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Electrochemical hydrogen discharge characteristics of Pd and Pd–Ni–Rh alloy hydride electrodes catalysed by Pd/Pt-black coatings

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The electrochemical hydrogen discharge characteristics of pure Pd and Pd–Ni–Rh alloy hydride electrodes, activated by a superimposed electrodeposited film of Pd/Pt-black, were investigated as a negative electrode for nickel oxide-metal hydride battery. The Pd/Pt-black superposed catalysts brought about high discharge rate characteristics of the electrodes. The best discharge characteristics were obtained for Pd–7.5 at % Rh and/or Pd–2.5 at % Ni–7.5 at % Rh alloy hydrides, the electrode surfaces of which were activated first with about 1–2 mg cm^{-2} of Pd-black and then almost the same amount of Pt-black.

1. Introduction

Recently, an attempt has been made to examine the electrochemical hydrogen charge–discharge characteristics of pure Pd, Pd–Rh, Pd–Ni and Pd–Li alloy hydride electrodes activated by electrodeposition of palladium-black as the negative electrode for rechargeable nickel oxide–metal hydride batteries [1]. Since Pd and Pd alloys are in general resistant to corrosion in alkaline electrolytes and have a high degradation-resistance for the charge-discharge process, they can be expected to have a higher degree of utilization as the negative electrode. However, in commercially produced battery systems, Pd and Pd alloy hydride electrodes are unlikely to be employed owing to their excessive cost, when much cheaper hydrogen storage alloys such as AB_5-type mischmetal based compounds, i.e., $MmNi_5$, and AB_2-type Laves phase alloys, e.g. $Zr(V, Ni, Mn)_2$ and $Ti(Mn, Cr)_2$ are now available and being commercially used [2–4].

The previous experimental results [1] of Pd and Pd alloy hydride electrodes activated with Pd-black alone have indicated that from the first cycle, each alloy foil electrode exhibited a high discharge capacity, C, e.g., for pure Pd the capacity was about $C = 195\,\mathrm{mAh\,g^{-1}}$ at 303 K, corresponding to an extent of H sorption of $PdH_{0.77}$ at a discharge current density of about $65\,\mathrm{mA\,g^{-1}}$. The C value of Pd–Rh alloy hydrides increased with increasing Rh content and exhibited a maximum at around 7.5 at % Rh of about $215\,\mathrm{mAh\,g^{-1}}$, corresponding to $H/M \simeq 0.85$, while the capacity of Pd–Ni alloy hydrides tended to decrease gradually with Ni content in the composition range 5.0 to 20.0 at % Ni, and that of Pd–3.1 at % Li alloy was a little higher than that of pure Pd.

Thus, the dependence of the discharge capacity on the composition of the alloys was approximately related to the extent of the $(\alpha + \beta)$ hydrogen miscibility gaps of the alloys studied at room temperature by measurements of *p-c* isotherms and of the lattice parameters at the phase boundaries [5–11]. Also, the discharge capacity seemed to be determined by a counterbalance between the high diffusivity of hydrogen in the bulk [12–16] and the stability of the hydrides, i.e. the $(\alpha + \beta)$ plateau pressure [5–8, 11].

However, when each of the electrodes was polarized cathodically or anodically a very rapid increase of the electrode potential, η_1 and η_1' [17–23], associated with charge and/or discharge of the double-layer capacitance through the Volmer reaction: $H_{ads} + OH^- \rightleftharpoons H_2O + e^-$, was observed instantly. However, in the case of Pd–Rh alloys, the overpotential was relatively small for all the compositions. Thereafter, the overpotential transients exhibited a slower growth of the electrode potentials, η_2 and η_2' [17–23]; this corresponds to the charge and/or discharge of the pseudocapacitance of the adsorbed hydrogen on the surface, and the process is concurrent with diffusion and reaction of absorbed hydrogen from the bulk to the surface, and *vice versa*. Such high overpotentials associated with charge transfer in the Volmer reaction during the charge–discharge processes should bring about a low efficiency of the rechargeable batteries.

