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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 31(2/3), 67-75
Issue Date	1984-03
Doc URL	https://hdl.handle.net/2115/28060
Type	departmental bulletin paper
File Information	31(2_3)_P67-75.pdf



RATES OF THE ELEMENTARY STEPS OF THE HYDROGEN ELECTRODE REACTION ON Pd-Au ALLOYS IN SULFURIC ACID

By

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(Received December 9, 1983)

Abstract

The charge-transfer elementary reaction rate on Pd-Au alloy electrodes in 0.5 M H₂SO₄ was evaluated by means of a galvanostatic transient technique and results were related to the surface alloy composition determined by XPS observations. The rate has a maximum near the equimolar alloy composition. Corresponding behaviour of the H-H recombination step rate was somewhat obscured by the H₂ diffusion control which occurred to set in, but the activity was likely to have a maximum at around 70% Pd. The Volmer-Heydrovsky mechanism was suggested on Au electrode.

Introduction

Catalytic activity of alloys of a metal of group VIII with one of group Ib has been the subject of a number of reports. Major interests in these investigations are placed on the role in catalysis of the vacancy in *d*-electron orbitals of the transition metal, which is likely to strengthen the adsorption of various reacting substances on the alloy, and on effects of diminution of the vacancy by filling it with *s*-electrons from the latter group metal which constitutes the alloy.

In the case of Pd alloyed with Au, the rate of the ortho-para (*o-p*) hydrogen conversion has been reported to be kept almost at a constant level or increased slightly with increase of Au content up to some 60%, but it then decreased sharply with its further increase. These have been accepted as evidence to support the vacant *d*-orbital concept.

Alloy systems, not necessarily confined in the VIII-Ib combination, are also interested in connection with the topic of surface modification of metal electrodes with foreign metal adatoms brought intentionally on the surface by *e.g.* the underpotential deposition. An increase of the electrocatalytic activity has been reported frequently, particularly for the electro-oxidation

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of simple organics, and its understanding is of a key importance in designing electrocatalysts.

It is aimed in the present work to investigate the rates of the elementary steps of the hydrogen electrode reaction (HER) on a series of Pd-Au alloys as a function of the alloy composition. As reported elsewhere¹⁾, owing to a high absorbability towards hydrogen of these alloys, the individual step rates of the discharge of proton and the catalytic H-H recombination process (plus H₂ diffusion in solution phase) can readily be measured by a transient technique in electrochemical systems.

Another factor which must be kept in mind in discussing electrocatalytic activity of alloys is the surface composition of the alloy components which may differ from the nominal bulk composition, namely, the possibility of the surface enrichment. Such information can be obtained from X-ray photoelectron spectroscopy (XPS). Fortunately, it has been indicated already in several reports that the surface enrichment is not significant in the Pd-Au alloys²⁻⁶⁾. In this respect, the present system is easier to be handled as compared with other systems, *e.g.* Pd-Ag, which appears to be associated with the surface enrichment of a significant extent²⁾.

Experimental

Alloys in the shape of a foil, 20 μm thick, were obtained from Tanaka Noble Metals, Co. (Tokyo). The nominal composition was Au₁₀Pd₉₀, Au₃₀Pd₇₀, Au₄₅Pd₅₅, and Au₆₀Pd₄₀. A Au foil (20 μm thick, Tanaka) and a Pd foil (12 μm thick, Ventron) were also used for comparison. The samples were usually prepared in 5 \times 10 mm size and held on Ta wire hair pins which were sealed in Pyrex glass tubings.

The cell and the electrodes were cleaned with hot chromic acid mixture at least overnight, followed by thorough rinses with water supplied from a Millipore pure water system. The electrolytic solution used was 0.5 M H₂SO₄. Anodic activation of the electrode was conducted in some cases as will be indicated later. Details of the polarization experiments by a transient technique have been reported elsewhere⁷⁾.

Surface concentration of Pd was determined after the polarization measurements by means of an ESCA apparatus (VG-III).

Results and Discussion

I. Surface analysis

Surface concentration of Pd, $c_{\text{Pd, surface}}$, was evaluated from XPS data. Typical spectra obtained with narrow range scans are shown in Fig. 1.

