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Electromotive force of metal hydride electrodes in gradient magnetic fields

I. Yamamoto[a,*], M. Fujino[a], M. Yamaguchi[a], F. Ishikawa[a], T. Goto[b], S. Miura[c]

[a]*Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[b]*Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106-8666, Japan*
[c]*Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980-8517, Japan*

Abstract

The electromotive force (emf) has been investigated for the hydride–hydride electrochemical cell under the influence of gradient magnetic fields. The thermodynamic consideration presumed the relationships between the emf and the gradient between the electrodes. The emf was measured for the array of the electrodes using the ferromagnetic metal hydride $LaCo_5H_x$ in the magnetic fields with the maximum gradient of 106 T/m up to 15 T at 293 K. The emf was proportional to the averaged gradient of magnetic fields and the distance between two electrodes and depended on the magnetic properties of the electrode material, which agreed well with the thermodynamic consideration.

Keywords: Metal hydride; Magnetic field effects; Gradient magnetic fields; $LaCo_5H_x$

1. Introduction

Magnetic field effects on chemical equilibria have been studied systematically by our group for metal–hydrogen systems. The magnetic energy in high fields for some ferromagnetic systems, such as $LaCo_5H_x$ and $SmCo_5H_x$, is large enough to influence chemical equilibrium. As a result, the pressure–composition isotherm (PCT) [1], equilibrium hydrogen pressure [2–5] and equilibrium hydride composition [6] were recognized to be changed by magnetic fields; for example, the hydrogen pressure P_{H_2} for the $LaCo_5$–H system is increased with increasing magnetic field as P_{H_2} is 0.12 MPa in zero field and 0. 18 MPa in 26 T at 293 K [5]. In these effects the magnetostatic energy of the hydride was converted into the chemical potential of hydrogen. Furthermore, a remarkable magnetic field effect on the electrode potential has been discovered [7,8]. The equilibrium potential for a $LaCo_5H_x$ electrode decreases 1.7 mV in the field of 15 T at 293.2 K [7]. In this effect the magnetic free energy is directly converted into an electrochemical energy. A thermodynamic consideration gave a relationship between the change in the electrode potential and the magnetic property of the hydride [9,10].

The above chemical effects occurred in homogeneous magnetic fields. In this paper the effect of gradient magnetic fields on the electromotive force (emf) for an electrochemical system is theoretically considered first. Introducing the term due to the magnetic fields into the free energy/chemical potential, which was confirmed previously in Refs. [9,10], gives a measurable magnitude of the emf in gradient magnetic fields. Next the emf of the metal hydride–hydride cell is observed in magnetic fields with the gradient of 106 T/m up to 15 T at room temperature. The gradient of the magnetic field is estimated finally.

2. Theory

The magnetization of the ferromagnetic hydride considerably changes with hydrogen composition. The saturation magnetization is linearly increased with decreasing hydrogen composition in the $\alpha+\beta$ and $\beta+\gamma$ regions of the hydride $LaCo_5H_x$. Then, the value ΔM_s is defined as the change in magnetization per desorbed 1 mol 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. The value ΔM_s is equal to 8.7 JT^{-1} mol^{-1} in the $\alpha+\beta$ region of $LaCo_5H_x$ [2,3]. The potential of the hydride electrode in a magnetic field is given by [10],

$$E = E_0 - B\,\Delta M_s/F \quad (1)$$

where, E_0 is the standard electrode potential, and B and F

*Corresponding author.

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are the magnetic flux density and the Faraday constant, respectively. Previous papers [7–9] confirmed that Eq. (1) is valid under the influence of homogeneous magnetic fields up to 15 T.

