ON ELECTRICAL PHENOMENA OF PALLADIUM FILAMENT OCCLUDING HYDROGEN II

Investigation of HIROTA and HORIUTI's Results

By

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Introduction

Migration of hydrogen dissolved in palladium along a potential drop was observed by COEHN and his co-laborators[1]. This phenomenon was further studies by DUHM[2], who determined the effective positive charge of the dissolved hydrogen according to the NERNST-EINSTEIN relation from the measured diffusion coefficient and the mobility.

The presence of cationic hydrogen in palladium was also concluded as follows by HIROTA and HORIUTI[3] from their experiments on electrical phenomena of a palladium filament occluding hydrogen. They balanced with a steady current a Wheatstone bridge comprizing in one of its arms a palladium filament sealed in a glass cell immersed in a thermostat at 100°C and filled with hydrogen of 10^{-1} mm Hg, and then left the circuit through the bridge open for one hour. On closing now the circuit, they observed a current through the galvanometer of the bridge, which decayed exponentially with time until the bridge was balanced again; on opening the circuit after the balance a current decaying similarly was observed in the reverse direction. These phenomena were interpreted as the migration of dissolved proton through potential gradient along the filament and the diffusion of the polarized proton back to the uniform distribution in the absence of the potential gradient.

The present author has pointed out in his previous paper[4] the discrepancies between HIROTA and HORIUTI's results and those of other authors. One of these discrepancies is that of the transference number of proton in palladium metal, *i.e.* the ratio of the current carried by proton to the total current carried by proton and electron. The transference number of proton in palladium amounts to at least 10^4 times as large as that extrapolated at 100°C from the results by WAGNER and HELLER[5] at 182°C and 240°C, as deduced from the

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HIROTA and HORIUTI's result attributing the above phenomena to the co-conduction of proton as shown in Appendix.

Experimentally, the HIROTA and HORIUTI's result could not now be reproduced, as reported previously[4]. It might however be possible on the basis of the observation by WAGNER and HELLER that the phenomena reported by HIROTA and HORIUTI is at least qualitatively reproduced, if the concentration of dissolved hydrogen in palladium is increased to 10^2 times as large as that of HIROTA and HORIUTI's experiment, and the sensitivity of the galvanometer is raised hundredfold as well.

The above conclusion has been thrown to the experimental tests as described in what follows.

Experimental and Results

A palladium filament of 10 μ was prepared by dissolving a silver integumentary layer of palladium Wollastone wire supplied by Ishifuku Metal Industrial Co. Ltd. Tokyo. The filament of *ca.* 1.5 cm length thus prepared was stretched between two platinum wires connected via nickel wires to Dumet wires sealed in a glass stem. The filament was now cathodically electrolysed by a constant current (0.1 mA) in a solution of 1/10 N H_2SO_4 against a platinum anode, until the resistance of the filament was steadily increased up to a value *ca.* 1.65 times the initial value as followed by means of 1000 c/s A.C. bridge.

The above increment of the resistance corresponds to the hydrogen concentration in terms of atomic ratio $H/Pd=0.7$[6], which is 3×10^2 times as large as that in the case of the HIROTA and HORIUTI's experiment, which was extrapolated from the observation of HOITSEMA[7], assuming that the dissolved hydrogen is in equilibrium with 0.1 mm Hg of hydrogen gas. The hydrogen thus dissolved was found to decrease, as followed by the resistance measurement described above, by anodic electrolysis or by keeping the filament in air at room temperature.

Mercury was now deposited on the filament of the high hydrogen content as mentioned above by a cathodic electrolysis in the 1/10 N H_2SO_4 solution containing 2×10^{-4} g $HgCl_2$ per 100 c.c. solution against the platinum anode. This procedure was found to have effectively checked the passage of hydrogen through the surface of the filament in conformity with the previous experimental result[4] that the desorption of hydrogen from the palladium filament at 100°C was retarded by the exposure of the filament to mercury vapor.

