

Palladium Hydride *pH* Electrode Equipped with Electrolysis System for Continuous Hydrogen-Charging

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In order to overcome the difficulties in the measurement of the hydrogen ion concentration, C_{H^+} , in aqueous solutions by the glass electrode, a palladium hydride electrode of improved type has been proposed. Using the electrode, it is possible to determine C_{H^+} in solutions containing fluoride ions or rather concentrated acid or base. The potential at the electrode is stable at least for 1000 hours in the absence of such strong oxidizing agents as dichromate and ferric ions in the test solution. The potential generating process at the electrode has been discussed.

KEY WORDS: Potentiometric measurement/ Hydrogen ion concentration/ Palladium hydride membrane/ Continuous hydrogen-charging/

INTRODUCTION

Because of the acid and the base errors, the glass electrode is not applicable to the measurement of the hydrogen ion concentration in solutions containing high concentration of acid or base. The other defect of the electrode is that glass is easily attacked by fluoride. In order to avoid these defects, other *pH* electrodes have been investigated.^{1,2)} A *pH* electrode based on a polymer-carrier system permeable to hydrogen ions has been described.³⁾ More commonly, electrodes based on *pH*-dependent electrochemical redox reactions have been used.

Electrodes for *pH* made of such metals covered with their oxide films as antimony,⁴⁾ iridium⁵⁾ and palladium⁶⁾ have been proposed. However, these metal metal-oxide electrodes were found susceptible to voltage drift problems, as it is difficult to prepare the oxide film of an appropriate thickness⁷⁾ as well as to maintain the thickness at constant especially when in the presence of reducing agents in the test solution.⁸⁾

Although the reversible hydrogen platinum electrode forms the basis for an operational definition of the *pH* scale, the use of the electrode on a routine basis is complicated by the need for a constant partial pressure of hydrogen in the test solution. Considerable informations on the palladium-palladium hydride electrode has been published for the measurement of *pH*.⁹⁾ Since hydrogen once adsorbed on and/or in palladium as an alloy escapes spontaneously from the alloy, however, the hydrogen-palladium system has limited utility, particularly in aerated solutions. *Jasinski* has extended the life of the electrode to a week or so in aerated solutions

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by the careful design of the measurement system.¹⁰⁾

The present work is devoted to the improvement of the palladium-palladium hydride electrode and to the investigation of the applicability of the improved electrode to solutions containing concentrated acid or base, fluoride ions, and reducing or oxidizing agents.

EXPERIMENTAL

The cell used for the potentiometric measurement of the hydrogen ion concentration is realized in Fig. 1. The inner solution, which was 0.5 M sulfuric acid in this work, was separated from the test solution by a palladium plate (more than 99.99% of purity, product of Tanaka Noble Metals Co.) of 0.2 mm thick and 154 mm² effective surface area which served as the hydrogen ion selective membrane. The palladium had been polished to be a mirror-like surface with the aid of carborundum powder. Two silver-silver chloride electrode (SSE, with saturated potassium chloride), RE1 and RE2, were set in the test and the inner solutions, respectively, and the potential differences between RE1 and palladium, RE2 and palladium, and RE1 and RE2 were measured by potentiometers (Model HE-101E, Hokuto Denko Co.). To implant hydrogen into the palladium plate, a controlled potential referred to a SSE, RE3, was applied to the plate by the aid of a counter electrode, CE2, of a platinum wire. A potentiostat (Model HA-501, Hokuto Denko Co.) was used for the electrolysis.

Voltammograms were recorded using the potentiostat, a function generator (Model HB-104, Hokuto Denko Co.) and an X-Y recorder (Model 3036, Yokogawa-Hokushin Denki Co.). The recorder was also used for the recording of potential difference-time curves.

