon the assumption that only the fraction of the intermetallic compound which participates in the storage process corrodes. When, on the other hand, the excess active mass also corrodes at the same rate, the calculated cycle life of this cell is reduced to only 1400 cycles. Obviously, this is not the case. After 2750 cycles this cell still operated well during repeated charging and discharging. Despite the fact that the number of four thousand cycles has not yet been reached, the cycle life already observed supports our model for the corrosion mechanism of the hydride electrode.

Furthermore, fig. 44 shows the high coulombic efficiency of this cell. Initially, for most cycles more than 95% of the charge input was recovered. Inefficiencies

Fig. 44. The high-rate capacity (solid line) and the total storage capacity (dashed curve) of a 300 mAh prismatic nickel-hydride cell (cell A) as a function of the cycle number; cf. table X.

were due to oxygen evolution at the nickel electrode (sec. 2.1.3). As a consequence small pressure peaks (0.03 atm) were observed at the end of the charging period. After approximately 1750 cycles a slight degradation of the nickel electrode became noticeable from a decreasing coulombic efficiency. This degradation was accompanied by larger pressure variations per cycle, for instance 0.09 atm for the 2700th cycle.

During fifty cycles (966–1015) the cell was charged and discharged over its complete capacity at 0.125 *C* rate with a coulombic efficiency of only seventy percent. Although the fraction of the charge input used for oxygen evolution is expected to increase with decreasing cycling rate, seventy percent efficiency is unusually low. Possibly, the history of the cell, being one of continuous charging and discharging at a high rate for almost a thousand times, has led to the formation of catalytic sites for the oxygen evolution reaction.

Three important voltage levels of this nickel-hydride cell are given as a function of the cycle number in fig. 45. The dotted line represents the voltages determined at the end of the charge process, $V_i(c)$. The open circuit voltage of the charged battery, $V_{oc}(c)$, was measured 30 seconds after $V_i(c)$. The cell voltage denoted as $V_{oc}(d)$ is the open circuit voltage measured 15 minutes after discharging was completed.

Fig. 45. Characteristic voltages of cell A as a function of the cycle number; $V_i(c)$ represents the cell voltage at the end of charging; $V_{oc}(c)$ and $V_{oc}(d)$ stand for the open circuit voltage of the charged and the discharged cell, respectively.

The lower voltage levels $V_i(c)$ and $V_{oc}(c)$ determined for the first thirty cycles (1 h, 0.25 *C*) and for the fifty cycles from $n = 966$ to $n = 1015$ (8 h, 0.125 *C*) indicate that the battery was incompletely charged. For the other cycles the three characteristic cell voltages remained almost constant: $V_i(c) = 1.56$ V, $V_{oc}(c) =$

1.52 V and $V_{oc}(d) = 1.22$ V. This demonstrates that the internal resistance did not change during the 9.5 months of testing. The voltage difference between charging and discharging, both at 1.0 C rate, was typically 140 mV. The internal resistance calculated from this voltage difference amounts to 0.24 Ω .

The maximum gas pressure in the cell increased almost linearly from 0.15 atm after 400 cycles to 4.70 atm after 2700 cycles. So, the average pressure rise was 2×10^{-3} atm-cycle⁻¹. The pressure rise may be attributed to the incomplete reduction of the evolved oxygen; note that in this cell 2×10^{-3} atm O₂ corresponds to only 0.23 mAh. However, since the pressure increase proceeded after reaching 2.5 atm, this explanation is improbable, as will be discussed in the next section. Alternatively, hydrogen gas might have caused the observed pressure rise. If the hydrogen gas formed by the corrosion of the intermetallic compound is not absorbed, the pressure increases at a rate of 1.3×10^{-3} atm-cycle⁻¹. At the observed low pressures (< 5 atm), absorption of the hydrogen gas might be hindered by the construction of the hydride electrode, which consisted of active mass embedded in a copper matrix with $m_{act}/m_{Cu} = 0.25$. This seems plausible because a similar pressure increase was not found for cell C and cell D.