To improve the electrocatalytic activity of the hydride electrodes, it is desirable to employ a platinum-black film, which has a higher exchange current density for the hydrogen evolution reaction, rather than palladium-black (for example [24]). Shirogami [25] has reported, in studies on a palladium–hydrogen permeable electrode in alkaline solution, that an electrode coated with Pd-black alone give poor reactivity in respect to polarization characteristics, while electrodes coated by Pt-black catalyst were very active. The same author [25] reported that the degree of reactivity depended on the

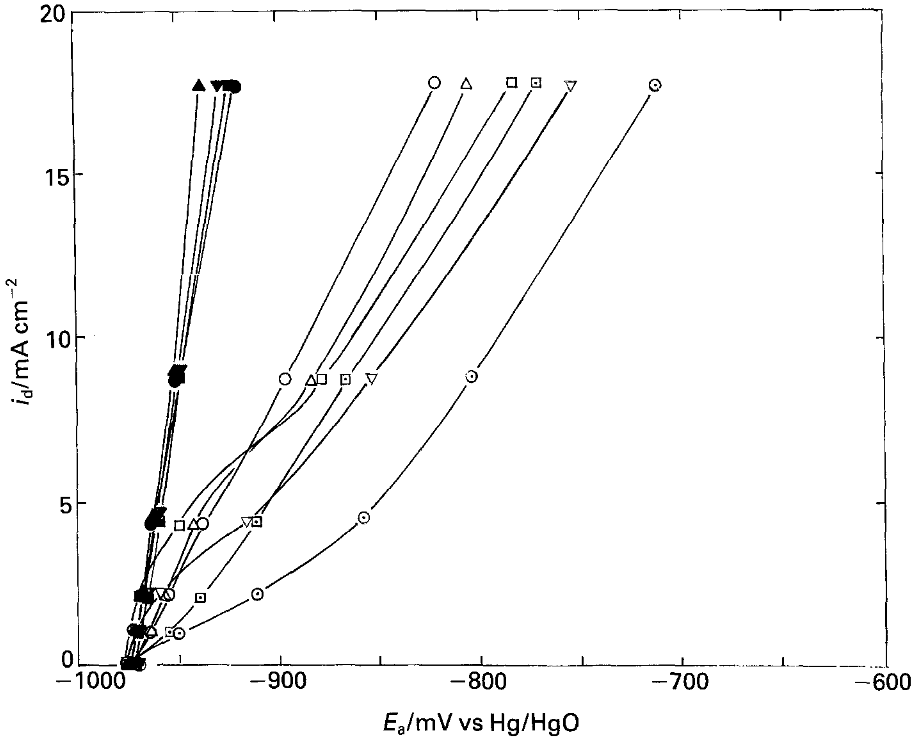

Fig. 1. Discharge current density against potential behaviours for Pd and Pd–7.5 at % Rh alloy hydride electrodes activated by electrodeposition of Pt-black alone, and Pd/Pt-black superposed catalysts, in addition to those for the hydride electrodes catalysed by Pd-black alone [1] at 5–7th cycles.

Legend	*Pd-black**		*Pt-black**
○ Pd	–		0.7
△ Pd	–		2.1
□ Pd	–		4.1
▽ Pd	–		5.3
● Pd	1.1	+	1.3
▲ Pd	1.3	+	2.5
■ 7.5 Rh	1.4	+	2.3
▼ 7.5 Rh	2.1	+	1.4
⊙ Pd [1]	1.3	+	–
⊡ 7.5 Rh [1]	1.6	+	–

* Measurements in mg cm^{-2}.

amount of platinum, and the best polarization characteristics were found with an electrode, the surface of which was coated with 10 mg cm^{-2} of Pd-black and then with 1–2 mg cm^{-2} of Pt-black. Bucur and Morariu [26] have reported, in a study on the anodic polarization resistance and surface properties of palladium–hydrogen electrodes in sulphuric acid solution, that the optimum quantity of Pt-black was 0.25 mg cm^{-2} which is much less than the best Pd quantity, found to be 3 mg cm^{-2}, because the polarization resistance increases owing to the decrease of the exit effective area of hydrogen atoms from the Pd electrode by the superposition of a hydrogen impermeable layer.