When the hydride electrode is exposed to a gradient magnetic field in an electrochemical cell, the electrode potential is different at different positions according to Eq. (1). Consequently, the emf δE, the difference in potential, is related to the difference in the magnetic field between two near positions δB.

$$\delta E = -\Delta M_s \, \delta B/F. \tag{2}$$

This means that the emf is generated by the same kinds of two electrodes in a gradient magnetic field. Integration of Eq. (2) between the position z_1 with the field of B_1 and the position z_2 with the field of B_2, yields,

$$\Delta E = -\Delta M_s(B_2 - B_1)/F \tag{3-1}$$

$$= -\Delta M_s DG/F \tag{3-2}$$

where D is the distance between positions z_1 and z_2 and G is the averaged gradient.

3. Experimental

The intermetalic compound $LaCo_5$ was made by arc-melting constituent metals in an argon atmosphere. The purity of metal was 99.9% for lanthanum and 99.99% for cobalt. Then, the ingots were annealed at 1223 K for 48 h. Powder X-ray diffraction indicated that the compounds were single phase with the desired crystal structures.

The electrodes were a mixture of pulverized compound and organic binder (polytetrafluoroethylene) with the weight ratio of 5:1. They were mechanically formed into small cylinders with a diameter of 3.2 mm. Their length and weight were about 6.5 mm and 0.4 g, respectively. The electrochemical cell was an open-air type filled with 30 wt.%KOH electrolytic solution and contained the hydride electrodes, the Ni positive electrode and a thermocouple. The hydride electrodes were linearly arrayed at nine planes, where a few electrodes were placed in the same plane, with each at a distance of 50 mm. The charging–discharging were repeated for ten cycles to activate all hydride electrodes. The cell was placed vertically along the central axis of the magnet.

Trapezoidal magnetic fields up to 15 T were applied to the cell. Each constant magnetic field was kept for about 5 min. Then, the field was decreased to zero at the same rate. The rising time of the magnetic field up to 15 T was 1 min. Both the field and the gradient were depended on the distance z from the center of the magnet as shown in Fig. 1. The maximum field and the maximum gradient were $B = 15$ T at $z = 0$ and $dB/dz = \pm 105.6$ T/m at $z = \mp 118$ mm, respectively.

The temperature of the cell was strictly controlled at 293.2 K at the accuracy of ± 0.03 K by using temperature-controlled water flowing through a water-jacket and a wire heater wound around the cell. Then, the magnetic field, the open voltage between the electrodes and the temperature were simultaneously measured and logged by a computer.