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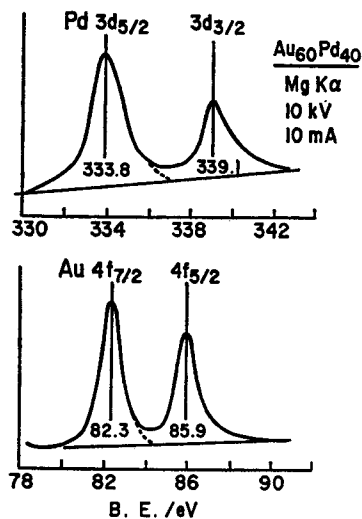


Fig. 1. XPS spectra on a $\text{Au}_{60}\text{Pd}_{40}$ alloy specimen.

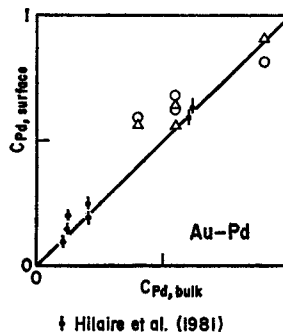


Fig. 2. Surface Pd concentration, as determined from XPS spectra, against bulk (nominal) concentration of various Au-Pd alloys. Data by Hilaire *et al.*⁴⁾ are also shown for comparison.

Signals at the binding energy value of 333.8 and 339.1 eV and of 82.3 and 85.9 eV were respectively assigned as Pd 3d (5/2 and 3/2) and Au 4f (7/2 and 5/2). The surface concentration was evaluated from the integrated areas of the Au 4f 7/2 and Pd 3d 5/2 signals.

Results are plotted in Fig. 2 against the nominal bulk concentration $c_{\text{Pd,bulk}}$. It is seen, in agreement with results reported in the literature²⁻⁶⁾, that $c_{\text{Pd,surface}}$ is in fair agreement with $c_{\text{Pd,bulk}}$. In view of the experimental error involved in this work, we conclude that the surface enrichment of Pd (or Au) is insignificant. In the following discussion, therefore, the surface concentration is taken as equal to the nominal bulk concentration and simply denoted as c_{Pd} .

II. Electrocatalytic activity of alloy electrodes

(A) The Volmer step

Typical galvanostatic overpotential rise and decay transients on $\text{Au}_{60}\text{Pd}_{40}$ specimen are shown in Fig. 3. The overpotential growth at the shortest time window shown ($\sim 10^{-4.5}$ sec) was almost straight. The slope gives the double-layer capacitance and hence the true surface area of the electrode.

It is seen that the overpotential component η_1 is readily evaluated from the plateau on the rise curve observed with the time window of $\sim 10^{-3}$ sec (or somewhat shorter at higher current density values). Results of the η_1 vs.

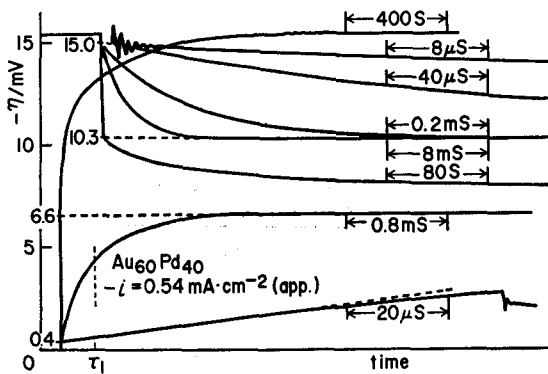


Fig. 3. Typical galvanostatic overpotential rise transients and decay transients on the $\text{Au}_{60}\text{Pd}_{40}$ alloy electrode, 0.5 M H_2SO_4 , 30°C. $-i = 0.54 \text{ mA cm}^{-2}$ (apparent, cathodic), $-\eta_{\text{ohm}} = 0.4 \text{ mV}$, $-\eta_1 = 6.2 \text{ mV}$, $-\eta_2 = 9.9 \text{ mV}$, $-\eta = 14.6 \text{ mV}$, $\tau_1 = 260 \mu\text{S}$.

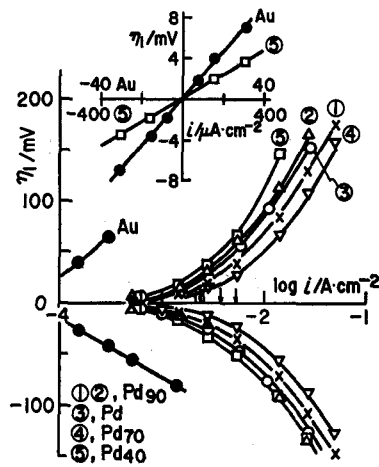


Fig. 4. Plots of η_1 against $\log i$ (apparent) on Au-Pd alloy electrodes of various compositions (before the anodic activation) i_{ov} evaluated from η_1 vs. i plots (inset) are indicated by the arrows on the abscissa. Data on the Au electrode are η and not η_1 .