The present study is primarily to make comparisons with the previous results [1] by examining the effects of Pt-black and Pd/Pt-black catalysts on the anodic polarization characteristics and the discharge capacity of pure Pd and Pd–7.5 at % Rh alloy hydrides, where the latter electrode has exhibited a maximum discharge capacity in a series of Pd alloy electrodes examined previously [1], and then, secondly to examine the discharge properties of Pd–Ni–Rh ternary alloy electrodes activated by Pd/Pt-black superposed catalysts.

2. Experimental details

The negative electrodes used were as follows: Pd–2.5 at % Ni and Pd–2.5 at % Ni alloys containing 2.5, 5.0 and 7.5 at % Rh, respectively, in addition to pure Pd and Pd–7.5 at % Rh alloy. They were prepared as previously described [1]. The sample electrodes were in the form of foils of about 60 μm thickness, 1.5 × 1.5 cm^2 in area and 130 to 170 mg in weight.

Prior to the experiments, all the samples were annealed *in vacuo* by slow cooling from about 1123 K for 2 h to room temperature; the surfaces were then activated by electrodeposition of a given amount of Pt-black and/or Pd/Pt-black superposed catalysts. In the latter case, Pd-black was firstly electroplated and then a further coating of Pt-black was deposited.

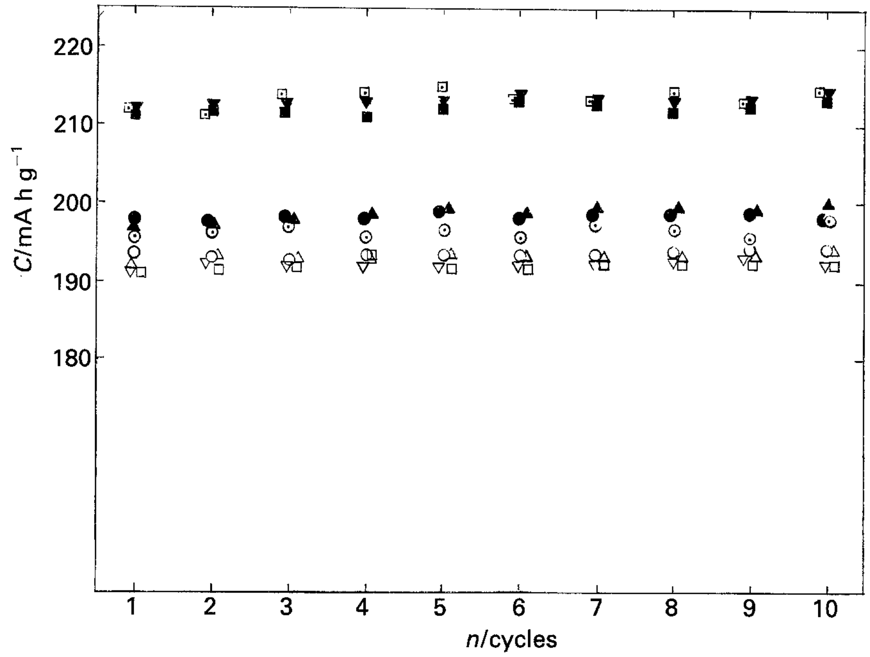

Fig. 2. Discharge capacity against cycle number, n, curves for Pd and Pd–7.5 at % Rh alloy hydride electrodes activated by electrodeposition of Pt-black alone, and Pd/Pt-black superposed catalysts, together with the previously determined capacity against n curves for the electrodes catalysed by Pd-black alone [1]. The discharge current is 10 mA ≃ 67 mA g^{-1}. Legend as in Fig. 1.

