Low pressure hydride anode materials for rechargeable batteries

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AB_5-type intermetallic compounds were prepared by induction melting. Electrodes were fabricated from metal powders by addition of a polymer binder and pressing at ambient temperature. Subsequently the electrodes were activated by amperodynamic cycling. Specific electrochemical experiments including rest potential measurements and potential controlled charge/discharge cycles were carried out to determine the thermodynamic and kinetic properties. The commonly used method for the determination of pressure–concentration isotherms was replaced by an electrochemical method. Potential measurements were carried out under equilibrium conditions at different states of charge enabling the calculation of pressure-composition isotherms from these data.

1. Introduction

The crucial requirements that have to be met for the use of hydrogen storage materials in rechargeable batteries are adequate capacity, sufficient corrosion stability and a low equilibrium pressure. Recently, research activities in this field were focused on the improvement of the properties of $LaNi_5$. The high capability of this material for hydrogen storage was discovered about 20 years ago, but technical application as an anode material was prevented by its poor corrosion resistance and an equilibrium pressure of 3.5 bar at ambient temperature. By replacing a fraction of the transition metal component Ni by Co, Mn and Al, the corrosion resistance could be improved and the equilibrium plateau pressure could be lowered by a factor of 10^2 to 10^3 [1].

Further advance is expected for the development of hydride anodes by the addition of hydride forming substituents, such as boron, silicon and other light elements, aiming at the improvement of the discharge capacity and the kinetic properties. Moreover, the performance of such electrodes should be improved by melt spinning of the basic materials [5].

A common method for the characterization of metal hydrides is the determination of pressure–composition isotherms by recording the weight changes of hydrogenated samples as a function of the equilibrium pressure during the absorption or release of hydrogen. This method is rather inaccurate when samples with low equilibrium pressures in the range from 10^{-2} to 10^{-5} bar are investigated. Uncertainties arise from the limited measuring range of pressure sensors and from leakage.

An additional problem is the development of a suitable preparation procedure for electrodes with adequate mechanical stability from metal powders to achieve satisfactory and reproducible electrochemical properties. To avoid recrystallization of melt spun materials the usual hot pressing of a mixture of PTFE and metal powders had to be replaced by a method applicable at ambient temperature.

2. Experimental details

2.1. Preparation of the intermetallic compounds

AB_5-type intermetallic compounds were prepared by induction melting and melt spinning. The composition of $LaNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$, a commercially available material was varied by addition of light elements (Si, B, Al) and different transition metals (Table 1).

2.2. Modification by thermal treatment

A series of samples was modified by melt spinning. Cooling rates up to $10^6\,K\,s^{-1}$ are reached by rapid quenching of the liquid metal on the surface of a rotating copper wheel in a protective gas atmosphere. This method is usually applied for the production of metallic glasses. Although a modification of the grain size and a distortion of the crystal lattice is indicated by X-ray and SEM examination, all of the investigated samples remained in a predominantly crystalline state.

2.3. Electrode preparation

The materials obtained were immersed in an aqueous copper solution and ground to a grain size below $5 \times 10^{-5}\,m$ in diameter.

Melt spun materials, which show highly elastic properties were immersed in liquid nitrogen during the grinding procedure to prevent oxidation and to enhance their brittleness.

The metal powders were coated with copper by chemical deposition, using an alkaline Cu^{2+}-solution and HCHO as a reducing agent. A variation of the amount of copper within a range from 5 to 20 mass %