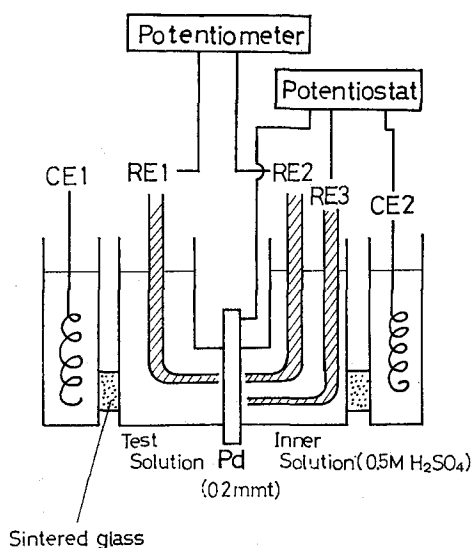


Fig. 1. Electrolysis cell

Palladium Hydride pH Electrode

The reduction-oxidation (Redox) behavior of hydrogen ion at the palladium electrode was investigated using a palladium disc electrode, 5.0 mm ϕ , which had been prepared and pretreated by the same procedure as that for the nickel disc electrode previously mentioned.¹¹⁾

All measurements were carried out at $25 \pm 0.5^\circ\text{C}$.

Apparatus

Clark-Lubs' and Kolthoff's¹²⁾ buffer solutions were employed as the standards of the hydrogen ion concentration.

All reagents used were of reagent-grades.

RESULTS

The redox behavior of hydrogen ion at the palladium electrode

The cyclic voltammogram at the stationary palladium disc electrode recorded at a scan-rate $1 \text{ mV} \cdot \text{s}^{-1}$ in 0.5 M sulfuric acid is realized in Fig. 2. A double-humped cathodic and a double-humped anodic peaks which correspond to the mono-layer adsorption of hydrogen atom on the surface of the palladium and its desorption,¹³⁾ respectively, were observed at the potential region between +0.3 and 0 V. A reduction current due to the evolution of hydrogen gas appeared at more negative potentials than -0.1 V .

Preparation of the hydrogen-implanted palladium membrane and the potential established at the membrane/solution interface

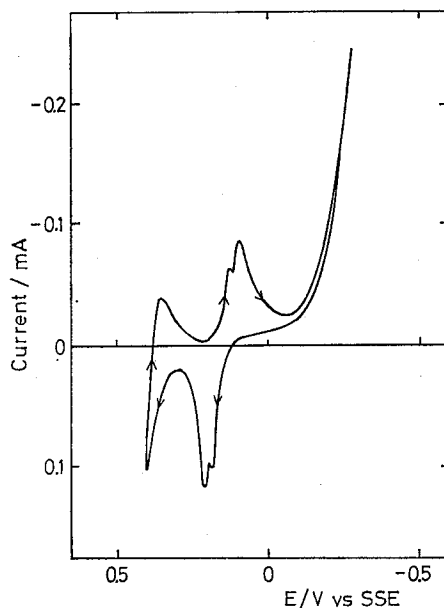


Fig. 2. Voltammogram at palladium disc electrode in 0.5 M sulfuric acid.
Scan-rate: $1 \text{ mV} \cdot \text{s}^{-1}$, Disc electrode: 5 mm ϕ .

Employing 0.5 *M* sulfuric acid as the inner and the test solutions (not deaerated), the controlled potential electrolysis at the inner solution/palladium interface was carried out for 2 min at -0.25 V vs RE3 in order to implant hydrogen into the palladium plate.¹⁴⁾

The time-course of potential differences between RE1 and palladium, ΔV_1 , measured as the potential of palladium vs RE1, between RE2 and palladium, ΔV_2 , measured as the potential of palladium vs RE2 and between RE1 and RE2, ΔV_3 , measured as the potential of RE1 vs RE2 are shown in Fig. 3. As ΔV_3 was the sum of $-\Delta V_1$ and ΔV_2 , it is clear that the potential gradient in the palladium plate is negligible.

At the beginning of the electrolysis, ΔV_2 abruptly shifted toward -0.25 V at the beginning and remained at this potential difference for further electrolysis. When the electrolysis was switched off, ΔV_2 rapidly shifted to a potential difference established by hydrogen in the palladium and hydrogen ion in the inner solution at the palladium/inner solution interface. About 3 min after the beginning of the electrolysis, ΔV_1 started to shift and reached at a constant potential difference, which was equal to $-\Delta V_2$, after 20 min. Hence, ΔV_3 was zero after 20 min. These potential differences were maintainable at constant for further 40 min.