The bath composition for plating of Pt-black was a 3 wt % $H_2PtCl_6.6H_2O + 0.02$ wt % $Pb(CH_3COO)_2$ solution, and the cathodic current density was 10 mA cm^{-2} at room temperature. The Pd-black plating was made from an electrolyte of 2 wt % $PdCl_2$ dissolved in 0.1 M HCl and containing 0.01 wt % $Pb(CH_3COO)_2$, using a cathodic current density of 150 mA cm^{-2}. The anode was a platinum foil.

The charge and discharge experiments were carried out at 303 ± 0.3 K with an open H-type cell using 6 M KOH as the electrolyte, with Hg/HgO reference electrodes and NiOOH–Ni(OH)$_2$ counter electrodes 4 × 9 cm^{-2} in area. The sample electrodes were charged at a current of 20 mA up to 140% of the theoretical capacities of $Pd_{1-x}X_xH_{0.7}$ and, after resting for 10 min, were discharged at the specified currents from 5 to 80 mA down to a cut-off voltage of 0.8 V with a battery charge-discharge cycle testing system. After resting for 10 min, the test experiment involved subsequent cycling of each electrode through more than ten charge–discharge cycles.

3. Results and discussion

3.1. *Effect of Pt-black and Pd/Pt-black catalysts on hydrogen discharge behaviour of pure Pd and Pd–7.5 at % Rh alloy hydrides*

Figure 1 shows the anodic polarization behaviour for Pd and Pd–7.5 at % Rh alloy hydride electrodes activated by electrodeposition of Pt-black alone in comparison with Pd/Pt-black catalysts, together with the

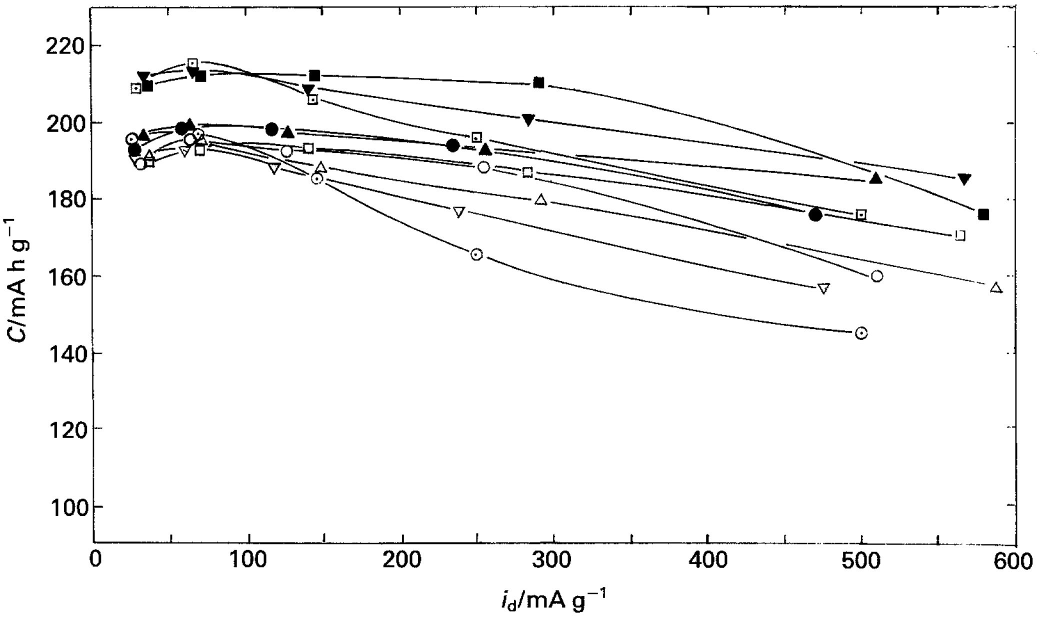

Fig. 3. Relationship between discharge capacity, C, and discharge current density, i_d, for Pd and Pd–7.5 at % Rh alloy hydride electrodes activated by electrodeposition of Pt-black alone, and Pd/Pt-black superposed catalysts, together with the previously determined C against i_d curves for the electrodes catalysed by Pd-black alone [1] at 5–7th cycles. Legend as in Fig. 1.

previously determined polarization behaviour for the electrodes catalyzed by Pd-black alone [1]. The electrode potentials correspond to the η_1' values which were observed instantly on discharging at various discharge current densities, where the electrodes had been charged up to 140% of their theoretical capacities. The η_1' values are averages for the 5–7th charge–discharge cycles.

