



THE INFLUENCE OF SILICON AND BORON ON THE ELECTROCHEMICAL BEHAVIOUR OF AB₅-HYDRIDES

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Abstract—AB₅-type intermetallic compounds were prepared by induction melting and melt spinning. The composition of a stoichiometric compound LaNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3} with a hexagonal CaCu₅ structure was varied by stoichiometric and nonstoichiometric addition of Si and B. Discharge capacity is increased considerably by addition of silicon in the range of 0.5–5 at% with a maximum value at about 1%. The highest capacity is achieved by a nonstoichiometric addition of 3 at% Si. The kinetic properties are additionally improved by the formation of a boron-rich second phase. Copyright © 1996 International Association for Hydrogen Energy

INTRODUCTION

Recent studies carried out with materials suitable for use as hydride anodes showed that capacities and discharge rates can be increased by partial substitution of LaNi₅-related intermetallic compounds by hydride-forming light elements. In particular, the replacement of La by Ca effects an increase in capacity, whereas corrosion stability decreases dramatically [1]. Although earlier studies [7] carried out by other authors described the use of silicon as a stoichiometric component of AB₅-hydrides, recent studies carried out with LaNi₅ in combination with a boron-containing second phase directed our attention to silicon and other hydride-forming light elements for the improvement of the reaction kinetics.

EXPERIMENTAL

LaNi₅-related intermetallic compounds with a hydride-forming hexagonal CaCu₅-structure were prepared by induction melting in an argon atmosphere. A series of samples were treated by melt spinning. In this procedure the liquid metals were quenched at cooling rates of 10⁶ K s⁻¹.

The resulting microcrystalline or amorphous metallic samples showed a marked change of their elastic properties.

Structural characterization

Structural characterization was carried out by the Debye-Scherrer method and SEM. The samples generally showed the hexagonal CaCu₅-structure of the pure intermetallic compounds. No evidence of a second phase

was found at a content up to 3% Si. The elastic lattice expansion caused by hydrogen absorption is reflected by a shift of the Bragg angles. A more detailed analysis shows that the *a/c*-axis proportion decreases with the hydrogen content, indicating that H-atoms are predominantly inserted into planes lateral to the symmetry-(c)-axis of the hexagonal unit cell. Low contents of B cause the formation of a second phase [2].

Electrode preparation

The metal samples were pulverized and the particles coated with a protective layer by chemical deposition of copper. The powders obtained were mixed with a fluoropolymer and attached to a nickel sheet serving as current collector by pressing at 200 kp cm⁻². A more detailed description of the procedure is given in Ref. [3].

A list of samples prepared by induction melting and of samples additionally modified by melt spinning is given in Table 1.

Determination of the hydrogen storage capacity

In order to investigate the influence of Si on the hydrogen storage capacity of materials based on LaNi₅ a series of samples containing different amounts of Si were examined. In addition, the influence of other substitutes or additives on the storage capacity was studied.

The storage capacity was determined by isothermal absorption/desorption cycles and electrochemical charge/discharge cycles. Table 2 shows a comparison of these results.

Table 1. Preparation method and composition of investigated samples

No.	Prepn	Ni	La	Co	Mn	Al	Si	Ta	Ti	B
847K	ind	59.0	16.8	12.4	6.6	4.9	—	—	—	—
25a	ind	58.4	16.5	12.2	6.4	4.9	—	2.0	—	—
27a	ind	56.7	16.1	11.9	6.3	4.8	—	—	2.1	1.9
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	—	—	—	—
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
41a	ind	59.9	16.3	12.1	6.2	4.9	0.5	—	—	—
42a	ind	60.7	15.8	11.7	6.1	4.6	1.0	—	—	—
33a	ind	61.3	15.3	11.3	5.9	4.6	1.5	—	—	—
34a	ind	61.7	15.0	11.1	5.8	4.4	2.0	—	—	—
35a	ind	62.8	14.3	10.6	5.6	4.3	2.4	—	—	—
36a	ind	63.5	13.8	10.2	5.4	4.0	3.12	—	—	—
37a	ind	64.3	13.2	9.8	5.1	4.0	3.6	—	—	—
38a	ind	65.2	12.8	9.5	5.0	3.7	4.0	—	—	—
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	—	—	—
32	MS	57.9	16.4	12.1	6.6	6.9	—	—	—	—

Electrochemical experiments

Activation. The electrodes were submitted to an activation procedure by ≈ 1000 amperodynamic current cycles ($+5\text{ mA}$ to 10 mA ; 1.5 mA s^{-1}). Constant capacity and reproducible behaviour was achieved by additional eight to 15 full charge/discharge cycles at 20 mA constant current (C_2).

Kinetic studies. Due to the low equilibrium pressure plateau of the basic material, the kinetic properties were estimated by comparing the potential increase during discharge at different electrodes.