A cell was constructed by fusing a blind tube of 1.2 cm inner diameter and 15 cm length to the glass stem, which supports the palladium filament as

described above. The cell was now connected to a vacuum line, evacuated for a short time, filled with hydrogen of *ca.* 60 cm Hg pressure and then immersed in a thermostat at 100°C.

The palladium filament thus enclosed in the cell was inserted to one arm of the Wheatstone bridge, which was the same as that previously reported[4], except for the galvanometer. The galvanometer used in the present experiment has a high voltage sensitivity, 3.45×10^{-8} V/mm in scale *i.e.* about 30 times higher than that of previously used, and a relatively low internal resistance, 25.8 Ω.

Procedures of the observation were the same as previous ones: the bridge were at first balanced by closing the circuit of a steady current through it passing 2×10^{-4} A through the filament for a quarter of an hour, then left for one hour with the circuit open, and thereafter again closed. No deflections of the galvanometer were found besides that arising from the zero point shift or the thermal electromotive force. The result was the same when the circuit was opened again after closed as above. The dissolved hydrogen in the palladium filament was retained almost unchanged as confirmed by the resistance measurement referred to above.

Discussion

COEHN and JÜRGENS[1] have observed the effect of the potential drop along a palladium wire on the diffusion of hydrogen dissolved at the middle portion toward the both ends. The effect was observed by measuring the ratio of the resistance of the negative half of the wire to that of the positive one by forming two arms of a Wheatstone bridge with the two halves of the wire connected at the middle. They have thus found that the ratio increases with the time, during which the potential drop was applied, but remains constant without the potential drop was applied.

The increase of the ratio was found, however, of the order of magnitude of 1/1000 as caused by a potial drop of 4.3×10^{-2} V/cm applied for 10 min., which shows that the migration of proton along the potential drop is extremely small.

On the other hand, the quantity of electricity conveyed by electron after opening the circuit through the bridge is, as calculated from the observation of HIROTA and HORIUTI*), nearly same to the total charge of proton dissolved in the filament at equilibrium with 0.1 mm Hg of hydrogen gas. This could only be the case, where the dissolved hydrogen is almost perfectly dissociated

*) Cf. Appendix.

into proton and electron in the palladium filament, and the proton is accumulated almost perfectly to the negative end after applying the potential drop 4×10^{-3} V/cm for 10 min. This conclusion is too far different from the result of COEHN and JÜRGENS, if there be more or less difference of the experimental condition *i.e.* dimension of the wires, strength of applied potential, and temperatures. It requires further investigation to elucidate the discrepancy.

Conclusion

The results described above show that the phenomenon reported by HIROTA and HORIUTI is not reproducible even under a more favorable condition.

The author wishes to express his sincere thanks to Professor J. HORIUTI for his advice and encouragement.

Appendix

The lower bound of the transference number of proton was calculated from the result of the HIROTA and HORIUTI's experiment as follows. We consider first as an ideal case a palladium filament *Pd*, which combines as shown in Fig. 1 the anodic compartment *A* and the cathodic one *C*, both filled with hydrogen gas of the same pressure, and is electrically connected at the both ends *a* and *c* respectively exposed to hydrogen in *A* and *C* to compose the Wheatstone bridge, under the following conditions.

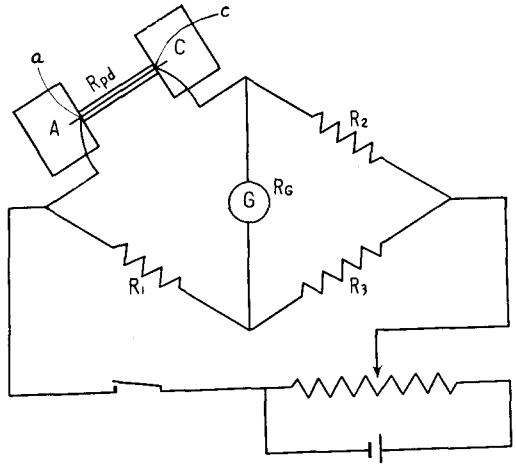

Fig. 1.