$\log i$ relation are shown in Fig. 4: These can be well expressed by the Volmer equation for a single electron transfer reaction with the symmetry factor value of some 0.6 (for the cathodic component rate).

To compare the electrocatalytic activity of electrodes of various compositions, one has to take into account the difference in the true surface area among the electrodes. (The roughness factor was usually 1.2~1.5.) For this purpose, it is convenient to observe the rise time τ_1 of short time overpotential rise transients. This is expressed further as $\tau_1 = R_1 C$ where R_1 is the polarization resistance with respect to η_1 and C is the double-layer capacitance of the electrode, both being defined per unit apparent surface area. As C is proportional to the roughness factor whereas R_1 is inversely proportional to it, τ_1 is free of the ambiguity due to difference in the roughness factor among different alloy specimens. As well known, R_1 for a single electron transfer reaction is related to its exchange current density, i_{ov} of the Volmer step in the present case, as $i_{\text{ov}} = (RT/F)/R_1$.

The overpotential rise up to η_1 was confirmed to be approximately of the type $\eta = \eta_1 [1 - \exp(-t/\tau_1)]$. Hence, τ_1 was evaluated at the time $\eta = 0.63 \eta_1$. As τ_1 tended to decrease with increase of η_1 (because of decrease of effective

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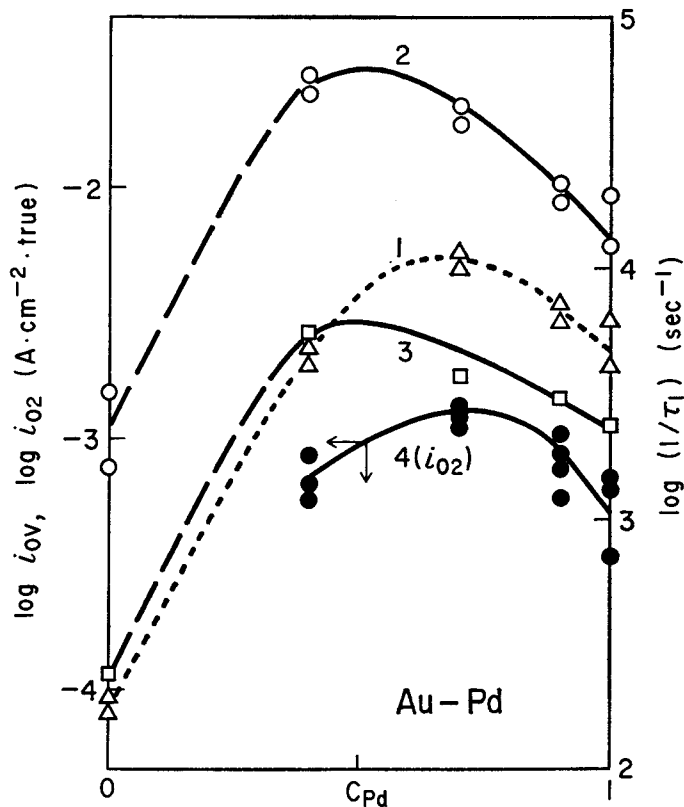


Fig. 5. Dependence upon the alloy composition of i_{0V} or $1/\tau_1$ (curves 1, 2 and 3) and of i_{02} (curve 4)

Curve 1: After a routine cleaning procedure

Curve 2: After anodic activation which followed curve 1

Curve 3: After standing the electrodes for two weeks, which followed curve 2.

R_1 with $|\eta|$), it was usually evaluated in the low polarization region, *i. e.*, $\eta_1 \leq 20$ mV.

Results of a typical series of measurements with the alloy electrodes are shown in Fig. 5 in terms of both τ_1 and i_{0V} , where the double-layer capacitance of $18 \mu\text{F cm}^{-2}$ (true) is assumed. Curve 1 was obtained on electrodes after a routine cleaning procedure whereas curve 2 was obtained after an anodic activation of the same electrodes by applying momentarily the potential of the oxygen evolution condition (~ 1.5 V RHE). The activity was much improved by the anodic activation and the shape of the curve became somewhat different as compared with curve 1. We may accept the behaviour of

curve 2 since essentially the same shape was reproduced even after two weeks of standing of the electrodes in the cell (curve 3).