It can be seen that the activation overpotential due to the charge transfer for the Pd electrode with about 1–2 mg cm^{-2} of Pt-black decreases about 100 mV at a discharge current density of 15 mA cm^{-2} (about 450 mA g^{-1}), compared to that of electrodes coated with about 1 mg cm^{-2} of Pd-black examined previously [1]. However, as has been observed [25, 26], excess amounts of Pt-black tend rather to increase the overpotential. On the other hand, the Pd/Pt-black superposed catalysts consisting of about 1–2 mg cm^{-2} of Pd-black and about 1–2.5 mg cm^{-2} of Pt-black cause a remarkable reduction of the overpotential at both Pd and Pd–7.5 at% Rh hydride electrodes. For instance, at $i_d = 15$ mA cm^{-2}, the overpotential decreases by about 230 mV compared to that of electrodes with a Pd-black coating alone [1]. Thus, it was confirmed that the electrocatalytic activity of Pd and Pd–7.5 at% Rh hydride electrodes is improved by a use of Pt-black in combination with the Pd-black catalysts. However, since the difference in the real areas per apparent cm^2 between the Pd/Pt and Pd-black coatings is unknown, it is difficult to evaluate how this real area factor may account for the difference of the polarization behaviour; the effects may not be truly 'electrocatalytic' in character but rather connected with decrease of real specific current densities.

Figure 2 shows the discharge capacity against cycle number curves, where the discharge current is 10 mA (2.2 mA cm$^{-2} \simeq 67$ mA g^{-1}). From the first cycle, each electrode exhibits a high capacity, and then the capacity remains almost constant over the charge–discharge cycles. The capacity of Pd hydrides coated with Pt-black alone are a little lower than that with Pd-black alone [1]; however, the C values for Pd hydrides coated with Pd/Pt-black are larger than that for Pd-black alone, although in the case of Pd–7.5 at% Rh hydrides, the Pd/Pt-black does not substantially improve the discharge capacity. Thus, it can be seen that the Pd-black, in respect to electrocatalytic activity, acts simultaneously as a hydrogen absorber, at least for Pd hydride electrodes.

Figure 3 shows the relationship between the discharge capacity and discharge current density, i_d, for Pd and Pd–7.5 at % Rh hydride electrodes coated with Pt-black alone and also with Pd/Pt-black at the 5–7th cycles. The discharge current density, i_d is defined in terms of mA g^{-1} according to convention in the field of nickel oxide–metal hydride batteries. The rate of decrease in the capacity with the i_d value for both electrodes coated with Pt-black and Pd/Pt-black catalysts is smaller than that for the electrodes coated with Pd-black alone [1], and especially it is found that the use of Pt-black in combination with Pd-black catalyst is excellent for attainment of high discharge rates; this is due to an increase of the overall exchange current anodized in the presence of Pt-black catalyst.

