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Magnetic Field Effects on the Electrochemical Potential*

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A novel magnetic field effect on chemical systems has been studied: The equilibrium potential was influenced by magnetic fields for the electrochemical systems including ferromagnetic hydrides such as $LaCo_5H_x$ and $Y_2Co_7H_x$. The change in the electrode potential ΔE for ferromagnetic hydrides was proportional to magnetic fields and ΔE was independent of the direction of the magnetic field. A 1.7mV decrease in the potential was observed for the $LaCo_5H_x$ electrode at 15T at 293.2K. The results agree well with the thermodynamic theory where the free energy of the system includes the magnetostatic energy.

KEYWORDS: magnetic field effect, electrode potential, electrochemical potential, metal hydride, $LaCo_5H_x$, $Y_2Co_7H_x$, $LaNi_5H_x$

1. Introduction

Magnetic field effects on chemical equilibria have been so far observed for ferromagnetic hydride-hydrogen systems. The pressure-composition isotherm (PCT), the equilibrium hydrogen pressure and the hydride composition are considerably changed by magnetic fields.[1-7] For example, the hydrogen pressure P_{H_2} for the $LaCo_5-H$ system is increased with increasing magnetic field as P_{H_2} of 0.12 MPa in zero field becomes 0.18MPa in 26T at 293K.[7] In these effects the magnetostatic energy of the hydride is converted into the chemical potential of hydrogen. Basically a similar magnetic effect is expected for the electrochemical system. That is, the equilibrium potential of ferromagnetic hydride electrodes is changed when magnetic fields are applied. This is considered to be a novel energy conversion between the magnetostatic and the chemical energies.

In this paper we review the theoretical and experimental results of the magnetic field effects on the electrode potential. In the theory, introducing the term of the magnetic free energy into the Nernst's equation gives a measurable change in the electrode potential. In the experiments the potential of the $LaCo_5H_x$ and the $Y_2Co_7H_x$ electrodes is observed in magnetic fields up to 15T at room temperature, resulting in a satisfactory agreement with the theory.

2. Thermodynamic theory

The magnetization of the ferromagnetic hydride considerably changes with hydrogen composition. The saturation magnetization is linearly increased with decreasing hydrogen composition in the $\alpha+\beta$ or the $\beta+\gamma$ region of $LaCo_5H_x$ as listed in Table I. Here, the value ΔM_s is defined as the change in magnetization for solid phase per desorbed 1mol hydrogen atom, where the sign of ΔM_s is positive or negative according to whether the magnetization is increased or decreased upon the desorption of hydrogen. On the other hand, the magnetization of $Y_2Co_7H_x$ shows periodically behavior with the hydrogen composition as illustrated in Fig 1.

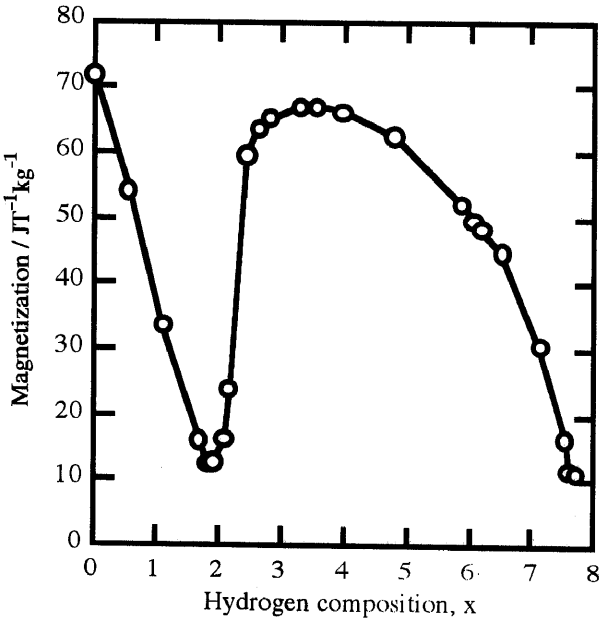

Figure 1. Saturation magnetization vs. hydrogen composition at 348.2K for $Y_2Co_7H_x$.