The potential shift indicates that hydrogen implanted from the inner solution/palladium interface diffuses in the palladium toward the test solution and the hydrogen concentration at both interfaces in the palladium becomes to be equal after an appropriate time. The gradual shift of ΔV_1 and ΔV_2 after about 60 min suggests the escape of hydrogen from palladium.

Using deaerated test solution, identical results with those mentioned above were obtained.

Figure 4 illustrates the time-course of ΔV_1 with various electrolysis time. The

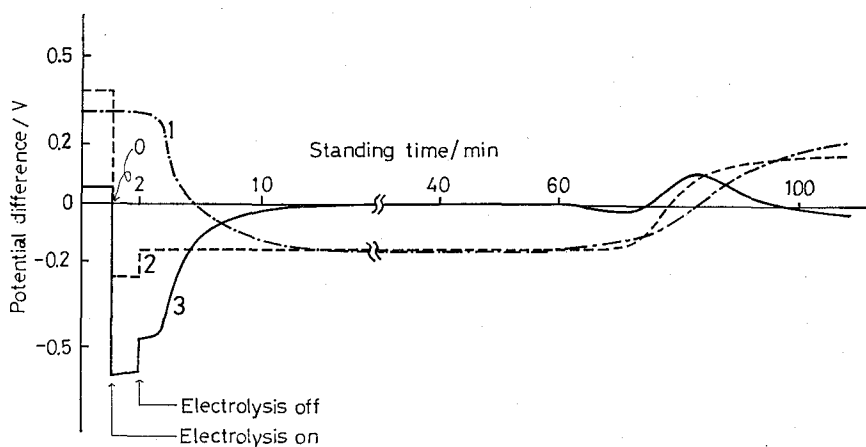


Fig. 3. Time course of potential differences during and after electrochemical implantation of hydrogen into palladium membrane. 1: ΔV_1 (between test solution and Pd), 2: ΔV_2 (between inner solution and Pd), 3: ΔV_3 (between test and inner solutions). Electrochemical implantation of hydrogen at -0.25 V vs SSE for 2 min. Test and inner solutions: 0.5 *M* sulfuric acid.

Palladium Hydride pH Electrode

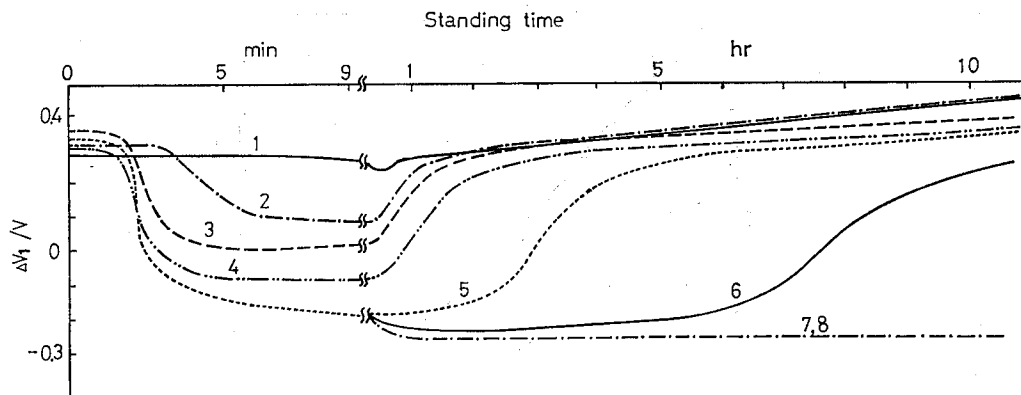


Fig. 4. Effect of electrolysis time for implantation of hydrogen. Electrolysis time: 1; 2 s, 2; 5 s, 3; 20 s, 4; 1 min, 5; 5 min, 6; 10 min, 7; 60 min, 8; continuous. Test and inner solutions: 0.5 M sulfuric acid.