In order to obtain more detailed information about the kinetic parameters and to detect the rate determining factors of anodic discharge reaction at high current densities, stationary galvanostatic current density/potential measurements were carried out at 50% charge state. Although the accuracy of the measurements were impaired by an inherent potential increase depending on the charge state at even higher current densities, b -values

and i_0 values could be determined by extrapolation of the Tafel lines in some cases.

RESULTS AND DISCUSSION

Storage capacity and efficiency

The results obtained from storage capacity determination with a series of electrodes containing different amounts of Si are given in Table 2. A comparison of the determined capacities shows that the coulombic efficiencies depending on the composition of the electrodes lie in the range of 50–70% related to a maximum value of 1:1 metal:hydrogen atomic ratio.

Obviously the capacity values and efficiencies are improved by the addition of Si. A series of samples containing different amounts of Si show a maximum discharge capacity at about 1 at% Si. At this low content no evidence of a second phase could be found by X-ray diffraction methods.

The coulombic efficiencies η_C are usually calculated from the discharge capacity related to the charge input

Table 2. Discharge capacities and efficiencies

Composition	Discharge capacity (mAH g ⁻¹)	Absorption capacity (wt %)	(mAh g ⁻¹)	η_C (%)
LaNi _{3.3} CO _{0.8} Mn _{0.4} Al _{0.3}	140			
La _{0.97} Si _{0.03} Ni _{3.57} Co _{0.72} Mn _{0.37} Al _{0.29}	137	1.3	348	39.4
La _{0.94} Si _{0.06} Ni _{3.61} Co _{0.70} Mn _{0.36} Al _{0.27}	209	1.16	311	67
La _{0.91} Si _{0.09} Ni _{3.64} Co _{0.67} Mn _{0.35} Al _{0.27}	201	1.33	356.5	56.4
La _{0.88} Si _{0.12} Ni _{3.62} Co _{0.65} Mn _{0.34} Al _{0.26}	206	1.15	308	67
La _{0.86} Si _{0.14} Ni _{3.76} Co _{0.63} Mn _{0.34} Al _{0.26}	202	1.08	289	70
La _{0.82} Si _{0.18} Ni _{3.76} Co _{0.60} Mn _{0.32} Al _{0.24}	154	1.04	279	55
La _{0.79} Si _{0.21} Ni _{3.83} Co _{0.58} Mn _{0.30} Al _{0.24}	130	1.3	348	37

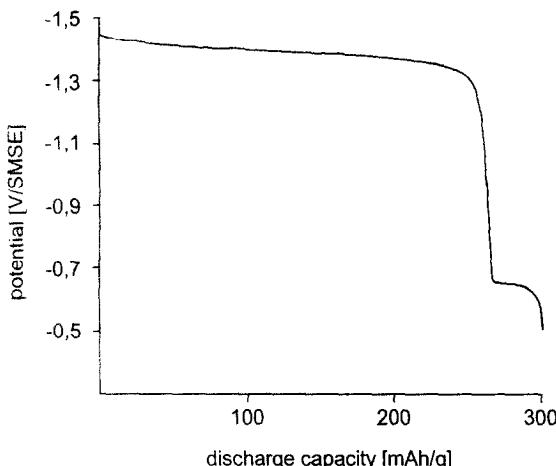


Fig. 1. Electrode potential during discharge.

during the charge process. The problems arising from H₂-losses in unsealed cells are matched by some authors [4], utilizing only a small range of the total capacity between 80 and 100% state of charge for the determination of η_C .

In order to provide a better approach to practical applications, the discharge capacities (mAh) refer to the capacity values determined by isothermic hydrogen ab-

sorption cycles. The electrode potential of electrode no. 29a as a function of the discharge capacity during the discharge process is shown in Fig. 1. At high current densities problems arise from a continuous potential increase depending on the charge state. In contrast to the straight lines expected from theoretical considerations, the potential plateau shows a distinct slope, especially in the case of melt spun material.

Moreover, the potential characteristics during discharge show a second plateau at about +0.8 V/RHE. In this potential range, metal dissolution may occur, but materials which had not undergone hydrogenation did not show this behavior. Considering the lower discharge capacities in comparison to the total storage capacities determined by isothermic hydrogen desorption, these findings indicate that a fraction of the initially absorbed hydrogen cannot undergo an oxidation reaction within a potential range which is of practical interest for the generation of electric energy. The correlation between different additives or substituent elements, respectively, and the discharge capacity is represented in Fig. 2.

Reaction kinetics

Because some of the i_0 values determined by extrapolation of the Tafel lines did not ensure the required precision and some electrodes did not even show linear sections in the anodic direction i_0 values were calculated from the charge transfer resistance at low overpotentials. A list of the determined i_0 values is given in Table 3.

