Electrocatalysis in Metal Hydride Electrode. II. Hydrogen Electrode Reaction and Related Properties of Group-IB Metal-Coated $LaNi_5$ Electrodes

Ken-ichi MACHIDA, Michio ENYO,* Gin-ya ADACHI,† Hiroki SAKAGUCHI,† and Jiro SHIOKAWA†

Research Institute for Catalysis, Hokkaido University, Sapporo 060

†Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

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Synopsis. Hydrogen storage type electrodes were fabricated from $LaNi_5$ powder after coating with group-IB metals by an electroless plating method, followed by press moulding. The hydrogen electrode reaction (HER) characteristics and mechanical stability during hydrogen charge/discharge cycles were then studied in 1.0 M (M= mol dm^{-3}) NaOH.

Storage type hydrogen/oxidant fuel cells using metal hydrides have been noted for their high energy storage capacities per unit weight.[1] There are, however, various problems to be solved before their realization, e.g. proper choice of systems with suitable pressure of the hydrogen charge/discharge cycles, prevention of pulverization of the hydrogen absorbing metals or alloys (metal hydrides) during use, etc. Ishikawa et al.[2] have reported recently that some hydrogen absorbing alloys can be "microcapsulated" with copper deposited by electroless plating so as to prevent the pulverization during repeated hydrogen charge/discharge cycles and that their hydrogen storage ability after the plating was maintained at the level comparable with those of the untreated alloys. We have reported elsewhere[3] that the electrocatalyst such as Pt or Ag, which possesses the greater rate of the Volmer over that of the Tafel step, namely the greater m_o ($=i_{oV}/i_{oT}$) value, is desirable as a surface modifier in the metal hydride electrode from the viewpoint of the energy efficiency in the charge/discharge cycles.

In this work, $LaNi_5$ powder was microcapsulated with a group-IB metal, and the electrochemical property in alkaline solution was investigated, together with their mechanical stability.

Experimental

Preparation of the Electrodes. $LaNi_5$ powder (particle size about 100 μm and the BET surface area 0.5 $m^2\,g^{-1}$) was subjected to electroless plating of Cu or Ag from conventional solutions,[4] or of Au by immersion of the powder in 2.5×10^{-3} M tetrachloroauric (III) acid solution. Amount of the deposition in weight (mol) % was 12.5 (48.6) for Cu, 12.5 (36.4) or 25 (57.2) for Ag, and 25 (42.3) for Au, respectively.

The microcapsulated $LaNi_5$ powder was pelletized into discs (13 mm diameter×1 mm thickness) with use of Ni nets (200 mesh) as electric leads under a static pressure of 400 Kg cm^{-2} and then heated at 770 K in vacuo (5×10^{-4} Pa) for several hours. The $LaNi_5$ samples bound with PTFE [poly(tetrafluoroethylene)] emulsion were prepared according to the method described in the literature.[5] In some occasions, a small amount of Pt was further deposited electrochemically. The nickel nets were spot-welded to Ta wires which were in turn sealed into Pyrex glass tubings.

Electrochemical Measurements. Galvanostatic polarization studies[3] were carried out in 1.0 M NaOH at 303 K. Real surface area of the test electrode was evaluated from the double layer capacitance data assuming a value of 18 μF cm^{-2} (true).

Results and Discussion

HER Characteristics. A series of microcapsulated $LaNi_5$ electrodes showed stable electrochemical behaviors in a similar manner as bare $LaNi_5$ electrodes. Thus, a typical plateau region was clearly observed on their short time (a few seconds) galvanostatic overpotential rise or decay transient curves respectively before the attainment of the steady-state polarization or of equilibrium potential. Through these observations, the electrodes are judged to possess a good hydrogen absorbability. Hence, as discussed previously,[6-8] we could estimate two overpotential components, η_1 and η_2', for the water discharge step and the hydrogen adatom recombination step, respectively.

The Tafel plots of η_1 on these microcapsulated electrodes showed a basic symmetry between the anodic and cathodic branches and the slope of the linear portion was reasonably close to 120 mV $decade^{-1}$. This indicates that η_1 represents the component overpotential for an one electron transfer reaction, namely the Volmer step. Its exchange current density (i_{oV}) estimated from the linear plots of η_1 vs. i, the applied current, near the reversible HER potentials was as follows: Cu/$LaNi_5$ 5.9, Ag/$LaNi_5$; 9.8, and Au/$LaNi_5$; 3.7×10^{-6} A cm^{-2} (true).