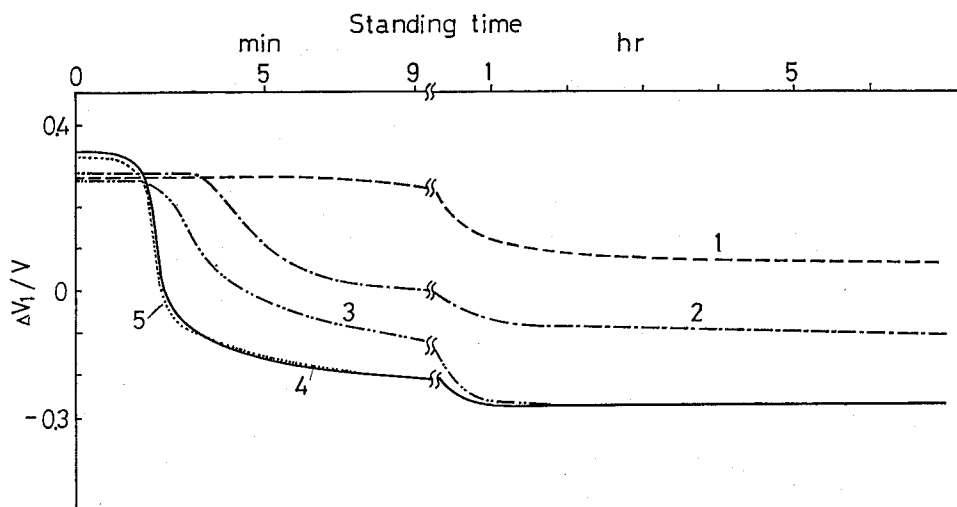
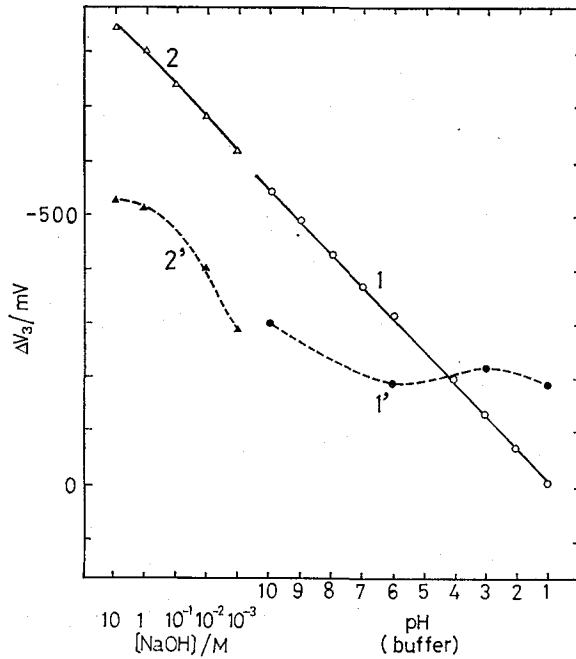


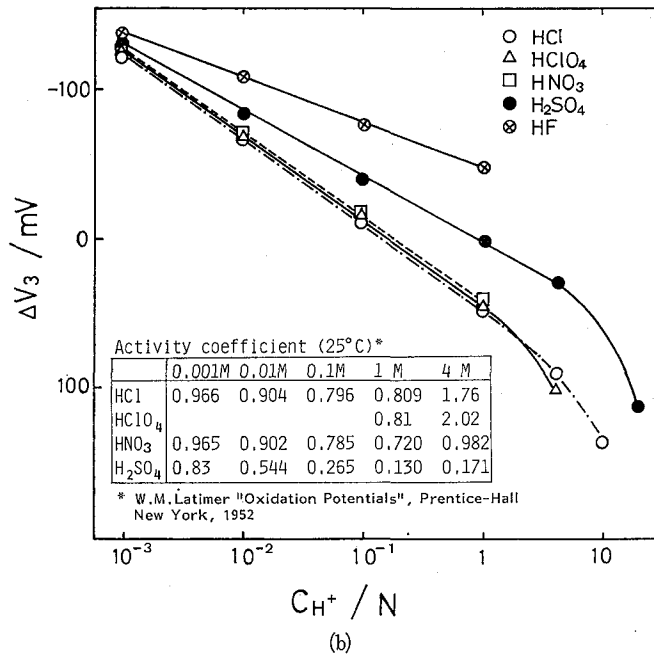
Fig. 5. Effect of electrolysis potential for implantation of hydrogen. Electrolysis potential (V vs SSE): 1; 0.00, 2; -0.10 , 3; -0.15 , 4; -0.25 , 5; -0.30 . Test and inner solutions: 0.5 M sulfuric acid.