5.4.2. Cell B; IEC test

After the activation of the electrodes, the C₅ capacity of this prismatic cell was determined from the tenth cycle. This means that the battery was charged for 16 h at 0.10 C rate, rested for one hour and then was discharged at 0.20 C rate until the cell voltage had declined to 1.0 V. The C₅ values found, 298 mAh, is almost the same as the rated capacity, i.e. 300 mAh.

Subsequently, the endurance of this cell was examined in accordance with the IEC procedures *Endurance in cycles* for testing sealed nickel-cadmium cells⁽²⁾. The cycle conditions are: discharging of a fully loaded cell for 2 h and 20 min, immediately followed by charging for 3 h and 10 min, both at 0.25 C rate. Thus, during each cycle the cell is overcharged at 0.25 C rate for 50 min. Every fiftieth cycle the remaining C₅ capacity has to be determined. The test is terminated when the actual C₅ capacity becomes less than 60% of the initial value. The required number of cycles for nickel-cadmium cells is at least four hundred.

During 1100 cycles we determined for this cell C₅ capacities between 82 and 88% of the initial value. Although, during each cycle the cell was 21% overcharged, the pressure variations were only 0.10 to 0.15 atm-cycle⁻¹. The maximum pressure in the cell remained approximately 2.5 atm. This appears to be the pressure level at which the oxygen gas, evolved at the nickel electrode is rapidly reduced at the hydride electrode. After nine months of testing, this cell showed no indication of an approaching failure.

5.4.3. Cell C; high-rate cycling

Analogous to the testing of the prismatic cell A, the endurance of the cylindrical cell C was examined by repeated charging and discharging over its complete, rated capacity at 1.0 C rate. The procedure for the activation of the electrode consisted of twenty lower rate cycles. The precise cycle regime is indicated in table XI.

TABLE XI
Cycle regime of cell C^{a)}.

cycle numbers	charging period, rate	discharging rate, V_{fd} ^{b)}
1- 2	10 h, 0.05 C	0.05 C, 0.9 V
3- 14	4 h, 0.25 C	0.25 C, 0.9 V
15- 20	2 h, 0.50 C	0.50 C, 0.9 V
21-1251	1 h, 1.0 C	1.0 C, 0.9 V

^{a)} Additionally to the listed regime, 0.125 C rate discharges were carried out regularly to determine the total storage capacity.

^{b)} V_{fd} : final discharge voltage (= cut off voltage).

On the assumption that the corrosion rate of the intermetallic compound is only 0.03%·cycle⁻¹ (table VI), the cycle life of this cell should be 2140 cycles according to fig. 41. If one accounts for the absence of 10% spare charge in the hydride electrode, a lifetime of 2580 cycles is calculated. When, on the other hand, not only the fraction of intermetallic compound that participates in the

Fig. 46. The high-rate capacity (solid line) and the total storage capacity (dashed curve) of a 600 mAh cylindrical nickel-hydride cell (cell C) as a function of the cycle number; cf. table XI.

Fig. 47. Characteristic voltages of cell C as a function of the cycle number; $V_c(c)$ represents the cell voltage at the end of charging; $V_{cc}(c)$ and $V_{cc}(d)$ stand for the open circuit voltage of the charged and the discharged cell, respectively.

in the storage process corrodes, but the excess active mass of the negative electrode also degrades, the expected cycle life is reduced to only 1200 cycles. The curves for the high-rate capacity and the total storage capacity of this battery are shown in fig. 46 as a function of the cycle number. It is clear that the capacity loss measured over 1251 cycles is negligible.

The open circuit voltages of both the charged and the discharged cell, $V_{cc}(c)$ and $V_{cc}(d)$, and the cell voltages measured at the end of charging $V_c(c)$ are plotted in fig. 47. These characteristic voltages did not change appreciably after the activation of the electrodes was completed. The open circuit voltages after charging and discharging, i.e. 1.53 and 1.22 V, respectively, were practically the same as those determined for cell A. The internal resistance of cell C was $0.42\ \Omega$ for cycling at 1.0 C rate. This rather high value, almost twice the value determined for cell A, is due to the use of a thicker separator. The thickness amounted to 0.4 mm instead of the mostly used 0.2 mm. However, there is no reason for applying a thick separator in a nickel-hydride cell. On the contrary, one should search for a very thin separator, as in such a cell there is no need to store an excess amount of electrolyte (sec. 5.1). The thicker separator, together with the larger 1.0 C current, resulted in a much higher end-of-charge voltage for this cell than that found for cell A: 1.72 versus 1.56 V.

