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ACTIVATION ENERGIES FOR HYDROGEN EVOLUTION REACTION AT LaM_5-TYPE ALLOY ELECTRODES

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The apparent activation energy for the cathodic evolution of hydrogen on LaM_5-type alloys (M: Cr, Fe, Co, Ni) was found to be closely related to the heat of formation of their ternary hydrides. The large heats of formation of $LaNi_5$ and $LaCo_5$ were presumed to be the chief cause of the synergistic effect in hydrogen evolution reaction at the alloy electrodes.

Since $LaNi_5$ and related alloys were proposed as hydrogen storage materials of great promise[1], their physical and chemical properties have extensively been studied[2]. In our previous paper[3], both $LaNi_5$ and $MmNi_5$ (Mm: mischmetal) were found to have a high electrocatalytic activity for hydrogen evolution, almost comparable to Pt and Pd electrodes. In this work, LaM_5-type alloy electrodes were prepared and their cathodic polarization characteristics in alkaline solutions, especially the activation energies for hydrogen evolution reaction, were studied in further detail with the intention of relating their electrochemical properties to chemical properties.

The test electrodes were prepared in the same manner as described previously[3], i.e. by melting the stoichiometric mixtures of La, Cr, Fe, Co, and Ni in an arc melting furnace under an argon atmosphere. Resulting alloy ingots were cut with a diamond blade, polished mechanically with fine emery papers and then mounted into glass holders with epoxy resin. The cathodic polarization characteristics were galvanostatically measured in 1 M KOH solutions at different temperatures ranging from 10 to 50 °C. The apparent activation energy for hydrogen evolution reaction at a given overvoltage, $Ea(\eta)$, was calculated from the Arrhenius plot or the plot

of log i vs. T^{-1}. The activation energy at equilibrium potential or zero overvoltage, Ea(0), was determined by extrapolating the Ea(η) vs. η plot to η = 0.

Figure 1 shows some plots of Ea(η) against $-\Delta H_f^\circ(AB_nH_{2m})$, the heat of formation of the ternary hydride, for LaM_5-type alloys. The values of $-\Delta H_f^\circ(AB_nH_{2m})$ were quoted from the reference[4]. As can be seen from Fig. 1, there exists a fairly good correlation between the electrochemical factor, Ea(η), and chemical factor, $-\Delta H_f^\circ(AB_nH_{2m})$.

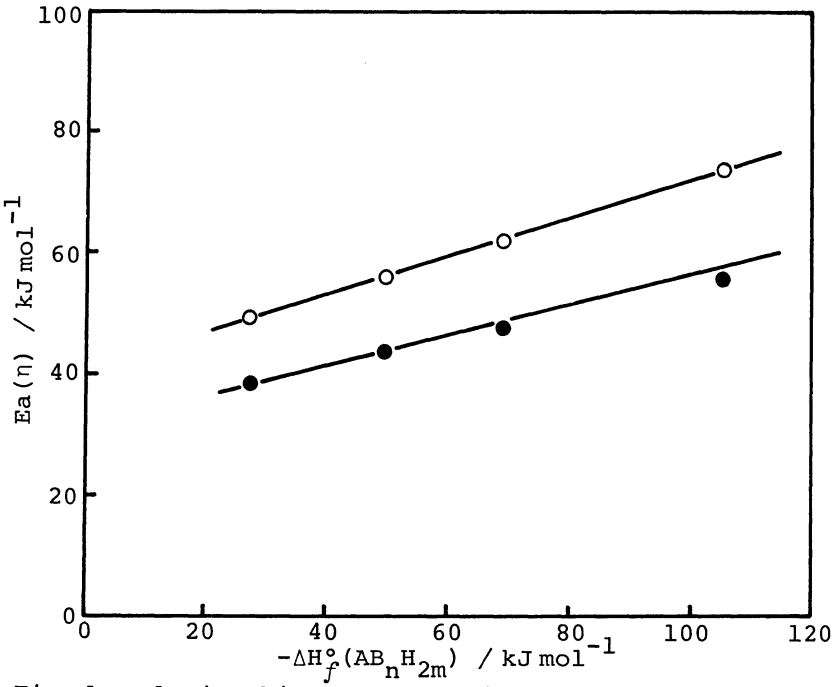

Fig. 1 Relationship between Ea(η) and $-\Delta H_f^\circ(AB_nH_{2m})$ for LaM_5-type alloys. ○:η = 0 V, ●:η = -0.3 V

