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A study of the hydrogen absorption reaction into α- and β-LaNi$_5$H$_x$ porous electrodes by using electrochemical impedance spectroscopy

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Abstract

The hydrogen absorption reaction into α- and β-phase LaNi$_5$H$_x$ porous electrodes in 6 M KOH solution has been investigated as a function of applied potential by analysing the a.c. impedance spectra complemented with cyclic polarization curves. The onset of the hydrogen evolution reaction (HER) can be accounted for in terms of the transition of the Warburg impedance to a capacitive loop at -0.980 V for the α-phase porous electrode and at -0.920 V for the β-phase porous electrode. The charge-transfer resistance, R_{ct}, values from the β-LaNi$_5$H$_x$ electrode are much smaller than those from the α-LaNi$_5$H$_x$ electrode over the whole applied potential range. The α- to β-phase transition at -0.980 V and the β- to α-phase transition at -0.920 V are discussed in terms of the applied potential dependence of R_{ct} for the hydrogen absorption reaction.

Keywords: Porous electrode; Hydrogen absorption reaction; Hydrogen evolution reaction; Impedance spectroscopy; Cyclic polarization; Lanthanum

1. Introduction

The absorption and release of large amounts of gaseous and electrolytic hydrogen by intermetallic compounds such as SmCo$_5$, LaNi$_5$, TiFe and their alloys have been reported [1,2]. Recently, nickel–metal hydride (Ni/MH) secondary batteries using these materials as an anode have been developed and commercialized because of their high energy density, high rate capability, and environmental acceptability [3,4]. In the Ni/MH secondary battery system, the hydrogen absorption reaction (HAR) into the MH electrode is usually accompanied by the hydrogen evolution reaction (HER) during hydrogen charging into hydride-forming electrodes such as LaNi$_5$ and TiFe [5,6].

The HAR into metal electrodes (such as Pt and Pd) has been investigated widely [7–9] by using a.c. impedance spectroscopy. The latter is an effective technique for analysing the mechanism of interfacial electrochemical reactions. The HAR into hydride-forming electrodes modifies the electronic and electrocatalytic properties of the electrode surface [10]. These properties are important from the point of view of hydrogen storage in Ni/MH secondary batteries. For example, the hydride formation on the active Pd surface influences the HAR into the Pd electrode [11,12].

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The present work is concerned with the HAR into the α- and β-phase LaNi$_5$H$_x$ porous electrodes as related to hydride formation on the electrode surface. For this purpose, a.c. impedance measurements supplemented by cyclic polarization experiments have been carried out in 6 M KOH solution. The charge-transfer resistance is determined from the measured impedance spectra by using a graphical method. The α- to β-phase transition is discussed in terms of the applied potential dependence of the charge-transfer resistance R_{ct} for the HAR.

2. Experimental

LaNi$_5$ alloy (Aldrich Chem. Co., purity 99%) was first pulverized by grinding into fine powder with an average particle size of less than about 45 μm (330 mesh). The powder was mixed with a binder of 10 wt.% polytetrafluoroethylene (PTFE) emulsion and then pasted on porous nickel plaque. The specimen was dried in vacuum at 100 °C. To activate the fresh LaNi$_5$ electrode specimen, potentiostatic hydrogen charging at -1.200 V for 7200 s and extraction at -0.600 V for 1800 s were repeated several times. Note, all potentials are reported with respect to a Hg/HgO reference electrode. After activation, the α-phase LaNi$_5$H$_x$ ($x=$ small value) and β-phase LaNi$_5$H$_x$ ($x=$ large value) electrodes were prepared by potentiostatic hydrogen extraction at

−0.600 V for 1800 s and charging at −1.200 V for 3000 s, respectively. Upon hydrogen charging, the α-phase electrode was fully transformed into the β-phase electrode and upon hydrogen extraction, the reverse transformation took place. The activated α- or β-phase porous electrode specimen was used as a working electrode. A platinum foil and a mercury oxide electrode (6 M KOH/HgO/Hg) were used as a counter electrode and a reference electrode, respectively. The electrolyte used was an aqueous 6 M KOH solution.

Cyclic polarization measurements were performed on the α-phase and β-phase porous electrodes in a decreasing and an increasing potential direction, respectively, over an applied range −0.600 to −1.200 V at a scan rate of 0.1 mV s^{-1}. This was achieved with a potentiostat (EG&G PAR, model 273) interfaced with an IBM compatible computer.

