Effect of Addition of Thiourea and Mercury on Hydrogen Evolution Reaction at Pd in Alkaline and Acidic Solutions

Ken-ichiro OTA*, Tokio KARIKOMI, Hideaki YOSHITAKE
and Nobuyuki KAMIYA

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Overpotential of Pd cathode was measured by current-step chronopotentiometry with addition of thiourea or mercury (II) chloride in H_2SO_4 and LiOH solutions. In H_2SO_4 , both additives increased overpotential components corresponding to discharge (η_1') and recombination (η_2') processes. The addition of thiourea into LiOH solution increased η_1' strongly while it decreased η_2' . On the other hand, η_1' and η_2' were both increased by the addition of HgCl_2 . The mechanism of these promotion/inhibition of hydrogen evolution electrochemical reaction was discussed in comparison with poisoning behavior of lithium cations against discharge and recombination processes.

1 INTRODUCTION

The hydrogen evolution reaction (HER) on Pd is utilized at the so called cold fusion research. In these process the hydrogen overpotential is a very important factor, and should be estimated precisely. The hydrogen overpotential is highly sensitive to electrolytes, impurities, or additives, and the extent of their influence on elementary processes --- discharge (Volmer), surface chemical (recombination, or Tafel) and discharge with recombination (ion + atom, or Heyrovsky) processes, --- has been discussed in several papers.^{1, 2)} It is generally difficult, however, to distinguish the elementary steps in detail. Current-step chronopotentiometry has been considered to be a possible way to measure the overpotential components of pure electrochemical process and surface chemical process separately by use of difference of time constants of these processes. This method is applicable to all kinds of electrodes in principle but these transients are usually rapid. On the other

hand, the overpotential transient on palladium has a quite long time constant corresponding to surface chemical process because it absorbs a large amount of hydrogen. Similarly, after terminating the current, hydrogen atom has to diffuse from the electrode bulk to the surface before the recombination. Thus the overpotential related with dividing the processes has been measured especially as for palladium in acidic solutions.³⁻⁵⁾

Cathodically polarized Pd electrode absorbs hydrogen much more than that under atmospheric pressure of hydrogen, but the value of H/Pd prepared electrochemically in H_2O or D_2O solutions was not precisely established in the literature; scattered between 0.7^{6, 7)} and 1.0⁸⁾ depending on the conditions. And it has been considered to be related with the condition of electrolysis, especially overpotential.^{3, 9, 10)} It has been demonstrated that the increase of the overpotential of Tafel process inhibit the recombination process to cause higher H/Pd.¹¹⁾ This system recently gathers interests especially on Pd cathodes in LiOD heavy water solution due to "cold fusion" phenomena reported by Fleischmann et al.¹²⁾

Thiourea additive was reported to increase hydrogen overpotential on palladium cathode in acidic solution.³⁾ In the pre-

Department of Energy Engineering, Faculty of Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240

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vious study of the series,¹³⁾ anomalously high overpotential has been observed and suggested to be due to inhibition of hydrogen evolution by the cations has been suggested in basic solutions. Especially the hydrogen recombination process was strongly suppressed in LiOH solution.¹³⁾ Achieving higher H/Pd by choosing the electrolytic conditions has been an important subject and in this paper we combine the inhibition effects of lithium ion and additives to investigate the overpotentials of elementary processes in order to offer the direction of the electrolytic condition to obtain high H/Pd.

2 EXPERIMENTAL

All electrochemical measurements were carried out in the acrylic cell containing 500 cm³ of solution to avoid the dissolution of the wall when glass cell was used. Palladium foil was used in this experiment for rapid stabilization of the composition and state of the electrode, i.e. 5 μ m 99.95% metal foil purchased from The Nilaco Corp was used. The surface area of the working electrode was 1.0 cm². A large area 99.95 % platinum wire from Tanaka kikinokoku was used for a counter electrode. The electrolyte solutions were prepared by the addition of Li metal (99 %+, Wako Pure Chemical Industries) or H₂SO₄ (98.0 %+, Wako Pure Chemical Industries) into Milli-Q water. Small amount of impurities possible in the solutions were removed by pre-electrolysis at 100 mA·cm⁻² for 12 h.

