

Absorption of Hydrogen into Palladium Foil Electrode: Effect of Thiourea

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ABSTRACT

Electrolytic hydrogen absorption into Pd foil (50 μ m thickness) was investigated in the absence and presence of 30 μ M thiourea (THU) in 0.5M H₂SO₄ and 0.4M LiOH. The amount of hydrogen absorbed under cathodic polarization was determined by integrating the ionization current of hydrogen when Pd electrode was polarized anodically.

After THU addition in the acidic and alkaline solution H/Pd increased by about 8% and 5%, respectively.

Further we tried absorption of deuterium into Pd foil and found a similar effect of THU to increase D/Pd only in the acidic solution.

1. Introduction

Cold fusion phenomena in Pd cathode has been said to occur when the deuterium loading ratio, D/Pd, is higher than 0.9. But it is not easy to attain such high value of D/Pd by an ordinary electrolysis method. Therefore it is very important to find the experimental condition to increase the loading ratio higher than 0.9.

Enyo *et al.*^{1) 2)} demonstrated that the hypothetical hydrogen pressure $P_{H_2}^*$ acting on the Pd hydrogen electrode was related to the overpotential of the Tafel step by the following Nernst type equation;

$$P_{H_2}^* = P_{H_2} \exp(-2F \eta_2 / RT)$$

where P_{H_2} is hydrogen gas pressure in the cell and η_2 the overpotential of Tafel step ($2H(a) \rightarrow H_2$) for hydrogen electrode reaction on palladium, and that thiourea ((NH₂)₂CS) in acidic solution poisoned Tafel step and accordingly increased η_2 .

So we reinvestigated absorption of hydrogen/deuterium into Pd electrode under cathodic polarization in aqueous solutions containing THU in expectation of a rise in H(D)/Pd value.

2. Experimental

The design of a glass cell for electrolysis is shown in Fig.1. We used a palladium foil ($50 \mu\text{m}$ thickness \times 5mm \times 5mm) which was pretreated in vacuum at 200°C for one hour as a working electrode. A platinum black mesh and a reversible hydrogen electrode (RHE) were used as an auxiliary and a reference electrode, respectively. All the experiments were performed in acidic solutions ($0.5\text{M H}_2\text{SO}_4$, D_2SO_4) or in alkaline solutions (0.4M LiOH , LiOD), bubbling nitrogen or argon gas throughout the experiment.

The absorption and desorption of hydrogen into/from Pd foil were carried out at 283K controlling the potential of Pd electrode as shown in Fig.2a. First hydrogen were absorbed into Pd foil under potentiostatic cathodic polarization. After a given period of electrolysis, Pd foil was then polarized anodically and all the absorbed hydrogen were desorbed from Pd. Fig.2b shows typical current response curve to these potential control. The negative and positive currents were integrated to give as "input charge" and "discharge charge", respectively, and loading ratio H/Pd was estimated as follows.

$$H/Pd = \frac{(\text{discharge charge})/(\text{Faraday constant})}{(\text{the mole number of Pd in the cathode})}$$

Hydrogen absorption and H/Pd measurement were performed using the same Pd foil repeatedly before and after the addition of $30 \mu\text{M THU}$.