The a.c. impedance was measured on the α- and β-phase porous electrodes by using a frequency response analyser (Zahner, IM5d). A single sinusoidal potential wave of 10 mV peak-to-peak was superimposed on the constant potential of −0.800 to −1.000 V over the frequency range of 10^{-3} to 10^5 Hz. The frequency was scanned from a high to a low value. The a.c. impedance measurements on the α- and β-phase porous electrodes were made in the direction of decreasing and increasing potentials, respectively.

All electrochemical experiments were performed at room temperature.

3. Results and discussion

Fig. 1 shows the cyclic polarization curve for the HAR into the α-phase LaNi$_5$H$_x$ electrode and hydrogen desorption from the β-phase LaNi$_5$H$_x$ electrode in a 6 M KOH solution at a scan rate of 0.1 mV s^{-1} in the applied potential range −1.200 to −0.600 V. As the potential is scanned in the positive direction, and then reversed in the negative direction, two
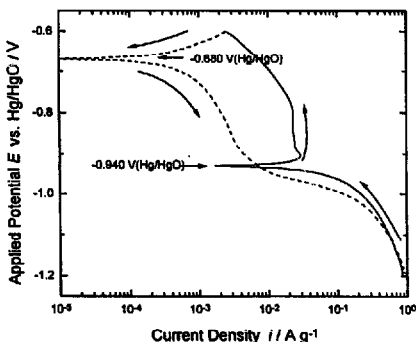

Fig. 1. Typical cyclic polarization curve for hydrogen absorption reaction into LaNi$_5$H$_x$ porous electrode in 6 M KOH solution at a scan rate of 0.1 mV s^{-1}. Potential scan in (——) positive direction and in (– – –) negative direction.

different open-circuit potentials (OCP) for the LaNi$_5$H$_x$ electrode appear at −0.940 and −0.680 V, respectively. This is due to the presence of the β-phase and the formation of an oxide film on the surface of the α-phase electrode.

Since the HAR into, and hydrogen desorption from, the MH electrode are reversible reactions, the OCP and the equilibrium potential of MH electrode, E(H), share almost the same value. The E(H) of the MH electrode is closely related to an equilibrium hydrogen pressure according to the Nernst equation, as previously reported by Balej [13]. The E(H) value of the MH electrode is given by Sakai et al. [4] and Balej [13] as

$$E(H) - E(Hg/HgO) = -0.9324 - 0.0291 \log P_{H_2} \quad (1)$$

where E(H)–E(Hg/HgO) is the value of the equilibrium potential against the Hg/HgO reference electrode at 20 °C and 1 atm of atmosphere in 6 M KOH, and P_{H_2} is the hydrogen partial pressure that is in equilibrium with solid solutions (hydrogen-alloy or hydrogen-alloy hydride) in a solid-gas phase system associated with the hydride electrode. At 20 °C, the equilibrium hydrogen pressure of the LaNi$_5$ is 1.86 and 1.36 atm upon hydrogen absorption and desorption, respectively [4]. Below a potential of about −0.940 V, which corresponds to the equilibrium hydrogen pressure, the transformation of α- into β-phase should occur in a 6 M KOH solution.

Provided that the hydrogen partial pressure is higher than the standard hydrogen pressure, 1 atm, (i.e. the value E(H)–E(Hg/HgO) lower than −0.932 V), the HER from the electrode dominates over the HAR into the electrode. The cathodic current density below about −0.940 V, on scanning in an increasing potential direction, was larger than that on scanning in a decreasing potential direction. This suggests that the HER on the β-phase electrode is stronger than that on the α-phase electrode. This is due probably to the enhanced electrocatalytic property of the β-phase LaNi$_5$H$_x$ for the HER, as indicated for hydride-forming Ni and Ni-glassy metal systems [14].