Table 1. Preparation method and composition of investigated samples

No.	Prep.	Composition/at %								
		Ni	La	Co	Mn	Al	Si	Ta	Ti	B
847 K	ind*	59.0	16.8	12.4	6.6	4.9	–	–	–	–
29a	ind*	58.0	16.4	12.1	6.5	4.9	2.0	–	–	–
30a	ind*	57.4	16.3	12.1	6.3	4.9	3.0	–	–	–
31a	ind*	56.1	15.9	11.8	6.2	4.9	5.1	–	–	–
32a	ind*	58.0	16.4	12.1	6.4	7.0	–	–	–	–
35a	ind*	62.8	14.3	10.6	5.6	4.3	2.4	–	–	–
39a	ind*	60.8	12.9	9.5	5.1	3.8	3.0	–	–	4.8
40a	ind*	53.9	15.3	11.3	5.9	4.6	3.0	–	–	6.0
42a	ind*	60.7	15.8	11.7	6.1	4.6	1.0	–	–	–
25	MS†	58.3	16.5	12.2	6.5	4.9	–	2.2	–	–
27	MS†	56.8	16.1	11.9	6.4	4.8	–	–	2.0	1.9
29	MS†	57.9	16.4	12.1	6.6	4.9	2.0	–	–	–

* ind: induction melting.
† MS: melt spinning.

showed no significant influence on the electrochemical properties of the electrodes.

The resulting agglomerated powders were suspended in an organic solution of a fluorpolymer ($10 \, g \, dm^{-3}$ Viton in acetone) and attached to a polypropylene disc with a nickel net as a current collector and pressed to electrodes at 19.6 MPa after drying in vacuum.

2.4. Activation

Electrochemical experiments were carried out in a polypropylene cell containing 6 M KOH and the usual equipment including a nickel sheet as a counter electrode, gas inlet tubes and a glass capillary for connection with a saturated mercurosulphate reference electrode (SMSE).

The electrodes were submitted to 1000 amperodynamic cycles ranging from +5 to −10 mA with a sweep rate of $1.5 \, mA \, s^{-1}$, followed by 8–15 constant current charge/discharge cycles to establish full capacity and reproducible conditions. The long and complicated activation procedure by submitting the electrodes to 100 charge/discharge cycles was replaced by this recently published method [3].

2.5. Characterization

Structure analysis of the metallic samples was carried out by the Debye–Scherrer method. Additionally the samples were examined by scanning electron microscopy and metallographic methods.

The hydrogen storage capacity was determined in a Sieverts apparatus by mass controlled isothermic desorption of hydrogen and by electrochemical charge-discharge cycles. Kinetic and thermodynamic properties of the different intermetallic compounds were investigated by potential measurements under equilibrium conditions.

2.5.1. Pressure–composition isotherms and storage capacity. The pressure–composition isotherms were determined from samples with a relatively high equilibrium pressure and at elevated temperatures respectively. As a consequence of the limited measuring range of the pressure sensors and of leakage the results became quite inaccurate when equilibrium pressures below 10^{-2} bar were measured. Experiments at higher temperatures showed shorter and less distinct pressure plateaux [2]. Figure 1
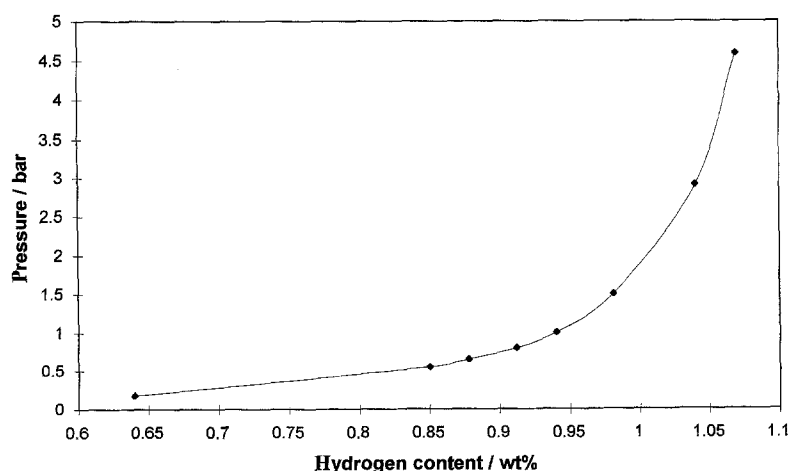