Electrode potentials against reversible hydrogen electrode, i.e., overpotentials η were measured by current-step chronopotentiometry. Potentio/galvanostat model 2020 (Toho Technical Research) was used with at constant current condition where the current was varied stepwise from higher values. Overpotential η after addition of thiourea or HgCl₂ was recorded when it became unvaried at each set current. Overpotential transients were recorded on a digital storage oscilloscope VC-6015 (Hitachi). When a current pulse is applied to test electrode, the potential rises rapidly and then increases gradually to reach a stable total overpotential(η). Thus, the total overpotential η is the sum of the rapidly rising potential(η_1)

and slowly rising potential component (η_2), namely, $\eta = \eta_1 + \eta_2$. When the current was terminated, the decay transient of the potential can be observed; the current decreases rapidly then slowly. The corresponding overpotentials are denoted as η_1' and η_2' , respectively, and we have $\eta = \eta_1' + \eta_2'$. It is believed that η_1 and η_1' are closely related with Volmer process and η_2 and η_2' are related with Tafel process.^{9, 10)} We measured η and η_2' on the overpotential decay transient through pulse generator 2320 (Toho technical research) after keeping a certain current for overnight. Appearance, collection and processing of the data were described in refs. 3 and 13 in more detail.

3 RESULTS

Overpotential growth at current density of 2 A·cm⁻² were drawn in the same time scale in Figure 1. Potentials in the system without additives became stable at 492 mV after 8 h in H₂SO₄ and both additives of HgCl₂ and thiourea were effective to increase overpotentials by 714 mV and 238 mV, respectively. As for LiOH, Hg containing system gave steady overvoltage of 1330 mV most rapidly and the steady states of systems with thiourea additives and no additives were attained slower in the similar manner. Comparing the

Fig. 1 The total overpotential growth for 5 μ m Pd cathode at 2000 mA·cm⁻². The temperature was 298 K. A, 1 M H₂SO₄ + 1 $\times$ 10⁻⁶ M HgCl₂; B, 1 M H₂SO₄ + 100 $\times$ 10⁻⁶ M thiourea; C, 1 M H₂SO₄; D, 1 M LiOH + 1 $\times$ 10⁻⁶ M HgCl₂; E, 1 M LiOH + 100 $\times$ 10⁻⁶ M thiourea; F, 1 $\times$ 10⁻⁶ M LiOH.

effects of Hg and thiourea, Hg is more effective in order to increase the overpotential.

The influence of thiourea on the Tafel plots of η and η_2' in H_2SO_4 is shown in Fig. 2. With the addition of thiourea (solid

Fig. 2 Tafel plots of cathodic region of palladium electrode in 1 MH_2SO_4 with (full line) or without (broken line) 1.4×10^{-5} M thiourea. $\blacktriangledown$: η , $\triangledown$: η_2' . $T = 298$ K.

Fig. 3 Tafel plots of cathodic region of palladium electrode in 1 MH_2SO_4 with (full line) or without (broken line) 1.0×10^{-5} M HgCl_2 . $\blacktriangledown$: η , $\triangledown$: η_2' . $T = 298$ K.

line) the total overpotential η and the overpotential component η_2' were increased, but the slope did not change appreciably. This tendency was also seen in the case of HgCl_2 addition as shown in Fig. 3; the slope did not change after the addition but η increased more than that in the case of thiourea addition while η_2' increased as large as in the case of thiourea in spite of different concentration. The difference between the additives were found in LiOH solution, as shown in Figs. 4 and 5. The slope of η was $179 \text{ mV} \cdot \text{decade}^{-1}$ and that of η_2' was $62 \text{ mV} \cdot \text{decade}^{-1}$ in solution without additives (broken line), but with addition of thiourea in Fig. 4, the slope of η increased to be $268 \text{ mV} \cdot \text{decade}^{-1}$ while values of η_2' were decreased with no change of the slopes. After the addition of HgCl_2 in Fig. 5 both of η and η_2' increased and especially η_2' showed a signif-

Fig. 4 Tafel plots of cathodic region of palladium electrode in 1 MLiOH with (full line) or without (broken line) 2.0×10^{-5} M thiourea. $\bullet$: η , $\circ$: η_2' . $T = 298$ K.

icant change, but the slopes were not changed.

The changes of overpotential by the additives are summarized in Table 1. In LiOH solution, the addition of thiourea increased η by 250 mV (minimum) and η_2' by -36 mV and,

Fig. 5 Tafel plots of cathodic region of palladium electrode in 1 M LiOH with (full line) or without (broken line) 1.0×10^{-5} M HgCl_2 . ● : η , ○ : η_2' . $T = 298$ K.

consequently, the influence was larger on the Volmer process. That of Hg increased η by 466 mV and η_2' by 415 mV and in this case the influence was larger in the Tafel process.