As is seen from the comparison of the figs 44 and 46, cell A and cell C operated with the same high coulombic efficiency. This is consistent with what should be expected. For, inefficiencies are due to oxygen evolution at the nickel electrode and are therefore not affected by the construction of the hydride electrode.

For cell C, the height of the cyclic pressure variations grew from 0.35 to 0.70 atm. The peaks coincided with the end of the charging period, which indicates that these variations are due to the evolution and reduction of oxygen. The maximum gas pressure in the cell remained below 1 atm during the first 900 cycles, as shown in fig. 48. Afterwards, the maximum pressure gradually

Fig. 48. The maximum gas pressure in cell C as a function of the cycle number.

increased to 5.7 atm at the 1250th cycle. This slow but steady pressure rise is attributed to the presence of a growing amount of hydrogen gas in the void volume of the cell. As follows from the pressure-composition isotherm of the $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}\text{-H}_2$ system (cf. the figs 28, 33 and 39), the hydrogen equilibrium pressure increases from approximately 0.4 to 10 atm as the hydrogen concentration in the intermetallic compound increases from 3.4 ($= \beta_0$) to 4.8 H/AB₃. As a consequence of the excess active mass in the hydride electrode, it will initially only be cycled over the fraction of the storage capacity that corresponds to hydrogen pressures below 0.4 atm. After storage capacity has been lost by corrosion, hydrogen will also be stored at sites corresponding to higher equilibrium pressures.

If it is assumed that after 900 cycles the low-pressure storage capacity of the hydride electrode became insufficient, a corrosion rate of $0.037\% \cdot \text{cycle}^{-1}$ is calculated. This value agrees well with the value determined from the half-cell experiments, i.e. $0.03\% \cdot \text{cycle}^{-1}$.

At the end of cycle 1251, the cell was overdischarged for 15 h at 1.0 C rate. This was caused by a defect in the measuring equipment and resulted in an increased internal resistance. While normal capacity values were still found for

0.25 C rate cycles, discharging at 1.0 C rate had become impossible. Testing of this cell was therefore terminated.

5.4.4. Cell D; overcharging and overdischarging

This cylindrical cell differs from cell C by the presence of ten percent spare charge in the hydride electrode and the use of a 0.2 mm thick separator. Similar to cell A and cell C, the applied cycle regime mainly consisted of charging and discharging at 1.0 C rate. Additionally, the performance of this cell during both overcharging and overdischarging was also examined.

A built-in reference electrode enabled us to record simultaneously the potential of the hydride electrode and the cell voltage. The charge/discharge curves of both the cell and the hydride electrode during a 1.0 C rate cycle are depicted in fig. 49. It is seen that the average voltage difference between the charge and the

Fig. 49. The variation of the cell voltage V_c and of the hydride electrode potential $-E_H$ (in fact: the reverse value of the electrode potential versus the Hg/HgO reference electrode) during a complete charge/discharge cycle at 1.0 C rate.

discharge curve of this cell is approximately 350 mV, when compared at the same state of charge. The internal resistance calculated from this value is 0.26 Ω . The overpotential for charging and discharging the hydride electrode at this high rate is only 50 mV. Fig. 49 also demonstrates the high coulombic efficiency of this nickel-hydride cell. For this particular cycle the coulombic efficiency was 98%. Generally, more than 85% of the charge input was recovered during discharging.

Prior to overdischarging, this cell was overcharged for eighty cycles primarily to test the gas transport in the wound electrode package used. The IEC cycle regime discussed in sec. 5.4.2 was applied. Whereas the height of the pressure

variations during each cycle was approximately 0.4 atm, the maximum pressure in the cell remained below 2.5 atm. The C_6 capacity after eighty overcharge cycles was 92% of the initial value. The oxygen recombination cycle thus proceeded as well in this cell as it did in cell *B*, despite the difference in cell construction.