On the other hand, the "Tafel lines" of η_2' in the cathodic region gave a slope of ca. 30 mV $decade^{-1}$, except in the region of very high current density where the slope became lower, and indicated that η_2' should be attributed to the Tafel step. The linear η_2' vs. i plots in the low overpotential region resulted in the following i_{oT} values: Cu/$LaNi_5$; 0.7, Ag/$LaNi_5$; 0.8, and Au/$LaNi_5$; 0.6×10^{-6} A cm^{-2} (true), which were roughly one order of magnitude smaller than the corresponding i_{oV} values. The values of i_{oV}, i_{oT}, and m_o ($=i_{oV}/i_{oT}$) estimated of the microcapsulated $LaNi_5$ electrodes are schematically summarized in Fig. 1, together with those observed on some Ni-based alloys[6-8] and PTFE-bound or Pt-modified $LaNi_5$ electrodes.

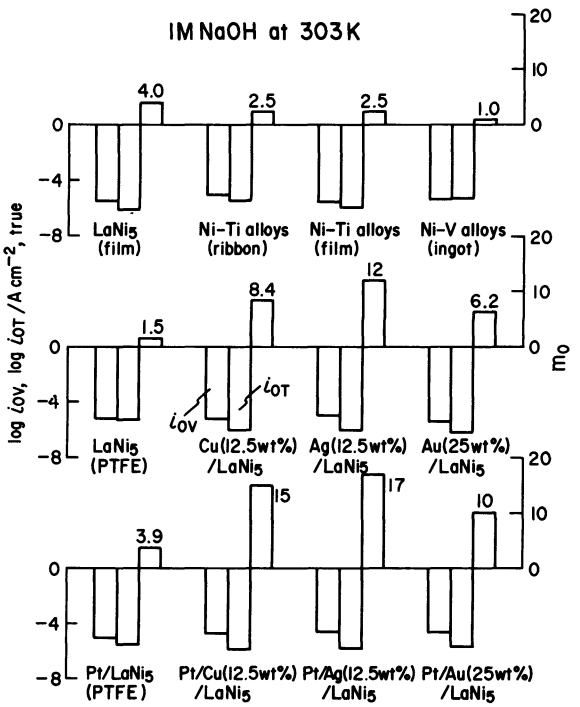

Fig. 1. Schematic diagram of the kinetic data obtained on Ni-based alloy ribbon or film electrodes, $LaNi_5$ electrodes coated with a series of group-IB metals, those further with Pt, and $LaNi_5$ electrodes bound with PTFE. 1.0 M NaOH, 303 K.

Table 1. Activation Energies for the Volmer and Tafel Steps and the Overall Reaction on Ni-Based Electrodes

Electrode	ΔE/kcal mol^{-1}		
	i_{ov}	i_{oT}	i_o
$Cu/LaNi_5$	9.0	4.5	4.6
$Ag/LaNi_5$	8.9	4.4	4.8
$Au/LaNi_5$	8.8	5.1	5.9

It was found that the microcapsulated $LaNi_5$ electrodes possessed much larger m_o values (6—12) than those (1—4) of the bare Ni-based alloys. Furthermore, they were considerably larger than those[3] observed on the group-IB metal electrocatalysts themselves. The larger m_o values were mainly caused by increased rates of the Volmer step and might indicate the existence of a synergistic effect between $LaNi_5$ and group-IB metals. A further increase up to m_o=17 was observed after a deposition of Pt on their surface. The PTFE-bound $LaNi_5$ electrode was mechanically very stable but the m_o value was relatively small (m_o=1.5): No polarization behaviors for HER could be studied with acceptable reliability, however, as hydrogen bubbles tightly adhered to the PTFE surface.

Mechanical Stability. The microcapsulated $LaNi_5$ electrodes prepared in this work were found to be stable even under polarizations up to η=−300 mV for a few ten hours. This was in agreement with the results reported on the hydrogen absorption/desorption cycles in gas phase[2] or in electrochemical system[9] of Cu-coated $LaNi_5$ specimens prepared in a similar manner as in this work. The electrodes were, however, damaged during polarizations over much longer durations even at potentials less than −300 mV.

Temperature Dependence. The activation heats evaluated from the Arrhenius plots of i_{ov}, i_{oT}, and i_o observed on the microcapsulated $LaNi_5$ electrodes are summarized in Table 1. The values were around 9 and 5 kcal† mol^{-1} for the Volmer and the Tafel step, respectively, and were in rough agreement with those observed on other Ni-based alloy electrodes.[6-8] Since the difference between the activation heats of two elementary reaction steps is appreciable (about 4 kcal mol^{-1}), m_o should significantly be increased at higher temperatures. This means that the energy efficiency may be improved if the hydrogen storage cells are operated at higher temperatures, but probably with the cost of decrease of the storage capacity.

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† 1 cal=4.18 J.