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Table I. Magnetic properties of $LaCo_5H_x$ hydrides

Phase(Hydrogen composition, x)	Magnetization [J/T/kg]	Two phase region	Temperature [K]	ΔM_S [J/T/molH]
α (0.3)	85		363.2	
		$\alpha+\beta$	363.2	8.67
β (3.4)	23		363.2	
β (3.4)	45		293.2	
		$\beta+\gamma$	293.2	16.4
γ (4.3)	11		293.2	

Table II. Data of hydride electrodes

Hydride	L [mm]	D [mm]	W [mg]	Magnetic property	$\partial E/\partial T$ [mV/K] obs.	calc.
$LaCo_5H_x$(I)	6.5	3.0	268.8	F	−0.74	−0.66
$LaCo_5H_x$(II)	6.4	3.0	231.5	F	−0.74	−0.66
$Y_2Co_7H_x$	4.8	3.5	303.6	F	−0.71	−0.61
$LaNi_5H_x$	8.8	3.0	314.6	P	−0.74	−0.56

F; Ferromagnetic, P; Paramagnetic

As a result of applied magnetic fields the free energy of hydrogen in the hydrides is changed as follows.

$$\delta G_{mag} = B\Delta M_S , \quad (1)$$

where B is the magnetic field. Here, we assumed that the magnetization is saturated and directed to the magnetic field used. Because ΔM_S is not zero for a ferromagnetic hydride, the change in the chemical potential is measurable. In contrast, such an effect is negligibly small in a non-ferromagnetic hydride. In the Ni/Hydrogen secondary battery, the metal hydride electrode reacts as,

$$MH + NiOOH = M + Ni(OH)_2. \quad (2)$$

where M and MH is the metal and the metal hydride, respectively. The potential of the hydride electrode E is related to change in the free energy of the hydride according to Nernst's equation,

$$\Delta G_{el} = -nFE , \quad (3)$$

where F is the Faraday constant and n is 1 for the reaction represented in eq. (2). Therefore the change in the electrode potential is caused by the change in the electrochemical potential,

$$\delta G_{el} = -F\delta E. \quad (4)$$

In the equilibrium δG_{mag} balances with δG_{el},

$$\delta G_{mag} = \delta G_{el}. \quad (5)$$

From eqs. (1), (4) and (5), the change in the electrode potential due to the magnetic field is given by,

$$\delta E = -B\Delta M_S/F. \quad (6)$$

This equation indicates that the magnetic field effects appear clearly in ferromagnetic hydride such as $LaCo_5H_x$ or $Y_2Co_7H_x$ with $\Delta M_S \neq 0$, but not in non-ferromagnetic hydride electrode such as $LaNi_5H_x$ with $\Delta M_S \cong 0$. Furthermore, the change in the electrode potential δE is proportional to the magnetic field.

Meanwhile the temperature dependence of the electrode potential obtained using the thermodynamic relation, $\Delta G = \Delta H - T\Delta S$. Thus,

$$\partial E/\partial T = \Delta S/2F. \quad (7)$$

The temperature dependence of δE, if it exists, is due to that of ΔM_S. If ΔM_S is independent of temperature, so is δE.

3. Experimental

The intermetallic compounds $LaCo_5$, Y_2Co_7 and $LaNi_5$ were prepared by arc-melting constituent metals in an argon atmosphere. The purity was 99.9% for yttrium and rare earth metals and 99.99% for cobalt. The ingots were annealed in argon at 1223K for 48h. Powder x-ray diffraction profile indicated that the compounds were single phase with the respective crystal structures.

The negative electrodes were made from the pulverized compounds which were mixed with an organic binder (polytetrafluoroetylene) at the weight ratio of 5:1. They were mechanically formed into small rods. The length(L), the diameter(D), the overall weight(W) and the magnetic properties of the hydride electrodes are listed in Table II. The electrodes were heated at 573K in a vacuum and were reacted with hydrogen at 4.5MPa at room temperature for an activation.

Two electrochemical cells, A and B, were prepared. Each cell consisted of the hydride electrodes, a Ni positive electrode, a platinel thermocouple and a Ag/AgCl electrode (SSE) as the reference electrode, and they were fully immersed in electrolytic solution with 30wt%-KOH. Cell A was unsealed type and includes the $LaCo_5H_x$ and the $LaNi_5H_x$ electrodes. Cell B includes the $Y_2Co_7H_x$ electrode and it is filled with hydrogen at the pressure of 43 or 26.7kPa. The electrode potential was measured in the temperature range between 288.2 and 313.2K for Cell A and between 288.2 and 344.1K for Cell B.