The Nyquist plots of the impedance spectra obtained from the α-phase LaNi$_5$H$_x$ electrode in 6 M KOH solution in the applied potential range −0.940 to −1.000 V are shown in Fig. 2. The a.c. impedance measurements were made in the direction of decreasing potential. The total impedance drops abruptly from 20 Ω at −0.940 V to 3.40 Ω at −0.980 V with decreasing applied potential. At the applied potentials above −0.980 V, the impedance spectra consist of one arc that represents the charge-transfer reaction and a Warburg impedance due to the finite-length diffusion process of hydrogen. By contrast, the impedance spectra are composed of three arcs below −0.980 V. The high-frequency arc corresponds to the contact resistance and the capacitance between alloy particles, the middle-frequency arc to the relaxation of the charge-transfer resistance and the double-layer capacitance, and the low-frequency arc to the relaxation of the hydrogen evolution resistance and the adsorption capacitance. The high-frequency arc, as well as the middle-frequency arc, is
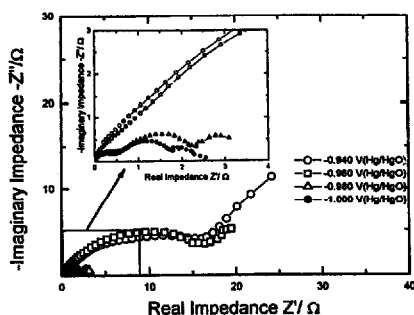
Fig. 2. Impedance spectra in Nyquist presentation for hydrogen absorption reaction into α-LaNi$_5$H$_x$ electrode in 6 M KOH solution at various applied potentials: (O) −0.940 V; (□) −0.960 V; (△) −0.980 V, and (●) −1.000 V.

severely depressed due to the porous nature of the LaNi$_5$H$_x$ electrodes.

The drastic change of the total impedance value and the appearance of the impedance spectra at −0.980 V indicate that, first, the formation of β-phase LaNi$_5$H$_x$ occurs just beneath the α-phase LaNi$_5$H$_x$ electrode surface and, second, the HER is just initiated below −0.980 V.

The Nyquist plots of impedance spectra obtained from the β-phase LaNi$_5$H$_x$ electrode in 6 M KOH solution in the applied potential range −1.000 to −0.900 V are given in Fig. 3. The a.c. impedance measurements were conducted in the direction of increasing potential. Below −0.900 V, the impedance spectra consist of three arcs. These three arcs represent the same relaxation processes that occur below −0.980 V from the α-phase LaNi$_5$H$_x$ electrode, as indicated in Fig. 2.

The Nyquist plots of impedance spectra obtained from the β-phase LaNi$_5$H$_x$ electrode in 6 M KOH solution at different
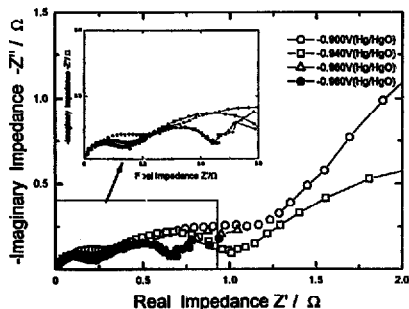
OCP of −0.916, −0.921, −0.928 and −0.932 V are presented in Fig. 4. In order to determine the electrocatalytic effect of the β-phase electrode on the HAR, the electrode used was transformed fully into the β-phase by application of −1.200 V for 3000 s and then maintained at open circuit for 500 to 1000 s. The OCP value increased slightly with holding time at open circuit due to the increased fraction of the α- to β-phase on the electrode surface. Thus, the β-phase is actually in equilibrium with the α-phase formed at the OCP. The a.c. impedance spectra in the low-frequency range change from the low-frequency arc below −0.928 V to the Warburg impedance above −0.921 V. The low-frequency arc represents the HER, whereas the Warburg impedance corresponds to the HAR. It should be noted that the size of the low-frequency arc decreases drastically with only a slight fall in OCP.

From the measured impedance spectra (Figs. 2–4), combined with the cyclic polarization curve (Fig. 1) it can be summarized as follows. The Warburg impedance to capacitive loop transition occurs at −0.980 V for the α-phase LaNi$_5$H$_x$ electrode and −0.920 V for the β-phase LaNi$_5$H$_x$ electrode. This indicates that the HER begins markedly at −0.980 V from the α-phase electrode and at −0.920 V from the β-phase electrode as hydrogen is charged into the electrode. Thus, the hydrogen evolution overpotential on the β-phase electrode is lowered by 0.06 V compared with that on the α-phase electrode.

In order to determine the charge-transfer resistance, R_{ct}, which is one of the crucial parameters for assessing the rate of the HER from the electrode surface, the electrical equivalent circuit (including the HER) previously suggested by Lim and Pyun [8] was adopted. The measured impedance data were so scattered and depressed due to the complexity of the porous electrode geometry that the complex, non-linear least-squares of data-fitting method [15] did not allow circuit parameters such as the hydrogen evolution resistance and the Warburg impedance to be determined accurately. Nevertheless, the R_{ct} values were determined from the middle-fre-
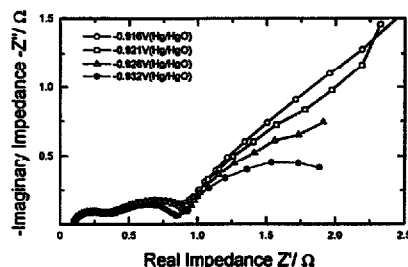

Fig. 3. Impedance spectra in Nyquist presentation for hydrogen absorption reaction into β-LaNi$_5$H$_x$ electrode in 6 M KOH solution at various applied potentials of: (O) −0.900 V; (□) −0.940 V; (△) −0.960 V, and (●) −0.980 V.