We performed four overdischarge experiments at 0.1 *C* rate and with the overdischarge period varying from 2 to 3 hours. In each case, the already discharged cell (with an open circuit potential of about 1200 mV) was further discharged at 0.1 *C* rate. The actual overdischarge process is considered to begin when the cell voltage has declined to 900 mV. After 20 to 30 minutes of overdischarging, the cell voltage reversed and hydrogen gas evolution started. The reversed cell voltage was initially -140 mV and increased to -300 mV after 3 hours of overdischarging. In the four experiments of this kind the pressure rise varied from 0.9 to 1.35 atm·hour⁻¹. Should hydrogen gas be formed and completely stored in the gas space at 0.1 *C* rate, a pressure increase of 10.14 atm·hour⁻¹ would be observed. Thus, during overdischarging at 0.1 *C* rate 87 to 91% of the evolved hydrogen was directly oxidized at the hydride electrode. The remaining 9 to 13% of the current at the hydride electrode was supplied by the oxidation of the spare charge of this electrode, as indicated by the gradual increase of the reversed cell voltage. When charge/discharge cycling was resumed immediately after these experiments, the gas pressure was seen to decrease to normal levels and no loss of storage capacity was observed.

Next, three overdischarge experiments at 0.05 *C* rate were carried out. During these experiments, the complete rated capacity was forced through the cell in the

Fig. 50. The variation of the cell voltage (solid line) and of the pressure in the cell (dashed line) during overdischarging at 0.05 *C* rate as a function of the time.

reverse direction. The variation of the cell voltage and of the pressure is presented for one of these experiments in fig. 50. Almost identical results were found for the two other experiments. Again, the discharged cell was additionally discharged, now at 0.05 C rate, and the actual overdischarge process was considered to start from 900 mV. Only after 2.5 hours, the cell voltage had declined to 900 mV and it took another 1.5 hours before the voltage reversed and the pressure began to rise. Similar to the overdischarge experiments at 0.1 C rate, the reversed cell voltage increased, but now from -110 to -210 mV. The initial pressure in the cell was 1.2 atm; this value resulted from repeated cycling at 1.0 C rate. The average pressure rise amounted to $0.33 \text{ atm} \cdot \text{h}^{-1}$. This means that 93% of the hydrogen evolved at the nickel electrode was simultaneously oxidized at the hydride electrode. Moreover, the pressure curve flattened as the hydrogen gas pressure increased.

In all cases, the hydrogen pressure in the cell decreased, even when cycling at 1.0 C rate was immediately resumed, and the space charge in the hydride electrode thus restored. The value of the storage capacity, determined from the first cycle after the twenty hours of overdischarging was still 79% of the rated capacity. Normal storage capacities were measured for the next cycles.

5.5. Conclusions

Four sealed nickel-hydride cells have been tested with the emphasis on the durability of the hydride electrode. The intermetallic compound $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ was used as active negative electrode material. The results obtained from these cells confirm that only the fraction of the intermetallic compound that participates in the cycling process corrodes. Moreover, these results indicate that the corrosion rate during cycling in sealed cells is approximately the same as the rate determined from half-cell experiments. Nickel-hydride cells, which comprise one of the newly developed stable intermetallic compounds, are therefore expected to withstand the standard endurance tests for rechargeable batteries. For instance, the cell which was examined in accordance with the IEC procedure exceeded the required cycle life by a factor of three without any indication of an approaching failure.

Moreover, it was shown that sealed nickel-hydride cells can be overcharged and overdischarged without building up an unacceptably high gas pressure. Both the oxygen recombination cycle during overcharging and the hydrogen recombination cycle during overdischarging proceed well provided that the cell is adequately designed.

The tested cells had been constructed with normal components but were not optimized for maximum energy density and/or maximum power density. However, a sealed nickel-hydride cell comprising a wound package made of a

56 cm² nickel electrode with 5.0 g Ni(OH)₂ and of a 60 cm² hydride electrode with 8.4 g La_{0.8}Nd_{0.2}Ni_{2.6}Co_{2.4}Si_{1.1}, which fits in a sub C size battery can, may be constructed in the same way. The capacity of such a nickel-hydride cell is 1.25 Ah and according to fig. 41 its lifetime will considerably exceed one thousand cycles.