The cell was placed in the center of an electromagnet and the hydrogen-charging/discharging processes were repeated. The temperature was strictly controlled at the accuracy of ±0.03K with temperature-controlled water flowing through

a water-jacket and electric heating around the cell. The rising time to the maximum field of 15T was 1min. The field was kept constant for 5min, and then it was decreased to zero. The electrode potential (vs. SSE) in an open circuit, the field, the temperature and the pressure were simultaneously measured and recorded.

4. Results and discussion

As a preliminary experiments, the temperature dependence of the potential for hydride electrodes were investigated in the absence of magnetic fields. These potentials were linearly decreased with increasing temperature. As listed in Table II its temperature dependence was obtained to be $\partial E/\partial T = -0.74$, -0.74 and -0.71mV/K for $LaCo_5H_x$, $LaNi_5H_x$ and $Y_2Co_7H_x$ electrodes, respectively. The linear temperature dependence follows the thermodynamic relation of eq. (7). These $\partial E/\partial T$ values agreed with the theoretical values for the hydride electrode according to eq.(7) with the ΔS values reported.[8] This confirmed that the present hydride electrodes work well as the hydrogen electrodes.

$LaCo_5H_x$ electrode

Figure 2 shows the time variations in temperature, the electrode potential (vs. SSE) and the magnetic field. At about t=600min. the base lines were lowered because of increasing temperature from 288.2 to 293.2K. The electrode potential for the $LaCo_5H_x$ electrodes were obviously changed in response to intermittently applied fields, while

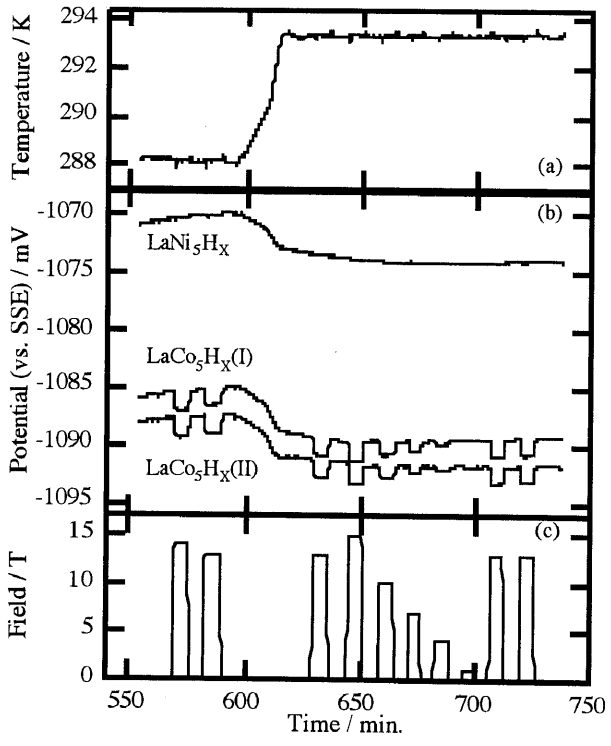

Figure 2. Time variations in the temperature, the electrode potential (vs. SSE) and the magnetic field for the $LaCo_5H_x$ and the $LaNi_5H_x$ electrodes.

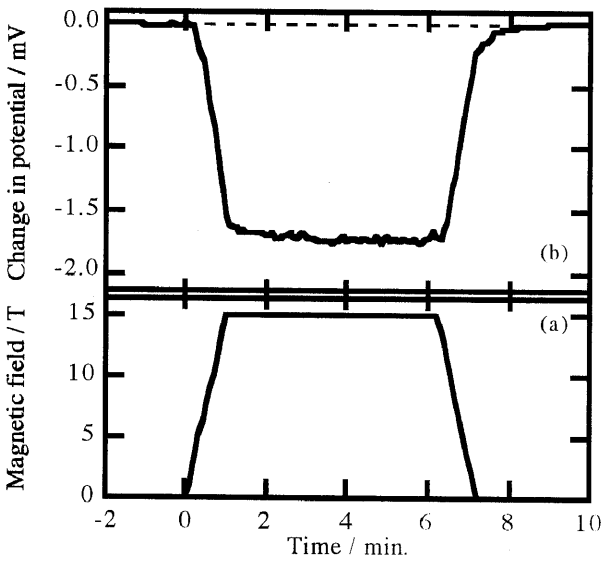

Figure 3. Time variations in the change in the potential of the $LaCo_5H_x$ electrode and the field at 293.2K.