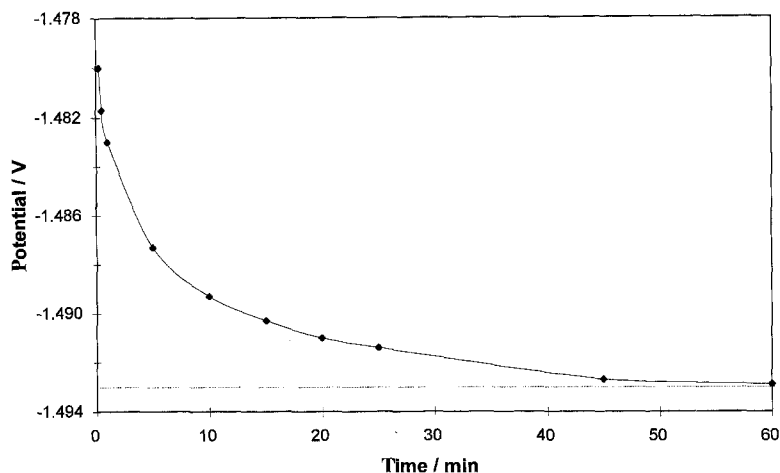Fig. 1. Pressure–composition isotherm at $T = 80 \, °C$ for electrode 29a.

Fig. 2. Time dependence of the rest potential. Key: (◆——◆) electrode 847 K at 80% state of charge; (·····) equilibrium potential.

shows the pressure–composition isotherm of sample 29a at 80 °C.

The hydrogen storage capacity was determined by measuring the mass difference between the pure inter-metallic compound and the sample in its hydro-genated state.

2.5.2. *Calculation of pressure–composition isotherms from rest potential measurements.* An alternative method suitable for the determination of low equilibrium plateau pressures is based on the measurement of the reversible electrode potentials as a function of the state of charge of the electrodes. Under equilibrium conditions a metal hydride electrode with a defined plateau pressure p_x behaves like a reversible hydrogen electrode at a hydrogen pressure p_x.

The dependence of the equilibrium potential on the partial pressure of hydrogen is expressed by the Nernst equation for gas electrodes:

$$E^\circ = E_0^\circ + \frac{RT}{F} \ln \frac{a_{H^+}}{\sqrt{pH_2}} \tag{1}$$

When no side reaction (e.g., a corrosion of the basic metal) takes place the equilibrium pressure can be calculated from potential values using Equation 1.

The electrode potentials were determined close to equilibrium conditions as a function of the state of discharge at different temperatures. Starting at a 100% state of charge the electrodes were discharged

at a constant current (20 mA). The discharge process was interrupted in intervals of 5 min. The rest potential was measured after 5 min at open circuit.

Figure 2 shows the time dependence of the rest potential at an extended timescale. As the potential decrease is about 50% within 5 min and the deviation from the equilibrium value (after 5 h at open circuit conditions) is only a few millivolts, the potential values after 5 min could easily be extrapolated to equilibrium values. Examples of the resulting characteristics are shown in Fig. 3.

From the obtained data pressure–composition isotherms were calculated. The results are shown in Fig. 4.

2.5.3. *Charge/discharge cycles.* Charge/discharge cycles were carried out at 20 mA constant current, which is nearly equivalent to a 2 h discharge cycle (C$_2$). Table 2 shows the discharge capacities and coulombic efficiencies of different samples. (Coulombic efficiencies refer to a hypothetical storage capacity with an atomic ratio Me/H 1 : 1 corresponding to the maximum capacity of the basic material LaNi$_{3.5}$Co$_{0.8}$Mn$_{0.4}$Al$_{0.3}$H$_6$.)