It was seen that the activity per unit true area was higher at intermediate alloy compositions than at pure Pd, with a maximum around the equimolar mixture of Au and Pd. The maximum activity was 3~5 times larger than the pure Pd foil. This indicates a synergistic effect between the two metals.

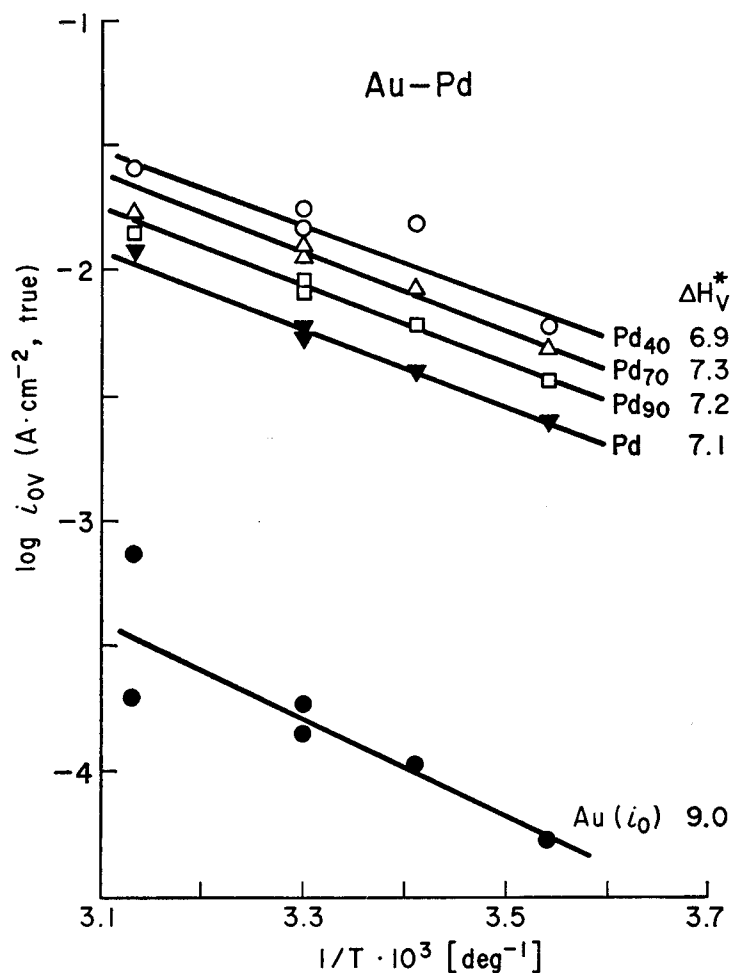


Fig. 6. Temperature dependence of i_{0V} and heat of activation, ΔH_V^* , of the Volmer step on Pd-Au alloy electrodes of various compositions (after the anodic activation). The data on Au represent i_0 and not i_{0V} .

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The temperature dependence of i_{ov} is shown in Fig. 6. The heat of activation obtained from the slope is approximately 7 kcal/mole, practically independent of the alloy composition. The data are, however, not accurate enough to decide whether or not the difference in the activity among the alloys of different compositions was caused by difference in the activation heat values (a difference of 1 kcal gives rise to the above difference in rates) or in the pre-exponential terms of rate expressions. Also shown in Fig. 6 are the results on Au electrode (for the overall reaction) which also has the activation heat of analogous magnitude (see Chapter III below).

(B) The Tafel step

The overpotential component η'_2 was reasonably well defined on the decay transients as shown in Fig. 3, indicating that permeation of hydrogen is sufficiently rapid in these alloys. Evaluation of η'_2 has hence been carried out on all the alloy specimens as well as on the pure Pd foil. As the kinetic behaviour of η'_2 on the alloys is very similar to Pd, the Tafel recombination step may be assigned to η'_2 as in the case of Pd^{1,7}.

The exchange current density i_{o_2} evaluated from the slope R_2 of the linear η'_2 vs. i plot at low η'_2 by the relation $i_{o_2} = (RT/2F)/R_2$ is also shown in Fig. 5 (curve 4). It is to be noted however, that the values are of the order of magnitude of $\sim 10^{-3}$ A cm⁻² (true), which is comparable in magnitude with the limiting current density, i_L , of hydrogen diffusion in the solution phase. Accordingly, the exchange current density observed is expected to be lower than i_{oT} of the Tafel step^{1,7} in accordance with the relation $i_{o_2} = (1/i_{oT} + 1/i_L)^{-1}$. The lack of a large composition dependence of the exchange current density may hence not necessarily mean such a behaviour of i_{oT} . Nevertheless, as i_L should be practically common in these data, it appeared likely that the catalytic activity for the H-H reaction would have a maximum at around 70% Pd. The result, therefore, supported the earlier work on the gas-phase *o-p* conversion reaction⁹ which indicated a maximum at about the same Pd concentration.