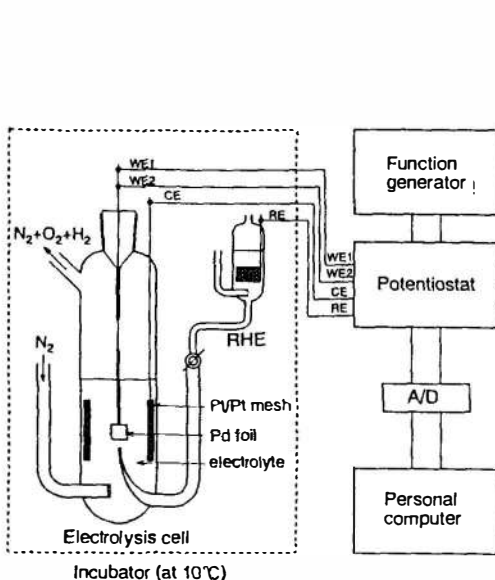


Fig.1. Schematic of experimental device

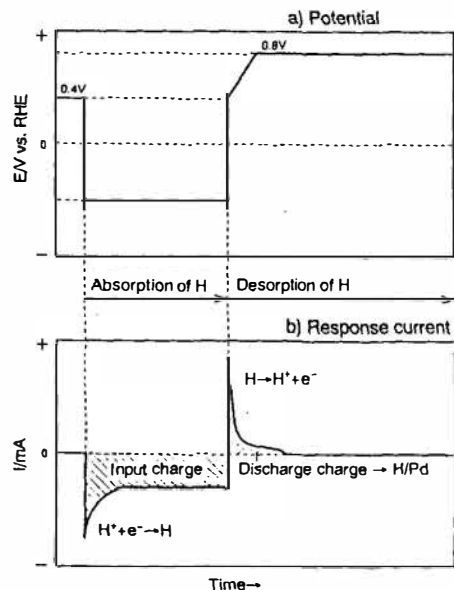
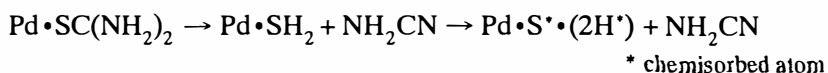


Fig.2. Charging and discharging process

3. Result and Discussion

Cyclic voltammetry of Pd foil electrode

Cyclic voltammograms for the Pd foil electrode in the absence and presence of THU in 0.5M H₂SO₄ are presented in Fig.3. After addition of THU in the electrolyte, two changes in voltammograms were observed; one was a decrease of the negative current peak at approximately +0.7V due to the reduction of the oxidized layer on Pd, and the other was an increase in anodic current above +1.0V. Bucur *et al.*³⁾ suggested that THU molecules were hydrolyzed and dissociated on the surface of Pd electrode as follows.



It was considered that resulting S* atom hindered oxidation of Pd and caused the decrease of the negative peak current due to reduction of the surface oxide, and that the increase in anodic current was due to oxidation of S* atom to SO₄²⁻.

Figure 4 shows voltammograms of the Pd foil for the extended potential sweep into the cathodic region. The current due to hydrogen evolution and absorption into the Pd foil were observed in the negative potential sweep, and upon the positive potential sweep discharging current due to the ionization of absorbed hydrogen desorbing from Pd was observed. The addition of THU led to the retardation of hydrogen evolution and absorption as well as of hydrogen desorption/ionization upon positive potential sweep.

A similar tendency was observed in 0.4M LiOH containing THU.

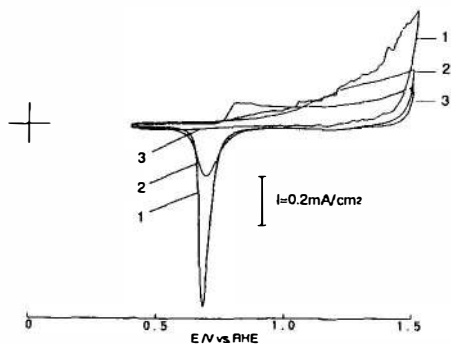


Fig.3. Cyclic voltammograms for Pd electrode in 0.5M H₂SO₄ containing
1: no THU, 2: 30 μM THU and
3: 200 μM THU.

sweep rate: 50mV/sec

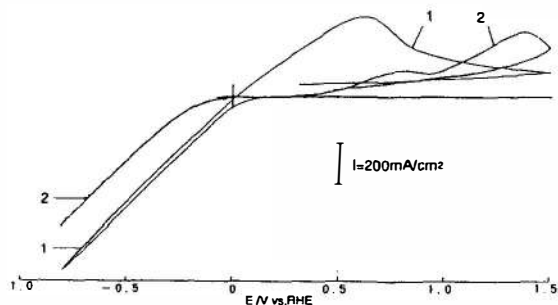


Fig.4. Linear sweep voltammograms for Pd electrode in 0.5M H₂SO₄ containing
1: no THU and 2: 30 μM THU.