potential difference attained an ultimate value ($-0.26_5 V$) 60 min after beginning of the electrolysis at $-0.25 V$ regardless with the electrolysis time of more than 30 min. The time required for the shift of ΔV_1 due to the escape of hydrogen from palladium was nearly proportional to the electrolysis time of longer than 1 min. With continuous electrolysis ΔV_1 , ΔV_2 and ΔV_3 were at constant at least for 1000 min after they attained the constant values.

When the continuous implantation of hydrogen was carried out at potentials more negative than $-0.15 V$, ΔV_1 attained the ultimate value ($-0.26_5 V$), as shown in Fig. 5. The electrolysis at more negative than $-0.5 V$, however, resulted irregular ΔV_2 and, hence, irregular ΔV_3 because of copious hydrogen gas evolution



(a)



Figs. 6-a and 6-b. Dependence of ΔV_3 on hydrogen ion concentration. Inner solution: 0.5 M sulfuric acid. 1, 2: with Pd membrane hydrogen-implanted, 1', 2': with Pd membrane without hydrogen-implanted.

at the inner solution/palladium interface.

Response of the hydrogen-implanted palladium, Pd(H), membrane electrode to the hydrogen ion concentration, C_{H^+}

The relation between the potential difference, ΔV_3 and the hydrogen ion concentration, C_{H^+} , in the test solution is realized in Fig. 6-a. In the measurement, 0.5 M sulfuric acid was employed as the inner solution. The electrolysis for the implantation of hydrogen into the palladium at $-0.25 V$ had been started 1 h prior to the measurement and was continued during the measurement.

Curves 1 and 2 were obtained with *Clark-Lubs'* buffer ($pH=1$ to 10) and sodium hydroxide solutions, respectively, as the test solutions. *Kolthoff's* buffer gave the same results as those in curve 1. Curves in Fig. 6-b are the results obtained with hydrochloric, perchloric, sulfuric and hydrofluoric acids solutions of different concentrations. There exists the *Nernstian* relation of slope 58 mV between ΔV_3 and the hydrogen ion activities in these solutions which was calculated taking the activity coefficients¹⁵⁾ of hydrogen ions and dissociation constants of these acids¹⁶⁾ into account. Also, the Nernstian relation was found when nitric acid of less than 1 M was used as the test solution. With nitric acid of higher concentration than 3 M, however, ΔV_1 was extremely positive, which may be due to nitrogen dioxide generated in the solution.

When palladium membrane without hydrogen implanted was used instead of Pd(H) membrane, no regular nor reproducible relation was found between ΔV_3 and C_{H^+} as broken lines in Fig. 6-a.

Effect of coexisting ions

The effect of coexisting ions on the determination of the hydrogen ion concentration, C_{H^+} , by the Pd(H) membrane electrode was investigated taking the use of the electrode in acidic solutions into account.

Even in the presence of 1 M of such ions neither oxidizable nor reducible in aqueous solutions as K^+ , Na^+ , Li^+ , Mg^{2+} , Cl^- , SO_4^{2-} and ClO_4^- , the determination of C_{H^+} could be performed and the results obtained agreed well with the calculated values being corrected for the ionic strength of the coexisting ions.

Table 1 Interference from oxidizing ions

Diverse ions	Potential difference, ΔV_3 (V)			
	Hydrogen ion concentration* (M)			
	10^{-3}	10^{-2}	10^{-1}	1
none	-0.112	-0.065	-0.008	+0.049
$10^{-2} M Cr_2O_7^{2-}$	-0.113	-0.062	+0.112	+0.160
$10^{-1} M Cr_2O_7^{2-}$	-0.112	-0.043	+0.480	+0.618
$10^{-2} M Fe^{3+}$	-0.110	-0.060	-0.007	+0.083
$10^{-1} M Fe^{3+}$	-0.112	-0.052	+0.220	+0.227

* added as hydrochloric acid.