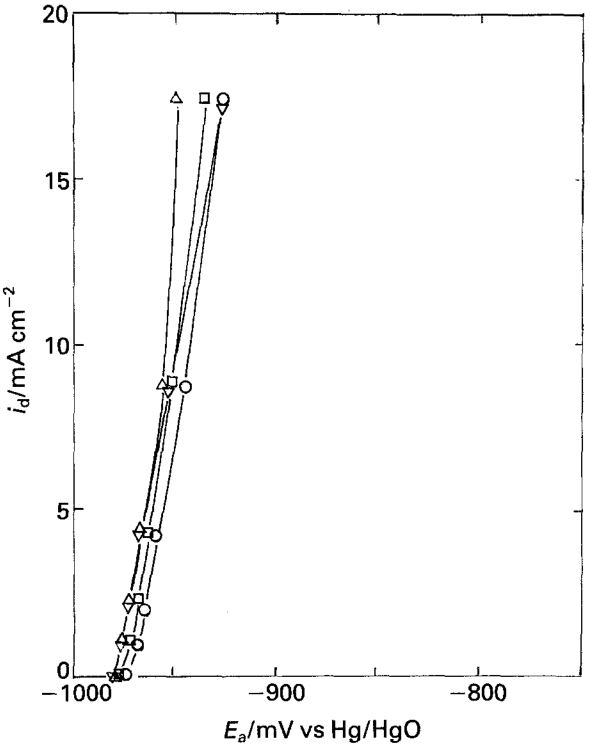

Fig. 4. Discharge current density against potential behaviours for Pd–Ni–Rh alloy hydrides catalysed by Pd/Pt-black at 5–7th cycles.

Legend	*Pd-black**		*Pt-black**
○ 2.5 Ni	1.1	+	2.2
△ 2.5 Ni–2.5 Rh	1.0	+	2.5
□ 2.5 Ni–5.0 Rh	1.3	+	2.3
▽ 2.5 Ni–7.5 Rh	1.4	+	1.2

* Measurements in mg cm^{-2}.

3.2. *Hydrogen discharge properties of Pd–Ni–Rh alloy hydrides coated with the Pd/Pt-black catalysts*

The anodic polarization characteristics for Pd–2.5 at% Ni and Pd–2.5 at% Ni alloys containing 2.5, 5.0 and 7.5 at% Rh, respectively, are shown in Fig. 4, where the overpotentials were measured in the same way as described above. It can also be seen that the activation overpotentials for each electrode are very low, even at high discharge current densities.

The relationship between the discharge capacity and cycle number at a discharge current of 10 mA, is shown in Fig. 5. The discharge capacity of a 2.5 at % Ni binary alloy hydride is lower than that of the ternary alloy hydrides containing Rh, but the capacity is higher than that of the previously characterized Pd–5.0 at % Ni alloy coated with Pd-black alone [1]. The discharge capacities of the Pd–Ni–Rh ternary

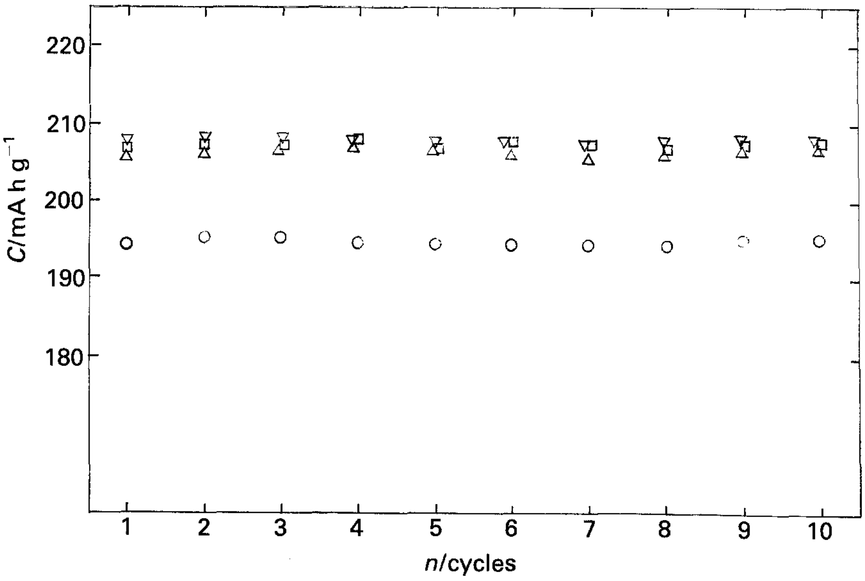

Fig. 5. Discharge capacity against cycle number curves for Pd–Ni–Rh alloy hydrides catalysed by Pd/Pt-black. The discharge current is 10 mA $\simeq$ 67 mA g^{-1}. Legend as in Fig. 4.

alloy hydrides tend to increase with increasing Rh content, although the difference is not substantial in the composition between 5.0 and 7.5 at % Rh. The observed capacity, C, of about 208 mA g^{-1}, corresponding to $H/M \simeq 0.81$ for Pd–2.5 at % Ni–7.5 at % Rh hydride is lower than that of the Pd–7.5 at % Rh binary hydride (Fig. 2).