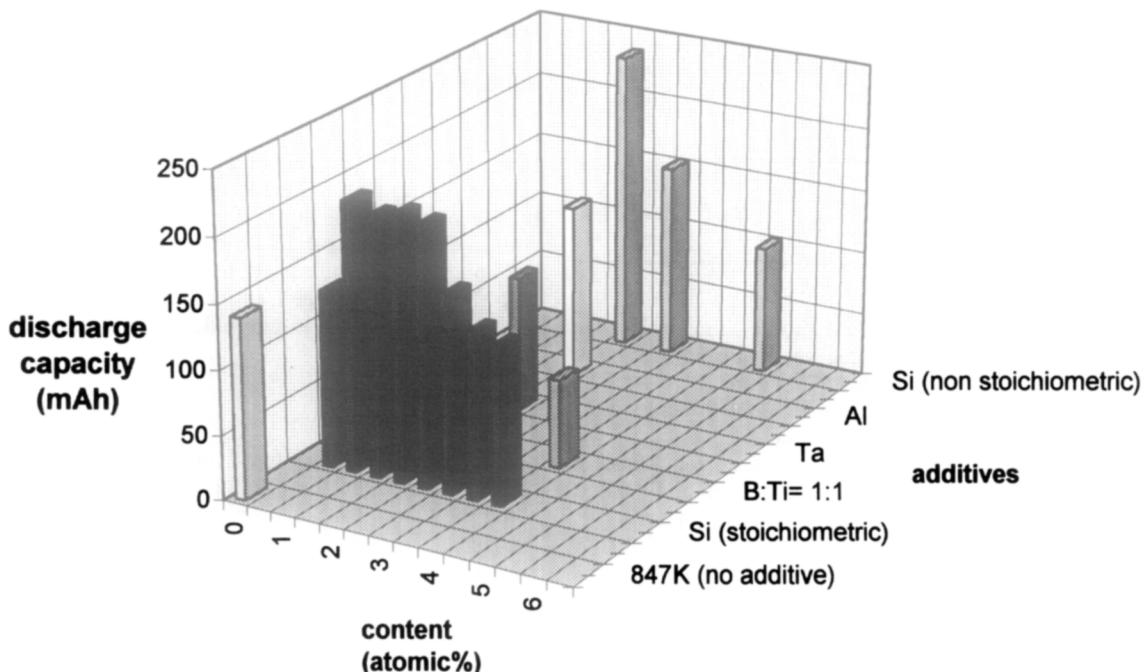


Fig. 2. Discharge capacity and composition.

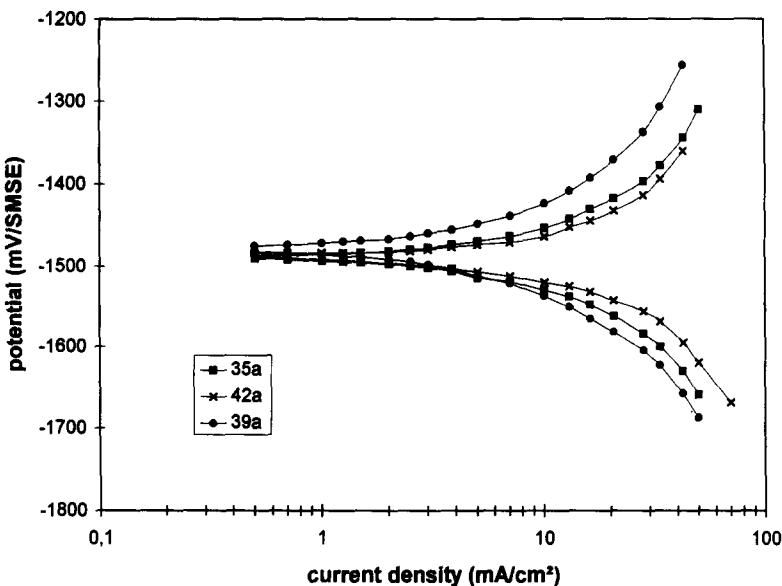


Fig. 3. Current density/potential characteristics.

Small deviations of the i_0 values were observed at different electrodes, indicating that the kinetics of the charge transfer reaction is only marginally influenced by the composition of the electrodes.

Table 3. Exchange current densities i_0^*

Electrode	847K	25	25a	27	27a	29
i_0^*	7.5	7.8	4.1	4.0	5.2	4.6
Electrode	29a	30	30a	31	31a	32
i_0^*	6.4	6.7	10.6	1.9	10.9	4.5
Electrode	32a	33a	34a	35a	36a	37a
i_0^*	7.8	7.4	6.1	8.3	6.4	8.2
Electrode	38a	39a	40a	41a	42a	—
i_0^*	3.0	3.9	5.0	4.1	7.4	—

Figure 3 shows cathodic and anodic characteristics of different electrodes. Control measurements with IR compensation revealed IR-drops ≤ 2 mV at 20 mA cm^{-2} . This indicates that the absence of Tafel slopes is more likely a consequence of polarization.