3. Results and discussion

The storage capacities of AB$_5$-type metal hydrides with a low plateau pressure based on LaNi$_{3.5}$Co$_{0.8}$Mn$_{0.4}$Al$_{0.3}$ that had been determined by
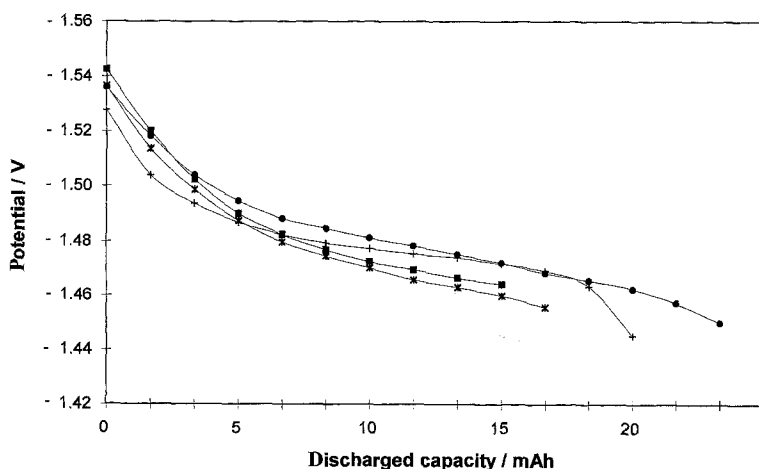

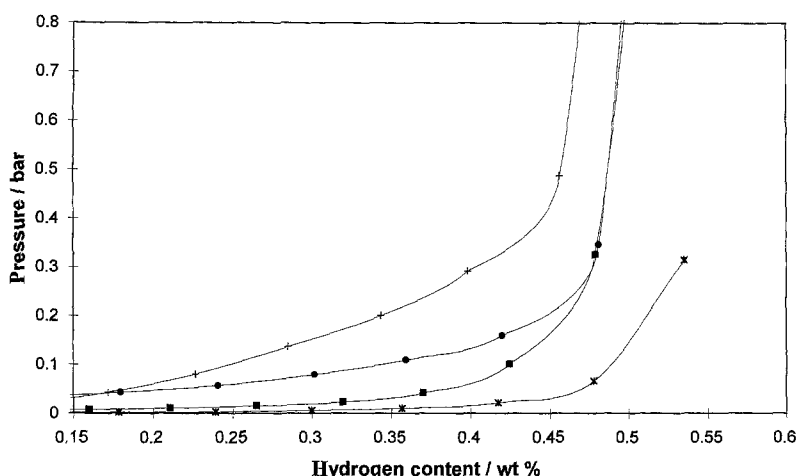Fig. 3. Rest potential against state of discharge at 20 °C. Electrodes: (■) 29, (×) 847 K, (+) 39a and (●) 29a

Fig. 4. Calculated pressure–composition isotherms at 20 °C. Electrodes: (■) 847 K, (×) 32a, (●) 35a and (+) 39a.

isothermic hydrogen desorption and by electrochemical discharge cycles differ by a factor of 1.5–2.0 depending on the composition and preparation procedure of the material. Capacity measurements carried out with pure LaNi₅ revealed an electrochemical discharge capacity of 90% of the theoretical value, although an additional loss of hydrogen had to be expected due to the high equilibrium pressure of this hydride (3.5 bar at ambient temperature). As no indication of corrosion was detected in any case and direct oxidation of hydrogen was prevented by the use of nitrogen as a protective gas, it is assumed that a fraction of the initially absorbed hydrogen cannot undergo an electrochemical oxidation reaction within a potential range which is suitable for the production of electric energy. This hypothesis is supported by the fact, that a second potential plateau appears in the discharge characteristics at a potential of +0.8 V vs RHE, although metal oxidation can occur at this potential.

Low equilibrium plateau pressures could be determined with sufficient accuracy by the calculation of pressure–composition isotherms from rest potential measurements (Table 3). When side reactions, for example, corrosion or oxygen reduction can be excluded, this method provides a suitable approach for the investigation of thermodynamic properties of metal hydrides which have a plateau pressure below 1 bar. The pressure range can also be extended by the use of a sealed cell compartment.

As the equilibrium potential of a hydrogen (or hydride) electrode decreases only by about 30 mV per order of magnitude of pressure increase, the wide measuring range of this method becomes evident.

Limitations concerning the accuracy of this method are due to diffusion potentials depending on the temperature and to experimental conditions that, although close to equilibrium, allow a determination of equilibrium values only by extrapolation.

A variation of the composition influences the storage capacity and the kinetic parameters. Small amounts of silicon lead to a significant increase of the storage capacity (Table 2) and a more pronounced potential (and pressure) plateau during discharge (Fig. 3).