Ascorbic acid, which is one of typical reducing agents and gives the serious interference with the pH measurement by the metal-metal oxide electrodes,⁶⁾ did not give any interference for the determination of C_{H^+} , between 10^{-2} and $1 M$, by the Pd(H) membrane electrode. Also, dissolved oxygen saturated under 1 atm O_2 at 25°C and $0.1 M$ of UO_2^{2+} , Cu^{2+} or Ni^{2+} coexisted in hydrochloric acid of concentration between 10^{-2} and $5 M$ gave no interference, when the activity coefficients were corrected for the ionic strength.

Strong oxidizing agents such as $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{3+} gave considerable disturbance in the measurement of C_{H^+} as seen in Table 1. The disturbance from these ions was decreased in solutions of pH higher than 2, because they change their chemical forms and, hence, their oxidizing power decreases.

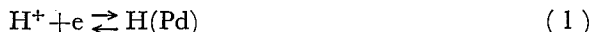
The effect of stirring of the test solution

The determination of C_{H^+} by the Pd(H) membrane electrode was affected with the stirring of the test solution. For example, when the test solution containing $10^{-3} M$ hydrochloric acid was stirred using magnetic stirrer at a rate of about 300 rpm, the potential difference ΔV_0 shifted about 60 mV toward positive.

DISCUSSION

Referring to Fig. 2 together with Fig. 5, it is obvious that potentials more negative than those for the adsorption of hydrogen on the surface of palladium should be applied to palladium in order to implant hydrogen into palladium. Hydrogen electrochemically implanted in palladium from its surface diffuses fairly quickly in the metal toward the other surface as indicated in Fig. 3. Though the hydrogen implanted is discharged spontaneously, the potential difference ΔV_1 , ΔV_2 or ΔV_3 does not change for fairly long time suggesting that the concentration of hydrogen at the surface of palladium is maintainable at constant even when that in the bulk of palladium decreases. This phenomenon is supported by the fact included in the voltammogram in Fig. 2 that the binding energy between hydrogen and palladium at the surface is much stronger than that between hydrogen atoms at the surface or that between hydrogen and palladium in the bulk of the metal. The hydrogen adsorbed on palladium may form the monolayer.¹³⁾ Because of the phenomenon mentioned above, if enough amount of hydrogen to maintain the monolayer of hydrogen adsorbed is supplied continuously to palladium by the electrolysis, the concentration of hydrogen at the palladium surface can be kept at constant.

The *Galvani* potential difference at the solution/palladium interface, ΔV_1 or ΔV_2 , in the present work is due to the reaction



Hence, the potential difference depends on C_{H^+} in the test solution when the concentration of hydrogen adsorbed on the surface of palladium, $\text{H}(\text{Pd})$, and C_{H^+} in the inner solution are at constant.

In the voltammetric interpretation of the potentials at ion selective electrodes, ISE, the authors advocated that potentials at ISE stable and responsive to the con-

centration of the objective ion in the test solution can be obtained only when the solution/electrode interface is depolarized by the objective ion, and demonstrated the idea based on the voltammograms for the ion transfer at the interface.¹⁷⁾

Voltammograms in Fig. 7 were recorded using the electrolysis cell of Fig. 1 equipped with Pd(H) membrane and scanning the current anodically or cathodically from 0 at a rate of $10 \mu A \cdot \text{min}^{-1}$ through the membrane by the aid of CE1 and CE2. During the current-scanning, the potential difference between the inner and the test solutions, ΔV_3 , were measured using RE1 and RE2. The inner solution employed in this measurement was 0.5 M sulfuric acid. The voltammograms sharply intersect the potential axis, where the current is 0, suggesting that the solution/Pd(H) membrane interface is depolarized by the reaction of eqn (1) even when an appreciable current is flowing. The ΔV_3 at zero-current, $\Delta V_{3,I=0}$, which correspond to the potentiometric potential, shifts with the activity of hydrogen ion in the test solution in the Nernstian way, and the relation of $pH - \Delta V_{3,I=0}$ agrees well with that realized in Fig. 6-a or 6-b. In this connection, in the absence of hydrogen implanted in the palladium membrane, the reproducible voltammograms could not be obtained.