REFERENCES

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- ²⁾ International Electrotechnical Commission, Sub-Committee 21 A: Alkaline Accumulators, publication 285.

6. FINAL CONCLUSIONS

The intermetallic compounds LaNi_5 and LaNi_4Cu are not suitable for application in rechargeable battery electrodes. The corrosion of these materials causes a strong decline of the storage capacity. However, by means of further alloying several very stable pseudo-binary AB_5 compounds have been found. For instance the capacity loss of a $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{0.1}$ electrode is only thirty percent after one thousand cycles.

The stability of hydride electrodes may be explained in terms of an unique transport process. The rate-determining step in the corrosion reaction is the transport of the lanthanide elements to the solid-liquid interface layer. Normally, the mobility of the atoms in intermetallic compounds is practically zero at room temperature. However, a zone of enhanced mobility induced by the distorted lattices is present in the intermetallic compound particles and located at the boundary between the hydrogen poor and the hydrogen rich phase. During charging and discharging, this zone travels through the particles, enhancing the transport of the rare earth elements to the surface. As a consequence, the corrosion takes only place during cycling and the corrosion rate changes in proportion to the lattice distortion. Thus, intermetallic compounds are more stable as they expand less during hydrogen absorption. Moreover, the stability of intermetallic compounds which contain small amounts of silicon or aluminium is further improved by the formation of an oxide layer which functions as an additional hindrance for the transport of the lanthanide elements to the solid-liquid interface.

Now that a viable hydride electrode has been found, sealed nickel-hydride batteries with a durability of more than one thousand cycles can be constructed. As both electrodes operate via a fast solid state transition mechanism, these batteries are capable of being charged and discharged completely in less than one hour, while still functioning at high efficiencies. An oxygen recombination cycle enables repeated overcharging of sealed nickel-hydride batteries. As a result of the absorption and oxidation of hydrogen gas by the hydride electrode, prolonged overdischarging is also possible without detrimental consequences for the further use of the battery.

In addition to the advantages already mentioned, the absence of poisonous heavy metals, such as cadmium and mercury, is expected to facilitate the widespread application of sealed nickel-hydride batteries.

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LIST OF SYMBOLS

A	Surface area	(m ²)
$a; b; c$	Lattice parameters	(Å)
C	Storage capacity	(mAh·g ⁻¹)
C_0	Initial storage capacity	(mAh·g ⁻¹)
C_t	Total storage capacity	(mAh·g ⁻¹)
D	Diffusion coefficient	(cm ² ·s ⁻¹)
d	Particle diameter	(cm or μm)
$E; (E_r)$	(Reversible) electrode potential	(mV)
E_c	Open circuit potential of a charged electrode	(mV)
E_d	Open circuit potential of a discharged electrode	(mV)
E_{fd}	Final discharge potential	(mV)
E_{he}	Hydrogen evolution potential	(mV)
F	Faraday constant = 96485	(C·eq ⁻¹)
ΔG°	Standard free enthalpy change	(kJ·mole ⁻¹)
$\Delta H_{\alpha/\beta}^\circ$	Standard enthalpy change for the α/β transition	(kJ·(mole H ₂) ⁻¹)
i	Current magnitude	(mA)
$j; (j_0)$	(Exchange) current density	(mA·cm ⁻²)
k°	Standard heterogeneous rate constant	(cm·s ⁻¹)
m	Mass	(g)
M_{AB_s}	Molecular weight of the AB _s compound	(g·mole ⁻¹)
n	Cycle number	(cycles)
n_t	Calculated cycle life	(cycles)
n^*	Stability constant	(cycles)
n_e	number of electrons involved in the electrode reaction	(eq·mole ⁻¹)
$p; (p_{H_2})$	(Hydrogen) pressure; 1 atm. = 1.013 × 10 ⁵ Pa 1 torr = 133 Pa	(Pa)
Q	State of charge	(mAh·g ⁻¹)
R	Molar gas constant = 8.3144	(J·(mole K) ⁻¹)
R_i	Internal resistance of a battery	(Ω)
R_u	Uncompensated electrolyte resistance	(Ω)
RHE	Reversible hydrogen electrode potential	(mV)
$\Delta S_{\alpha/\beta}^\circ$	Standard entropy change for the α/β transition	(J·(K·mole H ₂) ⁻¹)
S_{400}	Stability parameter	
SA	Specific surface area	(m ² ·g ⁻¹)
T	Temperature	(K or °C)
V	Cell voltage	(V)

