Theoretical Analysis of the Hydrogen Wave on Platinum Single Crystal Electrodes

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The hydrogen waves on the low index planes of platinum single crystal electrode except the square-wave part for Pt(111), were qualitatively explained by the Huckel method for the adsorbed hydrogen orbitals with the periodic boundary conditions. The square-wave part was explained by the free electron model in the two dimentional adsorption layer.

It is well known that the underpotentially deposited hydrogen (Upd-H) on platinum is markedly structure-sensitive. In H_2SO_4 solution, the hydrogen wave on Pt(111) consists of two parts : the square-wave part in 0.05-0.32 V and the following part in 0.32-0.5 V with a sharp spike at 0.45 V(50 mVs^{-1}). The square-wave pattern for the adsorption isotherm is out of the scope of analysis when the analysis is based on the simple Lungmiur model since the analysis gives always a bell shaped wave. The latter part with the spike has been discussed in connection with the specific adsorption of the hydrogen-sulphate ion[1] but the interpretations are still controversial.[2] What we have known is that the latter part disappears in $HClO_4$ solution and instead a new peak, so-called butterfly, appears in 0.55-0.8 V. The hydrogen wave on Pt(100) in H_2SO_4 solution gives a sharp but left-side tailing peak centered at 0.35 V. The hydrogen wave on Pt(110) in H_2SO_4 shows also a single but symmetrical main peak centered at 0.13 V. This main peak has been analysed satisfactorily with the Lungmuir model with the mutual interaction.[3] The mutual interaction (proportional approximation), came out to be attractive and amounted to 1.8 RT mol^{-1} at the full coverage.

The present work aims to analyze the structure-sensitive hydrogen waves observed at Pt(111), Pt(100) and Pt(110) in 0.1 M $HClO_4$ at a sweep rate of 50 mVs^{-1} by treating the mutual interaction among Upd-H by the Huckel method. The perchlorate ion is known not to specifically adsorb on the Pt planes.

In the analysis, we treated the lattice of the adsorbed hydrogens consisting of M and N lattice points in directions 1 and 2. The plane of interest consists of M × N lattice points. Each lattice point was numbered, 1,2, ・・・, i, j, ・・・・・. Each number has two coordinates because the two-dimentional lattices are concerned. These coordinates were represented with respect to i and j, as (i_1, i_2) and (j_1, j_2), respectively. Figure 1 illustrates j's lattice points neighbouring to i (i_1, i_2).

The matrix elements representing the interaction between i-th and the neighbouring j-th lattice points, $A_{i,j}$s, were expressed for the case of Pt(111) by the graph theory [4,5] in terms of the δ-functions as follows.

$$A_{i,j} \equiv \delta_{i_1 j_1 - 1}\cdot\delta_{i_2 j_2} + \delta_{i_1 j_1}\cdot\delta_{i_2 j_2 - 1} + \delta_{i_1 j_1}\cdot\delta_{i_2 j_2 - 1} + \delta_{i_1 j_1 + 1}\cdot\delta_{i_2 j_2} + \delta_{i_2 j_2 + 1}\cdot\delta_{i_1 j_1} + \delta_{i_1 j_1 + 1}\cdot\delta_{i_2 j_2 + 1} \quad (1)$$

The matrix elements of Pt(110) and Pt(100) were given by eliminating the third and sixth terms of Eq.(1) in both cases. The matrix was diagonalized by using Fourie type eigenvectors and then the periodic boundary conditions were introduced.[4,5] Details will be described elsewhere.