that for the $LaNi_5H_x$ electrode was not influenced by the magnetic field. The ferromagnetism of $LaCo_5H_x$ and the paramagnetism of $LaNi_5H_x$ result in this pronounced difference in the magnetic field effect. It must be noted that the present effect differs from the magnetohydrodynamic effect on the electrochemical system, in which the motion of ion carriers are modulated by fields.

Figure 3 presents the time dependence of the change in the electrode potential of the $LaCo_5H_x$ electrode when the field was applied up to 15T at 293.2K. The electrode potential was decreased with increasing field and the initial value is restored by removing fields. The electrode potential in 15T is 1.7mV lower than that in zero field. Moreover we confirmed that this effect is independent of the direction of the magnetic field; the sign and the magnitude of the change in the electrode potential are the same for both directions.

The change in the electrode potential is plotted as a function of the field up to 15T at 293.2K in Fig. 4. Through the experiment the $LaCo_5H_x$ hydride is in the $\alpha + \beta$ region because the equilibrium hydrogen pressure of 4kPa is lower than the atmospheric pressure (0.1MPa) at 293K. Therefore, ΔM_S is considered to be 8.67J/T/molH. The broken line denotes the value calculated from eq. (6) with ΔM_S=8.67J/T/molH. The decrease in the electrode potential was proportional to the field up to 10T and agreed well with the calculated value; the observed and the calculated ones are 1.0 and 0.9mV at 10T, respectively. In higher fields, however, the observed value tends to deviate from the calculated line. A similar deviation also appeared in the magnetic field-induced change in the equilibrium hydrogen pressure of the $LaCo_5H_x$[7], suggesting that both effects are due to the same origin.

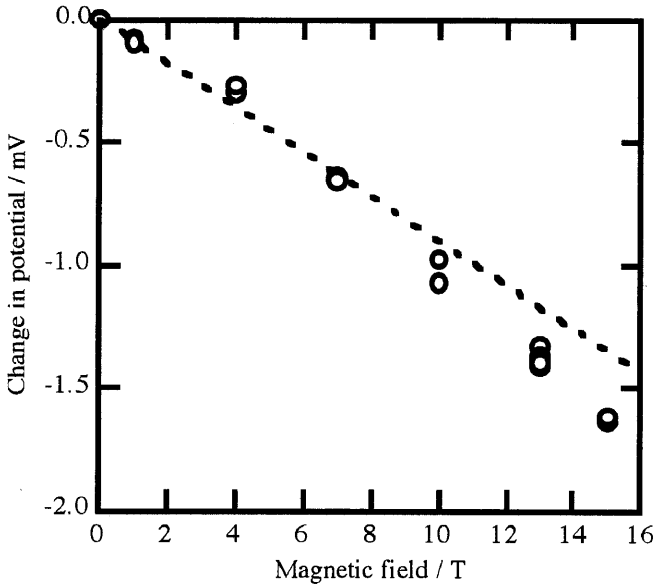

Figure. 4. Change in the potential vs. the field up to 15T at 293.2K for the $LaCo_5H_x$ electrode. The broken line denotes the value calculated according to eq. (6) with ΔM_S= 8.67J/T/molH.