sweep rate: 50mV/sec

Effect of THU on H/Pd (D/Pd) value

The relationship between H/Pd and input charge measured in 0.5M H₂SO₄ is shown in Fig.5. The amount of the input charge necessary for hydrogen to fill the Pd foil is 13~14 coulomb. While H/Pd in the electrolyte without THU kept nearly a constant value of 0.77 independent of input charge, after the addition of 30 μM THU in electrolyte the value reached 0.85; approximately 8% increase of H/Pd was observed.

Figure 6 shows the result in 0.4M LiOH. In the alkaline solution H/Pd value tended to rise with increase of input charge. H/Pd went up maximally by 5% after addition of THU. We could not compare the H/Pd values in the acidic solution directly with that in the alkaline solution, because the electrolysis potential was not the same. However the rise in H/Pd was confirmed in both electrolytes.

Further we studied absorption of deuterium into Pd foil in 0.5M D₂SO₄ and 0.4M LiOD. D/Pd value, 0.82, obtained in 0.5M D₂SO₄ containing 30 μM THU was 6~8% higher than in the electrolyte without THU. But little effect of THU on D/Pd was found in 0.4M LiOD at this concentration of THU.

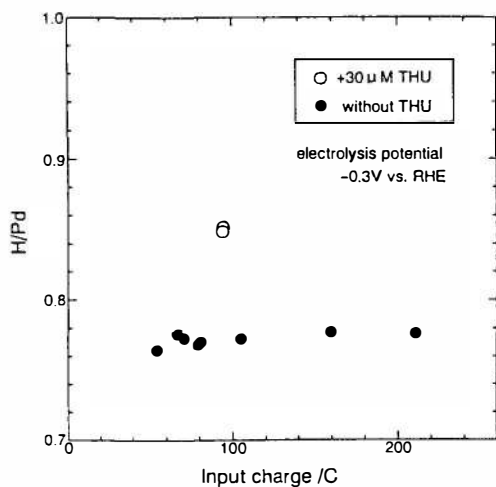


Fig.5. H/Pd vs. Input charge in 0.5M H₂SO₄ at 283K

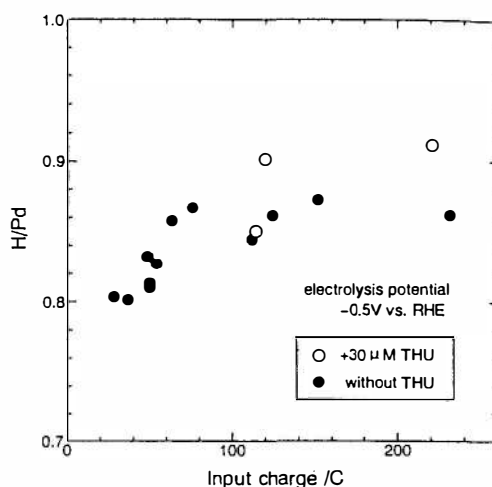


Fig.6. H/Pd vs. Input charge in 0.4M LiOH at 283K

4. Conclusion

The addition of 30 μM THU into electrolytes except 0.4M LiOD led increase of hydrogen loading ratio in Pd electrode. The effect of THU should be investigated further by varying the hydrogen overpotential on Pd and the concentration of THU.

5. References

- 1) T.Maoka and M.Enyo, *Surface Tech.*, **9**, 147 (1979)
- 2) T.Maoka and M.Enyo, *Electrochimica Acta.*, **26**, 607 (1981)
- 3) R.V.Bucur and P.Marginean, *Electrochimica Acta.*, **29**, 1297 (1984)