Due to the finding that the exchange current densities at different electrodes differ only within a small range, the kinetics of the charge transfer reaction is hardly influenced by the composition of the bulk electrode material. The electrocatalytic activity, which is reflected by the exchange current densities is mainly determined by the chemical composition and the structure of the electrodes surface. The catalytic activity of copper-coated samples should, therefore, be dominated by the properties of copper, a conclusion which is in good agreement with the experimental findings.

In addition to the protective function, surface coating with copper seems to be an adequate compromise to ensure sufficient catalytic activity for the formation or oxidation of metal hydrides. The use of a material with a higher catalytic activity, such as palladium or platinum as surface coating would implicate an increase of hydrogen evolution and lead to energy losses during the charge process and limit the charge currents applicable in an unsealed cell compartment.

On the other hand, the reaction kinetics at higher current densities obviously depend on the composition of the electrode material which is covered by a layer of copper, indicating that the reaction rate is also influenced by the properties of the bulk material. No Tafel lines could be detected at different electrodes. In these cases the concentration polarization range seems to overlap with the range of charge transfer polarization. Additionally the polarization is not influenced by stirring the solution.

Diffusion of hydrogen

In electrochemical systems transport limitations frequently occur at the phase boundary electrode/electrolyte solution within the liquid phase. As the diffusion of hydrogen atoms in a solid state metal hydride is much slower in comparison to aqueous solutions of molecular hydrogen, the rate determining process at high current densities occurs inside the bulk electrode material [3]. The diffusion coefficient of hydrogen differs from $10^{-5} \text{ cm } 2 \text{ s}^{-1}$ in aqueous solutions to $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ in LaNi_5 [5]. A diffusion-controlled process inside the electrolyte can, therefore, be excluded.

Obviously, the influence of Si addition is not limited to an improvement of capacity. A significant decrease of polarization at high current densities in the presence of a boron-containing second phase has been observed previously [2]. Although no evidence of the formation of a second phase is found at low contents of silicon, the addition of silicon seems to improve the diffusion controlled transport of hydrogen atoms inside the electrode in a similar way. It is assumed that the addition of Si or B influences the diffusion of hydrogen rather by the establishment of a second phase than by the formation of a single CaCu₅-structure with a high diffusivity for hydrogen atoms. Since the reaction rate is improved at contents up to 5% Si, at which the capacities are already decreasing, the improvement of diffusion is more likely due to the formation of additional grain boundaries and an enhanced interphase diffusion process along the grain boundaries of this additionally formed second phase. This assumption is confirmed by the detection of a second phase by Debye-Scherrer pictures at contents of more than 4% Si.

In contrast to the findings published by other authors [6] no improvement of the electrode behavior could be achieved with electrodes prepared by melt spinning in an argon atmosphere. Low capacities and a strong dependence of the electrode potentials on the state of charge are probably due to an increase of the mechanical stress during hydride formation as a consequence of the enhanced elastic properties of these materials.

CONCLUSION

The addition of silicon in a range from 0.5 to 3 at% Si to AB₅-hydrides based on LaNi_{3.5}Co_{0.5}Mn_{0.4}Al_{0.3}

improves the discharge capacities of hydride anodes. Contents up to 6 at% additionally improve the reaction kinetics by a promotion of hydrogen diffusion inside the bulk hydride. Modification of the materials by melt spinning in an argon atmosphere did not effect any improvement.

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REFERENCES

1. Z. P. Li and S. Suda, Abstract No. 33, Extended Abstracts of the Fall Meeting of the Electrochemical Society 1994, pp. 48–49.
2. M. Tadokoro, M. Nogami, Y. Chikano, M. Kimoto, T. Ise, K. Nishio and N. Furukawa, *J. Alloys Compounds* **192**, 179–181 (1993).
3. H. Kronberger, GDCh Monographie, Vol. 2, Elektrochemie und Werkstoffe, Gesellschaft Deutscher Chemiker, Frankfurt 1995.
4. Y. Fukumoto, M. Miyamoto, M. Matsuoka and Ch. Iwakura, *Electrochim. Acta* **40**, 845–848 (1995).
5. C. Lartigue, A. Percheron-Guégan, A. J. Dianoux and F. Tasset, *J. less-common Metals* **101**, 391–404 (1984).
6. R. Mishima, H. Miyamura, T. Sakai, N. Kuriyama, H. Ishikawa and I. Uehara, *J. Alloys Compounds* **192**, 176–178 (1993).
7. P. H. L. Notten, Europ. Patent Appl. 408 118 (1989).