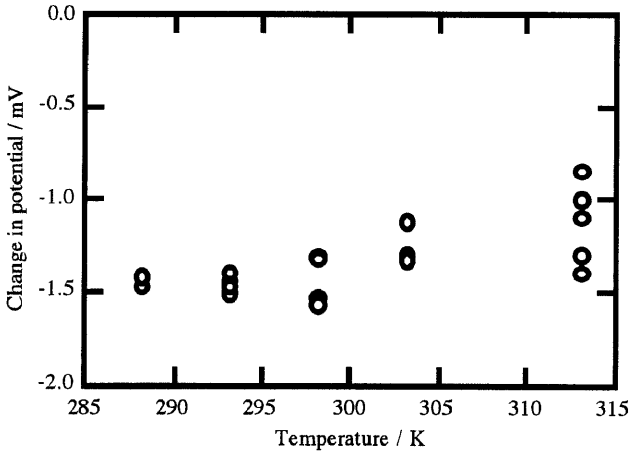

Figure 5. Temperature dependence of the change in the potential of $LaCo_5H_x$ electrode in 13T.

The change in the electrode potential was reduced in magnitude with increasing temperature between 288.2 and 313.2K as shown in Fig. 5. Equation (6) yields that the change in free energy of hydrogen in the hydrides is determined by the magnetic field so long as ΔM_S is independent of temperature. However, this is not the case for real hydrides. The ΔM_S value is sometimes changed with temperature because of the existence of Curie temperature T_c. For the $LaCo_5H_x$ system, T_c reduces from 840K for the α phase hydride to 360K for the β phase hydride.[8,9] Since the ΔM_S value is proportional to the difference between the magnetization of the α phase and that of the β phase, the ΔM_S value in the $\alpha + \beta$ region is increased with increasing temperature near room temperature. On the contrary to this prospect the observed

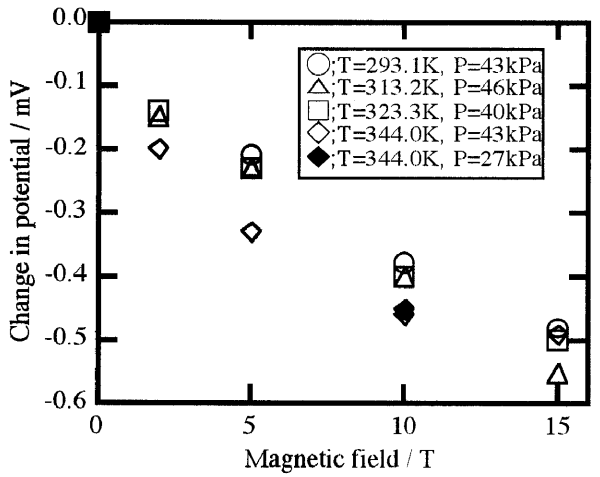

Figure 6. Change in the potential of the $Y_2Co_7H_x$ electrode vs. fields.

change in the electrode potential is increased with increasing temperature. This discrepancy is not fully understood at the moment.

$Y_2Co_7H_x$ electrode

The dependence of the electrode potential (vs. SSE) on field, temperature and hydrogen pressure was measured for $Y_2Co_7H_x$ electrode in the closed-type Cell B. Figure 6 illustrates the magnetic field dependence of the change in the electrode potential in the temperature range between 293.1 and 344.0K: The open symbols denote the results at the temperature of 293.1 (○), 313.2 (△), 323.3 (□) and 344.0K (◇), when the hydrogen pressure of the cell was controlled at 43±3kPa. The closed symbol (◆) presents the change in the electrode potential obtained under the hydrogen pressure of 26.7kPa at 344.0K, showing no pressure effect compared with that under 43.3kPa. The hydrogen composition of the $Y_2Co_7H_x$ electrode was not likely easily changed by temperature and pressure. Applying eq. (6) gives ΔM_S=3.2J/T/molH. This corresponds to the ΔM_S in the $\beta + \gamma$ region for $Y_2Co_7H_x$ (x=3~6).[5, 10]

5. Conclusions

Magnetic field effect on the electrode potential for ferromagnetic hydrides was theoretically presumed and experimentally confirmed using the hydrides $LaCo_5H_x$ and $Y_2Co_7H_x$. The electrode potential was considerably influenced by applied magnetic fields. The change in the potential of each electrode was proportional to magnetic fields and its proportionality constant was related to the magnetic properties represented by ΔM_S. This effect was independent of the direction of the magnetic flux. In the field of 15T, 1.7 and 0.5mV decreases in the potential were observed for the $LaCo_5H_x$ electrode at 293.2K and the $Y_2Co_7H_x$ at 313.2K, respectively. These results agree well with the thermodynamic consideration.

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