Eigenvalues, λ_k, were obtained as follows,

$$\text{Pt(111)} : \lambda_k = 2\,[\cos 2\pi k_1 / M + \cos 2\pi k_2 / N + \cos (2\pi k_1 / M + 2\pi k_2 / N)] \quad (2)$$

$$\text{Pt(100)} : \lambda_k = 2\,[\cos 2\pi k_1 / M + \cos 2\pi k_2 / N] \quad (3)$$

$$\text{Pt(110)} : \lambda_k = 2\,[\cos 2\pi k_1 / M + r \cos 2\pi k_2 / N], \quad (4)$$

where k_1 and k_2 are the components of wave vector, k, with respect to directions 1 and 2 and r is a parameter, being $0 < r < 1$. The parameter r originates from the unequal unit distances in directions 1 and 2 on Pt(110) and its value will be determined semi-empirically from the comparison with the hydrogen waves. Energies, ε_l , were given by the following expression according to the Huckel approximation,[6]

$$\varepsilon_l = \alpha + \lambda_l \beta , \quad (5)$$

where α and β are the Coulomb integral and the resonance integral of the hydrogen atom orbital, respectively. β was assumed to be negative according to our previous conclusion that the mutual interaction is attractive.[3] The densities of states, D.O.S. ($cm^{-2} \cdot eV^{-1} \cdot mol$), on the three kinds of lattices (sizes, MN= 200 × 400) were calculated by an electronic computer .

The hydrogen waves to be compared are represented in Figures 2a-2c with respect to Pt(111), Pt(100) and Pt(110) (dotted lines). In the calculation, α and β for each plane were determined as follows. In the case of Pt(111), α−2β was taken to correspond to the peak potential of the butterfly, 0.80 V, since D.O.S. became maximum at ε_l of α−2β. The values of α on Pt(100) and Pt(110) were taken from the energies which correspond to the peak potential at Pt(100), 0.35 V, and the center potential between the two peaks at Pt(110), 0.18 V, respectively. On the other hand, the value of α + 6β for Pt(111) which gives the lowest energy was taken to correspond to the cathodic terminal potential of the butterfly, 0.55 V. This implies that to explain the square-wave part on Pt(111) which appeared in a potential range of 0.05-0.35 V, an entirely different approach should be applied as discussed later. However, the values of α + 4β and α + 2(1+ r)β for Pt(100) and Pt(110) were taken to correspond to the cathodic end potential of the hydrogen wave, 0.05 eV. The respective α's and β's obtained were as follows,

Pt(111)	Pt(100)	Pt(110)
α = 0.74eV	α = 0.35eV	α = 0.18eV
β = −0.031eV	β = −0.075eV	β = −0.041eV (r =0.6).

In the presentation of the calculated results, the unit of the ordinate was adjusted so that the total number of energy levels becomes equal to the area of the corresponding hydrogen wave which gives the number of Upd-H when multiplied by N_A / F.

The calculated result for Pt(111), Figure 2a (solid line), shows only one peak which locates much more close (positive) to the highest energy allowed. Thus, the calculated curve reproduces the essential feature of the "butterbly" (dotted line). However, the hump-like behavior of the current on the left hand side of the peak was not reproduced. The shape of Pt(100) in Figure 2b (solid line) is symmetric and has only one peak but the experimental hydrogen wave (Figure 2b, dotted line) consists of two peaks at 0.29 and 0.35 V. Since the pre-peak is pretreatment-sensitive as in H_2SO_4 solution,[2,7] the peak at 0.35 V is taken as the main peak. In this sence, the theoretical result reproduces the essential feature of the hydrogen wave of Pt(100). The theoretical curve of Pt(110) has two peaks of the same height as shown in Figure 2c (solid line). The experimental one has also two peaks though the peak heights are different (Figure 2c, dotted line). The separation of the two peak was reproduced at $r = 0.6$.

The values of $|\beta|$ (attractive) were 1.2 RT, 2.9 RT and 1.6 RT mol^{-1} on Pt(111), Pt(100) and Pt(110), respectively. Our previous result of 1.8RT mol^{-1} for Pt(110)[3] is in a good agreement with the present value.

In the calculation, we changed the number of M × N (1000-16000) but the essential features of D.O.S. remained the same. The greater the mumber is, the more smooth curve was obtained. Effect of the removal of the periodic boundary condition for one of the two directions was also examined. The detail will be described elsewhere.