Voltammograms illustrated in Fig. 8 were obtained using 10^{-3} M hydrochloric acid as the test solution and 0.5 M sulfuric acid as the inner solution. When the test solution was stirred by a magnetic stirrer at a rate of about 300 rpm, the anodic limiting current due to the reduction of hydrogen ion in the solution was about

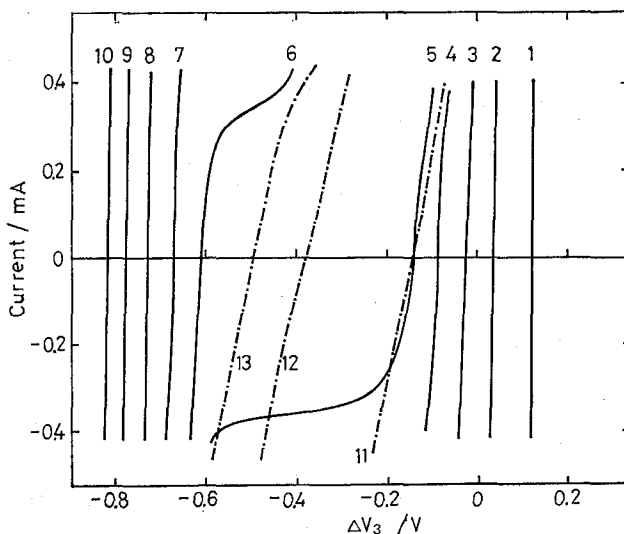


Fig. 7. Current-scan voltammograms (current $-\Delta V_3$ curves).
 Test Solution: 1; 10 M HCl, 2; 1 M HCl, 3; 10^{-1} M HCl, 4; 10^{-2} M HCl, 5; 10^{-3} M HCl, 6; 10^{-3} M NaOH, 7; 10^{-2} M NaOH, 8; 10^{-1} M NaOH, 9; 1 M NaOH, 10; 10 M NaOH, 11; $pH=3$, 12; $pH=7$, 13; $pH=9$, (3, 8); with 0.9 M NaCl, 4-7; with 1 M NaCl, 11-13; by Clark-Lubs' buffer)
 Inner solution: 0.5 M sulfuric acid. Hydrogen continuously implanted at -0.25 V vs SSE.

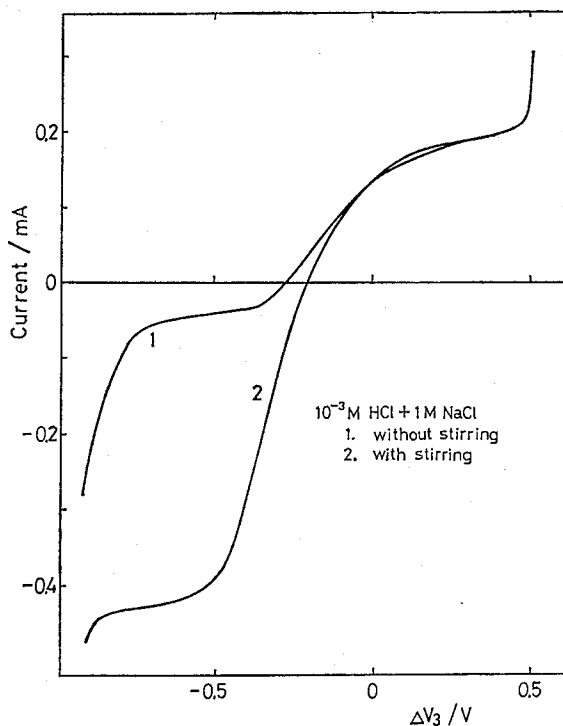


Fig. 8. Effect of stirring of test solution on voltammogram of 10^{-3} M hydrochloric acid.

10 fold of that without stirring. On the other hand, the cathodic limiting current due to the oxidation of hydrogen in or on the palladium was unaffected with the stirring. Accordingly, the $\Delta V_{3,I=0}$ was shifted about 60 mV more positive by the stirring, which explains the effect of the stirring on the measurement of C_{H^+} by the Pd(H) electrode.

ACKNOWLEDGMENT

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