The effect of concentration of the additive thiourea on overpotentials in LiOH is shown in Fig. 6, where overpotentials did not change in the range between 10^{-5} and 10^{-4} mol·dm⁻³. Total overpotential η decreased at the concentration above 10^{-4} mol·dm⁻³ while η_2' remained constant. On the contrary, for mercury, both overpotentials increased with the increase of HgCl_2 concentration, as shown in Fig. 7.

Fig. 6 Overpotential of palladium electrode at $100 \text{ mA}\cdot\text{cm}^{-2}$ in LiOH as a function of thiourea concentration. ● : η , ○ : η_2' . $T = 298$ K.

Table 1 Changes of the overpotentials related with discharge and surface chemical processes at current density from 2 to $200 \text{ mA}\cdot\text{cm}^{-2}$.

	thiourea addition			HgCl_2 addition		
	$\Delta\eta$	$\Delta\eta_1'$	$\Delta\eta_2'$	$\Delta\eta$	$\Delta\eta_1'$	$\Delta\eta_2'$
H_2SO_4	160	94	66	130	64	66
LiOH	250~418 ^a	286~454 ^a	-36	466	51	415

The values in the table is increase in the overpotential (mV) after the addition. The concentrations of additives were represented from Figs. 1 to 4. $\Delta\eta_1'$ was calculated by $\Delta\eta = \Delta\eta_1' + \Delta\eta_2'$. a, accompanied with the change of Tafel slope. The concentration of the additives was shown in Figs. 2 to 5.

4 DISCUSSION

4.1 Overpotential and additives in the mechanism of HER in sulfuric acid

The surface of the cathode in H_2SO_4 solution is usually considered to be clean enough to be investigated for the effect of strongly adsorbing additives on HER⁽³⁾. No evidence was found for the other processes occurring than Volmer-Tafel processes in our experiments. Thiourea adsorption takes more time to give steady overpotentials in comparison with the cases with no additives and HgCl_2 additives. This is explained that thiourea of neutral molecular species is adsorbed through slow surface processes, such as change of adsorption site and surface orientation change. On the contrary, a rapid process with HgCl_2 additives, as for that in pure H_2SO_4 , suggests that Hg ions are adsorbed rapidly enough to compose an electrode surface before the steady state attains in H_2SO_4 solution.

The addition of thiourea (Fig. 2) caused influence similar to steady overpotentials in the case of HgCl_2 (Fig. 3). Both η_1' and η_2' , which correspond to discharge and chemical processes, respectively, increased. These results suggest that thiourea and HgCl_2 inhibit both processes. But the difference $\Delta\eta_1'$ ($= \Delta\eta - \Delta\eta_2'$) was larger in thiourea addition than that in HgCl_2 addition while

Fig. 7 Overpotential of palladium electrode in LiOH at $100 \text{ mA} \cdot \text{cm}^{-2}$ as a function of HgCl_2 concentration. ● : η , ○ : η_2' . $T = 298 \text{ K}$.

$\Delta\eta_2'$ was almost the same for both (Table 1). This implies the suppression of discharge process, which is larger in Hg, and may be explained by the difference of the number of atoms blocked by these inhibitors.

It has been demonstrated that thiourea will be activated by the cathodic reduction into H_2S ⁽¹¹⁾. And it has been reported that H_2S may work as a promoter of the Volmer process on a steel⁽¹⁴⁾ unlikely to our results. Although the reason for this disagreement should be elucidated by the experiment further, it might be attributed to the difference in the strength of the surface S-metal bonds. The interaction between hydrogen and sulfur on surface will be weak on the surface with strong S-metal bond and it is possible that this effects on the Volmer process. Thiourea was reported as a promoter of hydride formation of nickel cathode in sulfuric acid⁽¹⁵⁾. This can be explained by the suppression of the recombination process and, consequently, agrees with our results. Palladium and mercury make an alloy easily⁽¹⁶⁾ and it is likely that the surface of the Pd cathode in the HgCl_2 added solution is alloy. Thus the mode of interaction of mercury species will be different from that of the molecular adsorbates like thiourea and may be like that of Li-Pd system.