$V_l(c)$	Cell voltage at the end of charging	(V)
$V_{oc}(c)$	Open circuit voltage of a charged cell	(V)
$V_{oc}(d)$	Open circuit voltage of a discharged cell	(V)
V	Unit cell volume	($\text{\AA}^3$)
V	Gas volume	(ml)
x	Hydrogen content = H/M-ratio	
y	(dis-)charge rate	(hours ⁻¹)
z	Composition parameter indicating the cobalt content	
α	Transfer coefficient in Tafel equation	
$\alpha; (\alpha_s)$	Hydrogen poor phase (saturated)	
$\beta; (\beta_o)$	Hydrogen rich phase (initially formed)	
δ	Diffusion layer thickness	(cm or μm)
η	Overpotential	(mV)
η_{he}	Overpotential for the hydrogen evolution reaction	(mV)
$\Sigma\eta_{c/d}$	Sum of overpotentials for charging and discharging	(mV)
θ	X-ray diffraction angle	(degree)
ρ	Density	($\text{g}\cdot\text{cm}^{-3}$)
σ°	Cross sectional area	($\text{\AA}^2$)

SUMMARY

In the present battery research, we aimed at a rechargeable cell, which could be charged and discharged at high rates and would function in any position for several years and without requiring maintenance. The metal hydride electrode is a rechargeable negative battery electrode based upon the reversible storage of hydrogen in metals. During the charging of such an electrode, hydrogen is formed by the electrochemical reduction of water and is subsequently absorbed by the metal. During discharging, the stored hydrogen is released and oxidized.

The intermetallic compounds LaNi_5 and LaNi_4Cu , both belonging to the group of metals which is capable of absorbing and desorbing large quantities of hydrogen at pressures around 1 atm and near room temperature have been considered most-promising materials for application in rechargeable batteries. However, during repeated charging and discharging the storage capacity of both LaNi_5 and LaNi_4Cu electrodes declines exponentially as a result of corrosion of these intermetallic compounds. Consequently, the durability of these electrodes is limited to approximately 100 cycles.

X-ray diffraction analysis and electron microscopy studies showed that during electrochemical charging and discharging intermetallic AB_5 compounds are converted into hydroxide needles of $\text{A}(\text{OH})_3$ and metallic precipitates of B. No further substantial reduction of the particle size occurs during electrochemical cycling, if one starts with metal powder with a specific surface area of about $0.25 \text{ m}^2\text{-g}^{-1}$, as determined by the BET method. The exponential decay of the storage capacity suggests that the corrosion reaction is affected by the repeated expansion and shrinkage of the intermetallic compound particles, which accompanies the charge/discharge cycles. We therefore hypothesized that hydride electrodes, made of an intermetallic compound which shows less lattice expansion than LaNi_5 on hydriding, should be more stable than LaNi_5 electrodes.

More than twenty different intermetallic compounds, in which lanthanum and nickel had been partially replaced by other elements, have been prepared to examine this hypothesis. As a result several multicomponent electrodes which exhibit an excellent stability have been found. For instance, the capacity loss of a $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ electrode is only thirty percent after one thousand cycles.

Comparison of the volume expansion of these LaNi_5 -related compounds and the stability of the corresponding electrodes demonstrates that the stability indeed increases in proportion to the decreasing volume expansion. The improvement in stability is considerably larger for intermetallic compounds which contain small amounts of aluminium or silicon. We have also established that cor-

rosion only occurs during charging and discharging and not during rest. These observations may be explained in terms of a unique mass transport process in the intermetallic compound particles.

Now that a viable hydride electrode has been found, sealed nickel-hydride batteries with a durability of more than one thousand cycles can be constructed. The properties of these batteries are measured. Sealed nickel-hydride batteries are capable of being charged and discharged in less than one hour. Both prolonged overcharging and overdischarging are possible. Furthermore, they do not contain poisonous heavy metals such as cadmium and mercury.