H. H. van Mal, K. H. J. Buschow and A. R. Miedema[4] have reported that LaM_5-type alloys obey the "rule of reversed stability" which can be formulated as

$$\Delta H_f^\circ(AB_nH_{2m}) = \Delta H_f^\circ(AH_m) + \Delta H_f^\circ(B_nH_m) - \Delta H_f^\circ(AB_n) \quad (1)$$

where $\Delta H_f^\circ(AB_nH_{2m})$ represents the heat of formation (the standard enthalpy of formation) of the ternary hydride, $\Delta H_f^\circ(AH_m)$ and $\Delta H_f^\circ(B_nH_m)$ are standard enthalpies of formation of binary hydrides for individual metals, and $\Delta H_f^\circ(AB_n)$ is the standard enthalpy of formation of the alloy. According to the above formula, the standard enthalpy of formation of the ternary hydride or the heat of hydrogen absorption by the alloy should be reduced with increasing standard enthalpy of formation of the alloy. In the case of the absence of any synergistic or cancelling effect in hydride formation reaction, $\Delta H_f^\circ(AB_nH_{2m})$ should be equal to the sum of $\Delta H_f^\circ(AH_m)$ and $\Delta H_f^\circ(B_nH_m)$. Consequently, the presence of a synergistic effect in the hydrogen

evolution reaction may be related to the large heats of formation of the alloy, $\Delta H_f^\circ(AB_n)$. For LaM_5-type alloys, $\Delta H_f^\circ(AB_n)$ have been calculated by A. R. Miedema[5]; -40 kcal mol^{-1} for $LaNi_5$, -17 kcal mol^{-1} for $LaCo_5$, +4 kcal mol^{-1} for $LaFe_5$ and +12 kcal mol^{-1} for $LaCr_5$. Clearly, one sees a large decrease of $\Delta H_f^\circ(AB_nH_{2m})$ from the sum of $\Delta H_f^\circ(AH_m)$ and $\Delta H_f^\circ(B_nH_m)$ for $LaNi_5$ and $LaCo_5$ but an increase of $\Delta H_f^\circ(AB_nH_{2m})$ from the sum of $\Delta H_f^\circ(AH_m)$ and $\Delta H_f^\circ(B_nH_m)$ for both $LaFe_5$ and $LaCr_5$, since the former two alloys have large negative values of $\Delta H_f^\circ(AB_n)$ while the latter two alloys have positive values of $\Delta H_f^\circ(AB_n)$. The decrease and the increase of $\Delta H_f^\circ(AB_nH_{2m})$ should lead to the decrease and the increase of Ea(η),respectively, because $\Delta H_f^\circ(AB_nH_{2m})$ and Ea(η) are linearly related with each other as was aforementioned. Therefore, the alloys with the large negative values of $\Delta H_f^\circ(AB_n)$ must show a synergistic effect of the electrocatalytic activity for hydrogen evolution reaction, whereas the alloys with the positive values of $\Delta H_f^\circ(AB_n)$ must reveal a cancelling effect of the electrocatalytic activity for the reaction as far as LaM_5-type alloys are concerned. The measured hydrogen overvoltages at 1 mA cm^{-2} for LaM_5-type alloy electrodes as well as those for corresponding M electrodes are given in Table 1.

Table 1 Comparison of hydrogen overvoltages at 1 mA cm^{-2} between LaM_5-type alloy electrodes and M electrodes at 30 °C.

M component / η /V	Ni	Co	Fe	Cr
LaM_5	-0.10	-0.11	-0.17	-0.43
M	-0.23	-0.25	-0.21	-0.41

The hydrogen overvoltage of La electrode is very high, compared with Ni, Co, Fe and Cr electrodes and is around -0.43 V at 1 mA cm^{-2} as reported in the previous paper[3]. Evidently, the hydrogen overvoltage increases in the order of $LaNi_5 < LaCo_5 < LaFe_5 < LaCr_5$ and the magnitude of synergistic effect decreases almost in the same order. Moreover, especially in the case of $LaCr_5$, the electrocatalytic activity is less than that of Cr electrode. These facts strongly support the above views. It may therefore be concluded that the small hydrogen overvoltage as well as the small standard enthalpy of formation of ternary hydrides are attained with these alloys having the large negative standard enthalpy of formation. The standard enthalpy of formation of LaM_5-type alloys may play an important role in arising a synergistic effect for hydrogen evolution reaction.

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References

1) J. H. N. van Vucht, F. A. Kuijpers and H. C. A. M. Bruning, Philips Res. Rept., 25, 133(1970).

2) e.g. Y. Osumi, A. Kato, H. Suzuki and M. Nakane, J. Less-Common Metals, 66, 67 (1979).

3) T. Kitamura, C. Iwakura and H. Tamura, Chem. Lett., 1981, 965.

4) H. H. van Mal, K. H. J. Buschow and A. R. Miedema, J. less-Common Metals, 35, 65 (1974).

5) A. R. Miedema, J. Less-Common Metals, 32, 117(1973).

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