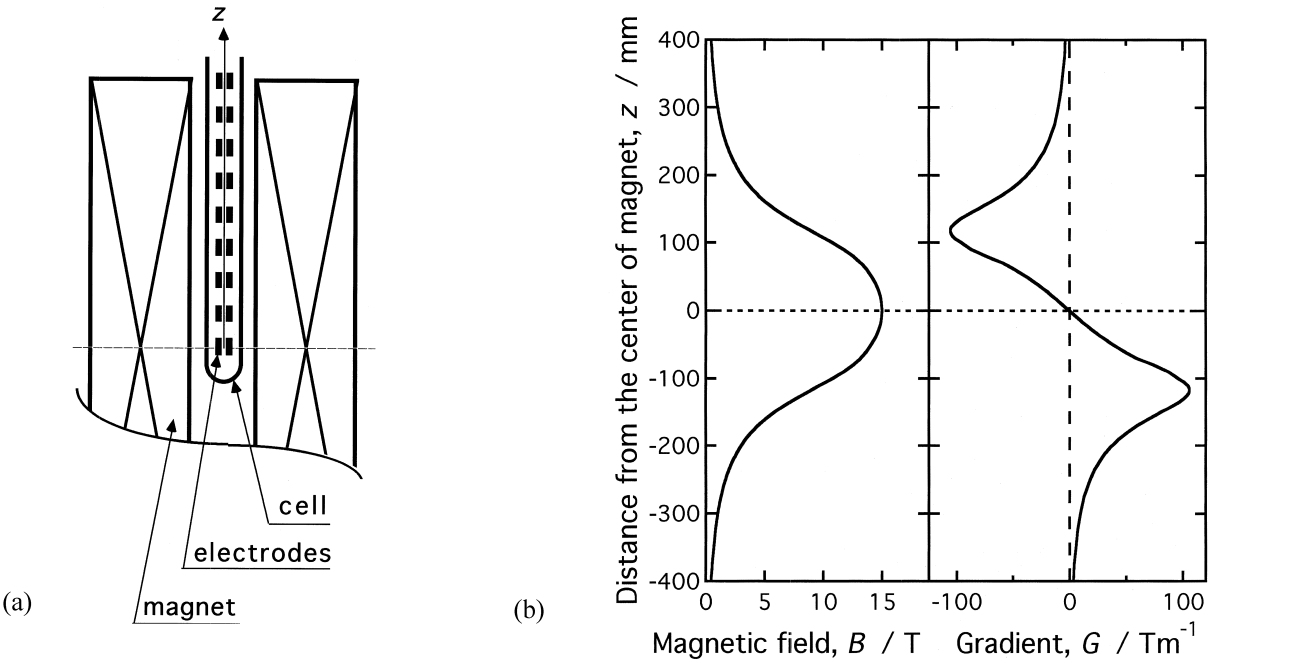

Fig. 1. (a) Arrangement of the cell and electrodes. The cell was placed at the upper side of the magnet. (b) Distribution of magnetic fields and gradients.

4. Results and discussion

The emf was not observed for the electrodes in the same plane of z. But the cell generated measurable magnitudes of emf between the electrodes which were located at different position of z. An example of the time variations in the magnetic field and the emf between two electrodes was illustrated in Fig. 2. Where the two hydride electrodes were exposed to the magnetic fields of 14.09 and 3.02 T. Noisy regions appeared in the emf signal with the application and removal of magnetic fields. The plateau region in the emf of 1.06 ± 0.05 mV was, however, observed while the magnetic field was fixed. The emf was expected to be 0.998 mV according to Eq. (3-1). The observed value and the theoretical one agreed with each other.

The emf was measured in different gradient fields for different pairs of hydride electrodes. Increasing the difference in the field resulted in the increase in the emf as shown in Fig. 3. Substituting the observed emf of $\Delta E =$ 1.06 mV at $z = 125$ mm and the distance of $D = 150$ mm into Eq. (3-2) gave the averaged gradient of the magnetic field, $G_0 = -78.4$ T/m. This agreed with the averaged gradient obtained from Fig. 1, $G_{av} = 73.8$ T/m. In spite of this good agreement of the emf between G_0 and G_{av}, they were about 30% lower than the gradient at the middle point of $z = 125$ mm, $G_m = -103.9$ T/m, where the distance was crossed over the peak of G_0 curve.

All estimations for the field gradient in various situations were summarized in Fig. 4. Meanwhile three kinds of the gradients were agreed for the other experiments when the cells were far from the center of magnet.

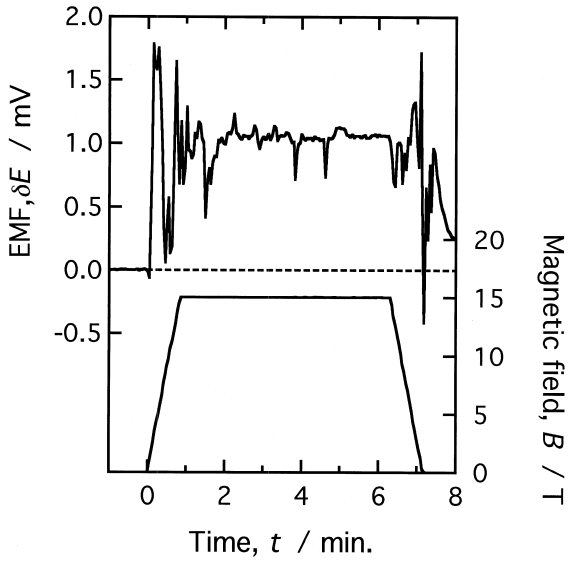

Fig. 2. Example of the time variation of emf under the influence of the trapezoidal magnetic field. Two hydride electrodes were located at $z = 50$ and 200 mm. The distance between two electrodes was $D = 150$ mm and the middle point between them was at $z = 125$ mm.