As can be seen from Fig. 6, the dependence of the discharge capacity on discharge current density for Pd–2.5 at % Ni and Pd–2.5 at % Ni alloy hydrides containing Rh coated with the Pd/Pt-black superposed catalysts is excellent, and is superior to that of the Pd–7.5 at % Rh binary alloy hydride. The decreasing extent of discharge capacity is about 5–7% even at $i_d = 500$ mA g^{-1}. The high discharge rate characteristics of these alloys is also superior compared to those of the commercially used alloys [2–4]. This is due to two effects: one is the improvement of electrocatalytic activity of the electrode surface by coating with the Pd/Pt-black catalysts; the other is an increase in instability of the Pd–Ni–Rh ternary alloy hydride by addition of nickel, albeit by only 2.5 at %, although hydrogen diffusivity through the bulk may decrease slightly by addition of the nickel [16].

On the other hand, the charge-available efficiency of hydrogen in these alloy electrodes with Pd and/or Pd/Pt-black coatings should tend to decrease more or less with increasing charge current densities, because the catalytic high area active Pd and Pd/Pt-black coatings will also catalyse cathodic hydrogen evolution.

Thus, it may be concluded that hydrogen charge–discharge characteristics of pure Pd and Pd–Ni–Rh alloy hydrides as the negative electrode for nickel oxide–metal hydride batteries is remarkably improved by electrodeposition of Pd/Pt-black superposed catalysts, especially in respect to high discharge rate characteristics. The best discharge characteristics are achieved with Pd–7.5 at % Rh and/or Pd–2.5 at % Ni–7.5 at % Rh alloy hydrides, the electrode surfaces of which had been electrodeposited first with about 1–2 mg cm^{-2} of Pd-black, and then with about 1–2.5 mg cm^{-2} of Pt-black.

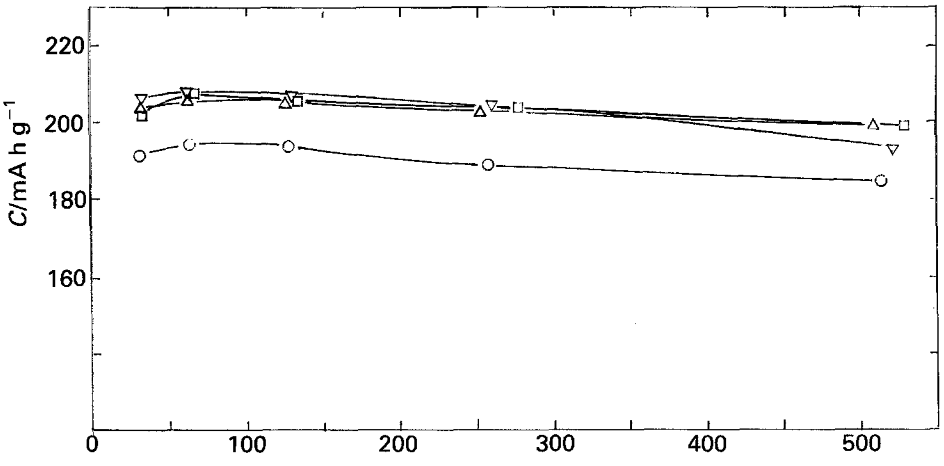

Fig. 6. Relationship between discharge capacity and discharge current density for Pd–Ni–Rh alloy hydrides catalysed by Pd/Pt-black at 5–7th cycles. Legend as in Fig. 4.

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