The number of the surface atoms of palladium electrode is around $1 \times 10^{15} \text{ atoms/cm}^2$, assuming smooth surface, while the number of the additives in the solution (molecules/500 cm^3) were 4×10^{13} (thiourea) or 3×10^{17} (HgCl_2) in Figs. 2-5. The degree of suppression of the current in the same overpotential is around 10^{-2} , which means 99 % of the surface is covered by the inhibitor in a physical blocking model. The working efficiency of the inhibitors can be calculated to be 0.3 and the number of the covered sites per that of the inhibitor in the solution is given as 3×10^{-4} for thiourea or 3×10^{-3} for HgCl_2 .

4.2 Overpotential and additives in the HER mechanism in LiOH solution

SIMS studies have been shown that Pd cathode absorb Li ion during the electrolysis of LiOH solutions^(17, 18). And the surface structure must reflect some lattices of the

phases of Pd-Li alloys^{19, 20}. In this sense, the behaviour of Li ion itself and those of the alloy forming additives is considered somewhat alike. The coworkers of the Li ion and the additives were not the simple sums of them as already seen in Figs. 4 and 5. It is probable that they depends on the interaction on the surface.

The profile of the potential growth (Fig. 1) was different to H_2SO_4 , i.e., $HgCl_2$ additives stabilized overpotentials more rapidly than the cases of thiourea additives and no additives. The latter cases are suggested to include the slow surface reaction before steady state of surface is attained.

Overpotential components for both of discharge and the Tafel processes in alkaline solutions are higher than those in the acidic solutions. These higher overpotentials can be attributed to the alkali metal-poisoning on the electrode surface in our previous report.¹³ This offers the possibility that the strongly adsorbing materials such as thiourea and mercury salt work even as promoters in competitive adsorption.

In fact, thiourea decreased overpotential η_2' of Pd cathode in LiOH solution as shown in Fig. 4. On the other hand, η and η_1' increased much more comparing with those in H_2SO_4 . Therefore, it may be said that thiourea is a promoter of the hydrogen recombination on the surface in LiOH solution but behaves as an inhibitor of the discharge process. This is reasonably explained as follows. Lithium cation works already as a poison to both processes but after the addition of thiourea it also affects on each process differently instead of Li occupant on the surface. Li on Pd surface may make a strong bond to hydrogen, but it is not likely to make such strong bond between thiourea on the surface and hydrogen. Since the adsorption of thiourea occurs easier than Li ion and the latter could be a stronger inhibitor than thiourea for hydrogen recombination process, thiourea in Li solution works as an apparent promoter for this process.

In addition to the change of slope after thiourea addition, increase of η_1' was much larger than in H_2SO_4 , which suggests the synergistic poisonous effects of Li and thio-

urea on the discharge process.

The same η_2' observed from 10^{-3} to 10^{-5} mol·dm⁻³ of thiourea (the concentration corresponds to $3 \times 10^2 \sim 3 \times 10^3$ of surface atoms) suggests that in this current range, the adsorption of thiourea suffers little modification. Decrease of η (and therefore η_1') above 10^{-3} mol·dm⁻³ thiourea is probably due to the change in lithium cation adsorption/desorption equilibrium.

The effect of $HgCl_2$ is different from thiourea; $HgCl_2$ modifies η_2' strongly rather than η_1' . And it directly corresponds to the strong suppression of the Tafel process and weak modification of discharge process. This is understandable if one consider the chemical nature of mercury, metallic but weak in interactive force with hydrogen. Mercury may work as a dischargable site and at the same time as an inhibiting site against chemical reaction of hydrogen.

The mode of the inhibition of mercury and lithium ions are alike in terms of alloy formation. And it is likely that the concentration of these element near surface of the cathode is not high because of the diffusion into the bulk. In fact the overpotential never reach the level of mercury cathode and the concentration of Li in the SIMS was at most 1 %^{17, 18}. Thus the ions can be absorbed almost independently of each other. Thus it is very reasonable that $HgCl_2$ addition increase η_2' even in LiOH solution just as LiOH solution shows high η_2' comparing other electrolytes; the effect of Hg ion on overpotentials is overlay on that of Li ion.

CONCLUSIONS

The overpotential of Pd cathode in H_2SO_4 and LiOH solution was measured by the addition of Hg_2Cl_2 and thiourea. In LiOH solution Hg addition was effective to increase the overpotential of the recombination step. From the result the addition of Hg might be effective to promote the hydrogen absorption into Pd metal and obtain the high H/Pd ratio.

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