i) Hydrogen is allowed to be absorbed or desorbed by the filament only through the surface exposed to hydrogen in either compartment but not through its surface in the intermediate region.

ii) Hydrogen diffuses only through the filament but not through the other leads of the Wheatstone bridge.

iii) The total resistance R_2+R_3 of the two arms of the Wheatstone bridge are extremely large compared with any of the resistances R_1, R_{Pd} of the filament and R_G of the galvanometer G similar to the case of the HIROTA and HORIUTI's experiment.

Consider now that the circuit through the bridge is closed, hence a quantity Q of electricity is passed through the filament causing an amount $n_p/2$ mol hydrogen to transfer from the anodic to cathodic compartment, to change the hydrogen pressure in both the compartments by an infinitesimal amount. The quantity of electricity carried by proton is expressed as

$$Fn_p = Q \cdot N, \qquad (1)$$

where F is Faraday and N the transference number of proton.

On opening the circuit, the pressure difference causes hydrogen to diffuse back through the filament from the cathodic to the anodic compartment. This results in a flow of a current through the bridge, insofar as the hydrogen dissolved in the filament is more or less dissociated. Let Q_G be the quantity of electricity passed through the galvanometer. The total amount of electricity conveyed by electron from a to c is, according to (iii), $Q_G\ (R_G+R_1+R_{Pd})/R_{Pd}$, which equals Fn_p provided that the dissociation of hydrogen into proton and electron were complete. In the general case, where the dissociation is more or less incomplete, $Q_G\ (R_G+R_1+R_{Pd})/R_{Pd}$ is not greater than Fn_p, *i.e.*

$$Fn_p \geq Q_G\ (R_G+R_1+R_{Pd})/R_{Pd}\,. \qquad (2)$$

We now compare the HIROTA and HORIUTI's experiment with the above ideal case, identifying R_1, R_2, R_3, R_{Pd} and R_G with corresponding quantities in the former case, where it is assumed that the conditions (ii) and (iii) are satisfied and the degree of dissociation is the same as in the ideal case. If, besides, the condition (i) were satisfied and further n_p protons were transferred by electricity of the quantity Q passed and crowded at the boundary of the very cathodic junction, leaving the filament at the uniform concentration of proton otherwise, the same quantity of electricity as that in the ideal case must be conveyed from the anodic junction to the cathodic one, hence (2) holds even in this case. In the real case of the HIROTA and HORIUTI's experiment, however, such distribution as described above can not be realized,

because of the back diffusion of protons from the cathodic junction and of the condition (i) being not necessarily fulfilled. Either of the above situations causes now the quantity of the electricity passed from the anodic to the cathodic junction on opening the circuit to decrease from that $Q_G\ (R_G+R_1+R_{Pd})/R_{Pd}$ in the above ideal case.

Let Q'_G be the quantity of electricity passed through the galvanometer in the real case in place of Q_G. We have in consequence

$$Q'_G < Q_G\,,$$

hence according to (1) and (2)

$$Q \cdot N > Q'_G\ (R_G+R_1+R_{Pd})/R_{Pd}\,,$$

which allows us to calculate the lower bound of the transference number N of proton from the HIROTA and HORIUTI's experiment.

Q was calculated at 1.2×10^{-1} coulomb from the result of the HIROTA and HORIUTI's experiment as the product of the current (2×10^{-4} A) passed through *Pd* and the time (10 min.) elapsed from the closure of the circuit to the balance of the bridge and Q'_G at 1.8×10^{-5} coulomb by integrating the observed current decaying to zero over the time. The value of $(R_G+R_1+R_{Pd})/R_{Pd}$ is given as 3 from the HIROTA and HORIUTI's experiment. We have hence 4.5×10^{-4} as the lower bound to N according to the above inequality.

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