The square-wave part of Pt(111) gives about two thirds of the monolayer charge of Upd-H. When the Upd-H coverage exceeds one third, the adsorption mode must be taken to change completely, giving rise to the square-wave pattern isotherm. Thus, we assume the model where the hydrogen atom or its electron moves freely in the two dimentional adsorption layer like the free electron model in metal. Taking the adsorption layer of a size of a × a, the energy, ε_n, is given as follwos.[6]

$$\varepsilon_n = (n_x^2 + n_y^2)\, h^2/(8ma^2), \qquad (6)$$

where the symbols have usual meanings. In the two dimentional quantum space consisting of n_x and n_y, the number of energy levels having a value of $\leqq \varepsilon_n$ is given as

$$N = \pi R^2/4, \text{ where } R^2 = n_x^2 + n_y^2. \qquad (7)$$

The factor of (1/4) in Eq. (7) is due to the condition that only positive integers are allowed for n_x and n_y. Then, the density of state is given from Eqs. (6) and (7) as

$$\text{D.O.S.} = dN/d\varepsilon = 2\pi ma^2/h^2 \qquad (8)$$

D.O.S. appears constant independent of ε and thus the above equation is in harmony with the square-wave pattern where the current is constant, being independent of the electrode potential. From the charge of the square-wave part, 160 μF cm^{-2}, we can calculate the number of Upd-H as 1.0 × 10^{15} cm^{-2}. Substitution of this number to D.O.S. of Eq.(8) gives the value of 12 × 10^{-30} kg to m which is far from 1.7 × 10^{-27} kg (static) of proton, but close to 0.91 × 10^{-30} kg (static) of electron. This verifies that the adsorbed hydrogen of the square-wave part releases its electron which moves freely in the adsorption layer. The hydrogen of the butterfly and other hydrogens on Pt(100) and Pt(110), on the other hand, localize their electrons near the adsorption sites.

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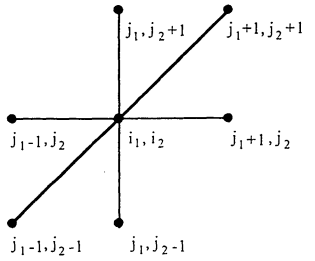

Figure 1. Neighbouring j's to i on Pt(111).

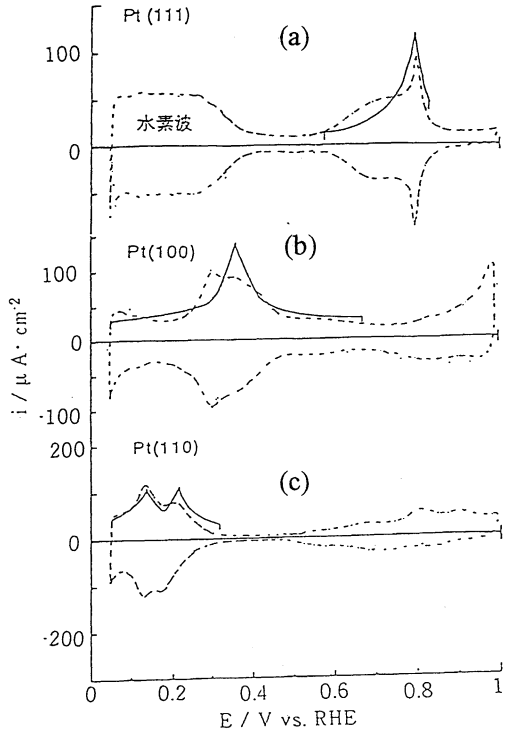

Figure 2. Hydrogen waves (dotted curve, 0.1M $HClO_4$, 50mV s^{-1}) and density of state (solid curve) on a) Pt(111), b) Pt(100) and c) Pt(110).

References and Notes

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