Figure 5 shows the rest potential of the basic material 847 K vs state of discharge at different temperatures. A more detailed analysis reveals that the temperature dependence of the rest potential (about $0.37 \, \text{mV K}^{-1}$) corresponds to a ΔS value of $71.4 \, \text{J mol}^{-1}$, which is about half of the value expected for the reversible hydrogen electrode, but this discrepancy is more likely due to liquid junction diffusion potentials than to a specific thermodynamic effect. For a reliable interpretation of this finding additional experiments would be necessary.

The formation of a second phase by addition of boron and its influence on the rate of hydrogen diffusion has been described in a previous report [3] and confirmed by the results published by other authors [4].

Although the formation of a second phase by addition of less than 3 at % Si could not be detected by the Debye–Scherrer method, a low polarization and an increase of the diffusion controlled maximum current density indicates that the diffusion velocity is promoted in a way similar to boron containing phases by the formation of a silicon-rich sec-

Table 2. Discharge capacities and coulombic efficiencies

Electrode	Capacity /mAh g⁻¹	Coulombic efficiency /%
25	101	28
27	73	20
29	91	25
32	72	20
25a	106	29
27a	69	19
29a	235	65
32a	137	38
39a	162	45
40a	161	44
847K	140	38

Table 3. Calculated equilibrium plateau pressures

Electrode	847K	29a	29	32a	35a	39a
Equil. pressure/mbar	6.3	35	10.4	1.7	32	16
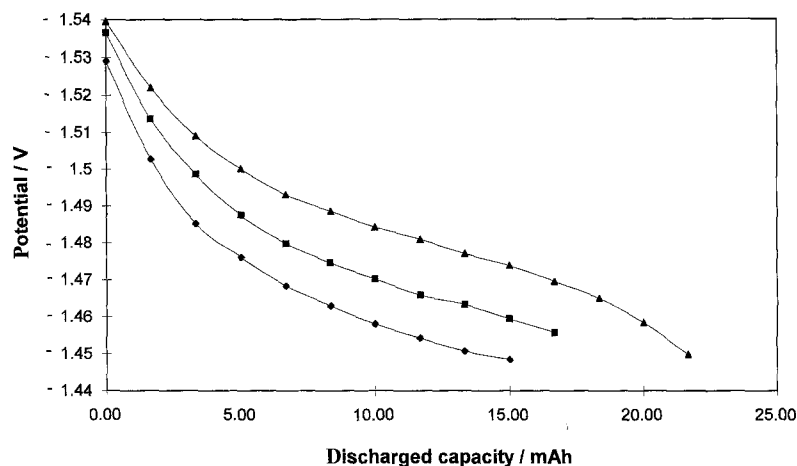
Fig. 5. Rest potential for 847 K against state of discharge at different temperatures. T: ($\blacklozenge$) 11.5, ($\blacksquare$) 21.5 and ($\blacktriangle$) 35.0 °C.

ond phase, effecting a higher diffusivity of hydrogen.

Melt spun samples of this series generally showed less capacity and higher polarization which is contrary to the results obtained by other authors from similar compounds [5]. Although some reasons for these discrepancies remain unclear and are probably due to differences in the preparation procedure, the highly elastic properties of melt spun materials implicate a persistent mechanical stress which effects an additional contribution to the decrease of potential (or increase of pressure) during hydrogen absorption. In materials with a high brittleness prepared by normal induction melting, the mechanical stress resulting from lattice expansion during the hydride formation is released by cracking and pulverizing of the polycrystalline metal. Despite the disadvantageous absorption behaviour of melt spun intermetallic compounds previous experiments [3, 5] showed that an appropriate long term cycle stability can be expected from their elastic properties by low mechanical and corrosive degradation.

4. Conclusion

The determination of equilibrium potentials at different states of charge provides a suitable method for the characterization of low pressure hydride anodes. Thermodynamic properties can be determined within a wide measuring range with sufficient accuracy. Enhanced discharge capacity and power density is achieved by the addition of small amounts of silicon and boron.

Acknowledgement

References

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