(C) The overall reaction

As i_{o_2} was much lower than i_{ov} , the former would practically represent the overall electrocatalytic activity of these electrodes. Accordingly, we may expect an analogous shape of composition dependence of the overall exchange current density i_o . Such a behaviour was, however, not in agreement with the one reported in the literature⁸.

III. Catalytic and electrocatalytic activity of Au

The electrocatalytic activity of Au with respect to i_{ov} was not obtainable in this work, as η_1 was not defined experimentally. Nevertheless, as the Volmer step is certainly involved in the overall HER, the steady-state polarization data obtained on Au should indicate the lower limit value of i_{ov} . These are therefore also plotted in Fig. 5 in order to be compared with the data on the alloys. The resultant value was 1~2 orders of magnitude lower than those on Pd and the Au-Pd alloys; it was interesting that the difference was far smaller than one would anticipate from the *o-p* hydrogen conversion reaction data where the difference has been reported to be 8~10 orders of magnitude⁹.

The galvanostatic overpotential rise and decay transients on Au electrode are almost of simple RC charge (discharge) type with the time constant of $\sim 10^{-2}$ sec. The overpotential value reached should represent the steady-state overpotential value as it was then kept constant for much longer polarization times. Such a short time-constant value indicates that the pseudocapacitance due to hydrogen adsorption is practically absent.

The exchange current density i_0 of the overall reaction on Au was determined by the linear η vs. i plot. Extrapolation of the cathodic Tafel line, which had the slope of around 60 mV, to $\eta=0$ also yielded analogous magnitudes (Fig. 4). The value is of usual magnitude for the HER as often reported^{8,10-12}) but it is much higher than the rate of catalytic H-H recombination reactions represented *e.g.* by the *o-p* hydrogen conversion in the gas phase¹³). Thus, the above-mentioned value corresponds approximately to 5×10^{-9} mole H_2 $sec^{-1} cm^{-2}$ at 30°C, whereas the *o-p* hydrogen conversion rate after extrapolated to 1 atm is¹³) roughly 1×10^{-11} mole H_2 $sec^{-1} cm^{-2}$ at 77°C, or with the heat of activation of 18 kcal $mole^{-1}$, roughly 2×10^{-13} mole H_2 $sec^{-1} cm^{-2}$ at 30°C. The rate of (the slowest elementary step of) the HER is therefore 10^4 times more rapid than the gas phase H-H reaction. Likewise, the heat of activation, which is 9 kcal $mole^{-1}$ in the HER on Au as shown in Fig. 6, is considerably lower than the above-mentioned value of 18 kcal $mole^{-1}$ in the gas phase reaction.

These discrepancies indicate either one of the following two possibilities, namely (i) the H-H recombination reaction is common in the HER and the *o-p* conversion reaction but the rate is extensively augmented by the existence of water in the case of the former reaction, or (ii) the elementary step in the HER is not the H-H recombination type as on many electrocatalytically active metals¹⁴) including Pd, but the Heyrovsky step, $H_2 \leftrightarrow H + H^+ + e$, as often suggested^{10,11}). The former possibility is, however, very unlikely as the

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existence of water may retard, rather than enhance, the mobility of hydrogen on the surface and indeed, on other catalytically active metals such as Pt, the rate of *o-p* conversion was reported to be more rapid than, or at least comparable with, that of the HER¹⁵. Similarly, the lower value of heat of activation in the HER than in the gas phase reaction as quoted above should be difficult to be accounted for.

On the other hand, the cathodic Tafel slope of ~ 60 mV on Au, which was much lower than ordinary 120 mV, supports the latter possibility, the Heyrovsky step connected with the rapid Volmer step. The fact that the slope was higher than 40 mV, the value anticipated for the Heyrovsky mechanism in the simplest case, required further consideration. Such a value on Ag electrode was explained by Krishtalik in terms of the barrierless model¹⁶.

The anodic Tafel line was in harmony with the present argument as it has a linear portion of ~ 100 mV slope (Fig. 4), rather than tending to give a steep overpotential rise approaching a limiting current density which should be expected for the Tafel mechanism.

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