SAMENVATTING

Dit batterijenonderzoek was gericht op de ontwikkelingen van een gesloten herlaadbare cel, die snel geladen en ontladen kan worden en die gedurende meerdere jaren goed funktioneert in elke stand en zonder dat onderhoud vereist is. De metaalhydride-elektrode is een herlaadbare, negatieve batterij-elektrode, die gebaseerd is op de reversibele opslag van waterstof in metalen. Tijdens het laden van een dergelijke elektrode wordt waterstof gevormd door de elektrochemische reductie van water en vervolgens geabsorbeerd door het metaal. Tijdens ontladen komt de opgeslagen waterstof vrij en wordt geoxideerd.

De intermetallische verbindingen LaNi_5 en LaNi_4Cu , die beide behoren tot de groep van metalen die in staat is grote hoeveelheden waterstof te absorberen en desorberen bij kamertemperatuur en drukken van ongeveer 1 atm, leken aanvankelijk veel belovende materialen voor toepassing in herlaadbare batterijen. Echter, als gevolg van corrosie van deze intermetallische verbindingen neemt de opslagcapaciteit van zowel LaNi_5 als LaNi_4Cu elektroden exponentieel af tijdens herhaald laden en ontladen. Hierdoor is de levensduur van deze elektroden beperkt tot slechts circa 100 cycli.

Met Röntgen-diffractie analyse en elektronenmicroscopie is aangetoond dat de intermetallische AB_5 verbindingen tijdens elektrochemische laad/ontlaadcycli omgezet worden in naaldvormig $\text{A}(\text{OH})_3$ hydroxide en metallische B precipitaten. Uitgaande van metaalpoeder met een specifiek oppervlak van ongeveer $0.25 \text{ m}^2 \cdot \text{g}^{-1}$ (BET methode) treedt vrijwel geen verdere verkleining van de deeltjesgrootte op tijdens elektrochemisch laden en ontladen. De exponentiële afname van de opslagcapaciteit doet vermoeden dat de corrosiereactie beïnvloed wordt door de herhaalde uitzetting en inkrimping van de metaaldeeltjes, waarmee de laad/ontlaad-cycli gepaard gaan. Daarom hebben wij verondersteld dat hydride-elektroden, die gemaakt zijn van een intermetallische verbinding waarvan het volume door waterstofabsorptie minder toeneemt dan dat van LaNi_5 , stabielere zouden zijn dan LaNi_5 elektroden.

Met deze veronderstelling als werkhypothese zijn meer dan twintig verschillende intermetallische verbindingen, waarin lanthaan en nikkel gedeeltelijk zijn vervangen door andere elementen, bereid. Hierbij zijn meerdere multi-komponenten elektroden met een uitstekende stabiliteit gevonden. Zo is bijvoorbeeld het capaciteitsverlies van een $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.6}\text{Co}_{2.4}\text{Si}_{1.1}$ elektrode slechts dertig procent na duizend cycli.

Uit een vergelijking van de volume-uitzetting van deze LaNi_5 -achtige verbindingen met de stabiliteit van de corresponderende elektroden blijkt dat de stabiliteit inderdaad evenredig toeneemt met afnemende volume-expansie. De

stabiliteitsverbetering is aanzienlijk groter voor intermetallische verbindingen, die kleine hoeveelheden aluminium of silicium bevatten. Ook is vastgesteld dat corrosie alleen optreedt tijdens laden en ontladen en niet tijdens rust. Deze waarnemingen kunnen verklaard worden in termen van een uniek massatransport-proces in de metaaldeeltjes.

Door de vinding van een levensvatbare hydride-elektrode kunnen gesloten nikkel-hydride batterijen met een levensduur van meer dan duizend laad/ontlaad-cycli worden gemaakt. De eigenschappen van deze batterijen zijn gemeten. Gesloten nikkel-hydride batterijen kunnen in minder dan 1 uur geladen en ontladen worden en zijn langdurig overlaadbaar en overontlaadbaar. Bovendien bevatten ze geen giftige zware metalen zoals cadmium en kwik.