Fig. 4. Impedance spectra in Nyquist presentation obtained from β-LaNi$_5$H$_x$ electrode in 6 M KOH solution at different open-circuit potentials of: (O) −0.916 V; (□) −0.921 V; (△) −0.928 V, and (●) −0.932 V, after hydrogen charging at −1.200 V for 3000 s.
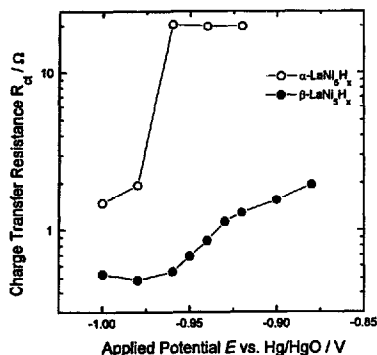
Fig. 5. Applied potential dependence of charge-transfer resistance for hydrogen absorption reaction into (○) α-LaNi₅Hₓ electrode and (●) β-LaNi₅Hₓ electrode in 6 M KOH solution.

quency arc in the Nyquist plots by a graphical method [15] providing reliable data of the R_{ct}.

The dependence of R_{ct} on applied potential for the HAR into the α- and β-phase LaNi₅Hₓ electrodes in 6 M KOH solution is shown in Fig. 5. As hydrogen is absorbed into the α-phase electrode, i.e. decrease in applied potential, the R_{ct} value remains constant up to -0.960 V and then decreases abruptly at -0.980 V, followed by a gradual decrease up to -1.000 V. The R_{ct} value from the β-phase electrode decreases slightly with decreasing applied potential in the range -0.880 to -1.000 V. The R_{ct} value from the β-phase LaNi₅Hₓ electrode is much lower than that from the α-phase LaNi₅Hₓ electrode, irrespective of applied potential.

From the appearance of two different OCPs (Fig. 1) and the drastic fall in the R_{ct} for the HAR into the α-phase electrode (Fig. 5), it is indicated that the α-phase is transformed into the β-phase just beneath the α-phase electrode surface at -0.980 V. The lowered hydrogen evolution overpotential (Figs. 2 to 4) and R_{ct} value (Fig. 5) from the β-phase LaNi₅Hₓ electrode as compared with the α-phase LaNi₅Hₓ electrode, suggest that the HER proceeds more readily from the β-phase electrode than from the α-phase counterpart. This may be due to the greater electrocatalytic effect of the β-phase on the HER, as usually found for hydride-forming electrodes, for example, the Ni hydride electrode [14].

4. Conclusions

A study has been made of the hydrogen absorption reaction (HAR) into and the hydrogen evolution reaction (HER) at α- and β-phase LaNi₅Hₓ porous electrodes in 6 M KOH solution by analysing the a.c. impedance spectra together with cyclic polarization curves as a function of applied potential. The following conclusions are reached.

1. The Warburg impedance to capacitive loop transition occurs at -0.980 V for the α-phase electrode and at -0.920 V for the β-phase electrode. The charge-transfer resistance, R_{ct}, value and hydrogen evolution overpotential on the β-phase electrode are lower than those on the α-phase electrode. It is concluded that the HER begins at -0.980 V for the α-phase electrode and at -0.920 V for the β-phase electrode, below which the HER proceeds more vigorously at the β-phase electrode than at the α-phase electrode.

2. As the potential is scanned in the positive direction and then reversed in the negative direction, two different open-circuit potentials for the LaNi₅Hₓ electrode appeared at -0.940 and -0.680 V. The R_{ct} for the HAR into the α-phase electrode displays a drastic fall at -0.980 V. This suggests that the α-phase electrode undergoes a strong transition to the β-phase at -0.980 V, below which the β-phase is stable.

3. In contrast to the α-phase electrode, the R_{ct} for the HAR into the β-phase electrode exhibits a relatively small positive dependence on the applied potential. This means that the β-phase electrode undergoes decomposition of the β- to α-phase sluggishly at -0.920 V, above which the α-phase is stable.

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