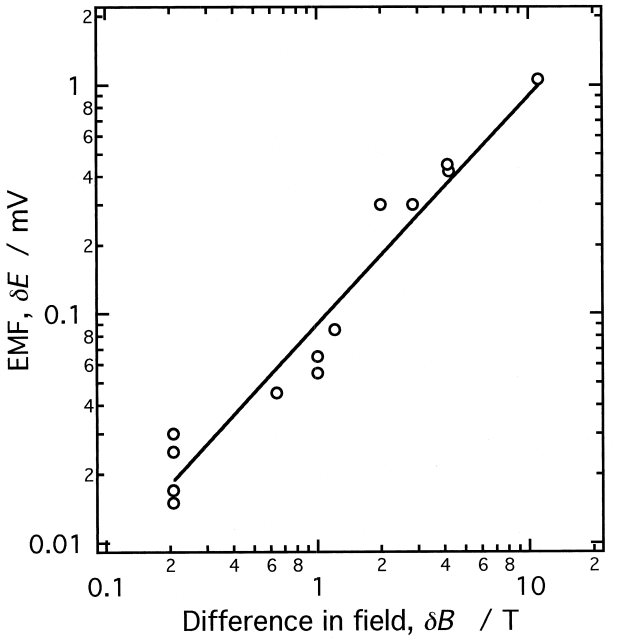

Fig. 3. Observed emf as a function of the difference in magnetic fields between electrodes for $LaCo_5H_x$–$LaCo_5H_x$ cell at 293.2 K. The solid line denotes the calculation due to Eq. (3-1).

5. Summary

Gradient magnetic fields applied to a hydride–hydride cell were theoretically presumed to produce an emf and

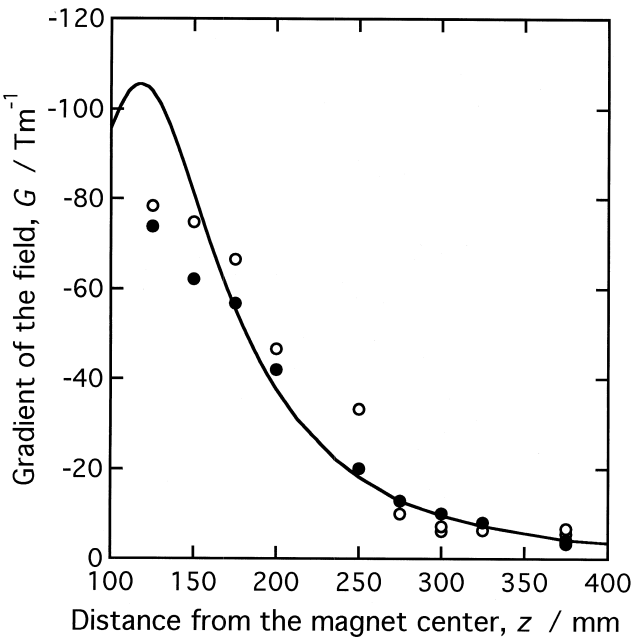

Fig. 4. Dependence of the distance from the magnetic center on the gradient of fields obtained according to Eq. (3-2) and averaged. The open and closed symbols denote the G_0 and G_{av}, respectively. The curve indicates the gradient of fields at the middle point between electrodes, G_m

experimentally confirmed using the ferromagnetic metal hydrides $LaCo_5H_x$. The emf between the same kinds of electrodes was generated in gradient magnetic fields as a function of the distance between the electrodes. The field gradient of -74 T/m resulted in the emf of 1.06 mV at room temperature. The emf was proportional to the averaged field-gradient between the electrode positions. Its proportionality constant was related to the magnetic properties of the electrode material $LaCo_5H_x$, represented by ΔM_s and the Faraday constant. The emf was also depended on the distance between the electrodes because of the difference in the magnetic fields at the electrode positions. These results agree well with the thermodynamic consideration.

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