LEVENSLLOOP

Han Willems werd op 6 mei 1955 te Eindhoven geboren, en behaalde het diploma HBS-B aan het Rythovius College te Eersel in 1972. In hetzelfde jaar begon hij met zijn studie Scheikundige Technologie aan de Technische Hogeschool Eindhoven. Het kandidaatsexamen werd in 1976 afgelegd, waarna op 25 april 1979 deze studie met lof werd afgesloten. Zijn afstudeeronderzoek verrichtte hij in de vakgroep Elektrochemie onder leiding van prof. E. Barendrecht. Daarnaast vervulde hij in deze vakgroep diverse student-assistentenschappen.

Van mei 1979 tot juli 1984 was hij werkzaam als wetenschappelijk medewerker van het Philips Natuurkundig Laboratorium te Eindhoven. Hier werd in de groep Grensvlakchemie, die geleid wordt door Dr. G. Frens, het onderzoek verricht op grond waarvan dit proefschrift tot stand kwam.

Sinds augustus 1984 maakt hij deel uit van de Philips' produktdivisie Verlichting en Batterijen.

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Stellingen bij het proefschrift:

Metal Hydride Electrodes
Stability of LaNi_5 -related
Compounds

J. J. G. Willems

2 november 1984

T.H. Eindhoven

1.

Het anormale autodoteringsgedrag van boor tijdens de epitaxiale groei van silicium kan verklaard worden door rekening te houden met chemische reacties in de gasfase.

S. B. Kulkarni and A. A. Kozul, *Electrochem. Soc. Meeting* 80-2, Hollywood, Florida, Ext. Abstr. No. 540 (1980).

2.

De stabiliteit van de, door Schoonman en medewerkers gebruikte sonde voor de elektrochemische bepaling van het waterstofgehalte in metalen zal aanzienlijk toenemen indien bij kamertemperatuur het palladiumhydride $\text{PdH}_{0.6}$ wordt gebruikt als referentie-elektrode.

J. Schoonman, D. L. Franceschetti and J. W. Hanneken, *Ber. Bunsenges. Phys. Chem.* **86**, 701 (1982).

3.

In ionogene kristallen is altijd ruimtelading aanwezig. De overmaat aan lading, die onmiddellijk onder het oppervlak is gelokaliseerd in een dunne laag, wordt gecompenseerd door extra lading van tegengesteld teken, die zich dieper in het kristal in een meer uitgestrekte laag bevindt.

4.

De mogelijke toepassing van perfluoroverbindingen ter verbetering van de waterhuishouding in zink-lucht-cellen biedt interessante vooruitzichten.

5.

Het verschil in snelheid waarmee het etsproces van het halfgeleidermateriaal InP verloopt in zoutzuur, enerzijds, en in oplossingen van HCl in gekonsentreerd azijnzuur, anderzijds, kan niet verklaard worden met een zuiver elektrochemisch oxydatiemechanisme.

S. Adachi and H. Kawaguchi, *J. Electrochem. Soc.* **128**, 1342 (1981).

P. H. L. Notten, *J. Electrochem. Soc.*, verschijnt najaar 1984.

6.

Uit het waterstofabsorptiegedrag volgt dat amorf LaNi_5 opgebouwd gedacht kan worden uit vele mikrogebiedjes, die zich onderscheiden door verschillende lanthaan/nikkel-ratio's.

7.

Tegen de, door Stadler en Boehm getrokken konklusie dat de deeltjesgrootte van fotochemisch neergeslagen platina op TiO_2 eenvoudig beheersbaar is, bestaan ernstige bedenkingen.

K.-H. Stadler and H. P. Boehm, Proc. 8th Int. Congress on Catalysis, Berlin, 2-6 July 1984, Vol. IV, p. 803-814.

8.

Een herlaadbare batterij is een chemische reaktor waarin chemische energie omkeerbaar wordt omgezet in elektrische energie. Vanwege hun gekompliseerdheid verdienen de processen in dergelijke reaktoren ook de aandacht van proceskundige chemici.

9.

Het verdient aanbeveling om in leerlingendossiers niet langer het beroep van de vader op te nemen.

10.

De opdracht van een proefschrift aan geliefde personen wekt de indruk dat het proefschrift voor hen is geschreven.