

Determination of adsorption energy distribution function on monocrystalline platinum

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Abstract

Hydrogen underpotential deposition (upd) on monocrystalline platinum was studied by cyclic voltammetry. Hydrogen adsorption isotherms were determined from cyclic voltammetric experiments and the corresponding adsorption energy distribution functions were calculated. The distribution function of the first kind. Hydrogen upd in HClO₄ was studied and the standard adsorption energies was determined. In the case of Pt(100) the standard adsorption energy distribution of the interaction parameter was linear with coverage. The standard adsorption energy distribution function of the first kind was determined and a good agreement was obtained between the calculated and experimental values.

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planes of platinum is a complex process. Hydrogen isotherms determined from cyclic voltammetric experiments were used to calculate the adsorption energy distribution functions. This problem leads to the Fredholm integral equation of the first kind. Hydrogen adsorption isotherms were determined assuming a local Langmuir isotherm and the distribution function of the first kind. The distribution functions obtained are much narrower so the local Frumkin isotherm was used and the standard adsorption energy distribution function of the first kind. The distribution functions obtained were used to reconstruct the isotherms and experimental isotherms. The proposed method gives good insight into the interactions of H-Pt.

1. Introduction

The determination and understanding of adsorption isotherms belong to the most fundamental problems in catalysis and electrocatalysis. Even in simple cases, adsorption isotherms are complex because of the heterogeneity of surfaces and interactions between adsorbed species.

One of the simplest electrocatalytic processes is hydrogen underpotential deposition (upd) on metals, especially on platinum. However, this process is quite complex, even on well-defined Pt surfaces [1]. This is principally related to the overlap of the H and ionic

adsorption, surface reconstruction, etc. Until now we do not have any general models explaining these processes, mainly because of the lack of detailed experimental isotherms of the individual species.

Recently [1], we have studied isotherms of hydrogen upd on Pt(100), (110) and (111) in HClO₄ and H₂SO₄ and determined Gibbs energies of adsorption as functions of hydrogen surface coverage, standard Gibbs energies of adsorption and interaction parameters and their derivatives. Only in the case of Pt(100) in HClO₄, Pt(110) in H₂SO₄ and Pt(111) was the Gibbs adsorption energy, $\Delta G_{\text{ads}}(\Theta_H)$, a linear function of the surface coverage, Θ_H , indicating a Frumkin-type adsorption isotherm; in the other cases the isotherm was more complex and nonlinear.

In general, any adsorption isotherm may be treated as distributed and the adsorption energy distribution function may be described, without any assumptions, by the Fredholm integral equation of the first kind

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$$\Theta_H(E) = \int_a^b K(u, E) f(u) du, \quad (1)$$

where $\Theta_H(E)$ is the potential dependent surface coverage by adsorbed hydrogen, $f(u)$ is a dimensionless distribution function, $K(u, E)$ is the equation kernel, that is the assumed local adsorption isotherm, $u = \Delta G_{\text{ads}}/RT$ is the dimensionless hydrogen adsorption function, and E is the electrode potential [2,3]. The main assumptions in the above equation are that the adsorption may be described locally by the isotherm described by the kernel, e.g., simple Langmuir isotherm, the adsorption energy on different areas of the surface, u , is different, and the distribution of adsorption energies is described by the function $f(u)$. The main difficulty with determination of $f(u)$ from Eq. (1) is that this is an ill-posed problem and so-called regularization techniques are used to stabilize the solution [4–6]. This technique is widely used in the heterogeneous adsorption studies from the gas phase. Its main advantage is that it can be used to analyze directly the experimental data Θ or $d\Theta/dE$ vs. E without any other assumptions about the distribution function. Although this method is often used in the heterogeneous adsorption from the gas phase, because of a quite limited amount of data in these measurements quite often the (mathematical) shape of the distribution function is assumed and only its parameters are determined. The electrochemical method provides a lot of high quality experimental points permitting such an analysis without the assumptions about $f(u)$.

In our earlier work [6] we have applied such a technique to determine the upd hydrogen adsorption distribution function on polycrystalline and (531) platinum. As the kernel, the Langmuir isotherm was used

$$K(u, \eta) = \theta_H = \frac{1}{1 + \exp(u + F\eta/RT)}, \quad (2)$$

where θ_H is the local adsorption isotherm, and η is the hydrogen overpotential. Then, the integral Eq. (1) becomes

$$\Theta_H(\eta) = \int_{u_1}^{u_2} \frac{1}{1 + \exp(u + F\eta/RT)} f(u) du. \quad (3)$$

In practice, it is possible to determine $d\Theta_H/d\eta$ directly from the cyclic voltammograms and it is preferable to use the derivative kernel [6]

$$\begin{aligned} K(u, \eta) &= \frac{d\theta_H}{d\eta} = \frac{F}{RT} \theta_H(1 - \theta_H) \\ &= \frac{F}{RT} \frac{\exp(u + F\eta/RT)}{[1 + \exp(u + F\eta/RT)]^2} \end{aligned} \quad (4)$$

and

$$\frac{d\Theta_H}{dE} = \int_{u_1}^{u_2} \frac{(F/RT) \exp(u + F\eta/RT)}{[1 + \exp(u + F\eta/RT)]^2} f(u) du. \quad (5)$$

The derivative form of the equation, Eq. (5), is less sensitive to the experimental errors than the direct isotherm, Eq. (3) [6]. In the present paper we have analyzed hydrogen upd adsorption on three Pt basal planes (100), (110) and (111) in 0.1 M HClO₄ and 0.5 M H₂SO₄. Determination of the distribution functions is much easier using the electrochemical rather than the gas adsorption technique, as many more experimental points of $d\Theta_H/d\eta$ are available from the cyclic voltammograms than from the classical adsorption experiments.

In the present manuscript we have applied this method to the basal Pt(*hkl*) surfaces. In our earlier paper [6] we have shown that there is a formal equivalence between the Frumkin or Temkin isotherms and the distribution of sites (see Figs. 3 and 4 in [6]). Although there is no statistical-mechanistic proof that there is a continuous distribution of sites on monocrystalline surfaces, because of this equivalence it seems reasonable to assume that, because of the presence of adsorbed hydrogen atoms at different interatomic distances on the electrode surface, there are different effective adsorption energies for different atoms.

2. Experimental

Cyclic voltammograms were obtained from Professor Juan Feliu, University of Alicante, Spain and are the same as in our earlier work [1]. More experimental details were given in our earlier paper [1]. Details of the solution of the integral Fredholm equations were given in [6]. Integral equations were solved in the Matlab program using subroutines developed by Hansen [5,7]. Curves of $d\Theta_H/d\eta$ vs. η were analyzed using several regularization methods and the automatic selection of the regularization parameter from the L-curve [5,7]. As the results obtained using different methods described in [5,7] gave similar results, only the results obtained using Tikhonov regularization are shown here. Comparison of different regularization methods will be published elsewhere.

3. Results

3.1. HClO₄

3.1.1. Pt(111)

As was discussed earlier [1] the ionic adsorption on Pt in HClO₄ is not observed or it is relatively weak. The parameter $d\Theta_H/d\eta$ was determined directly from the voltammograms for Pt(111) but for Pt(100) and (110) it was corrected for the possible contributions from

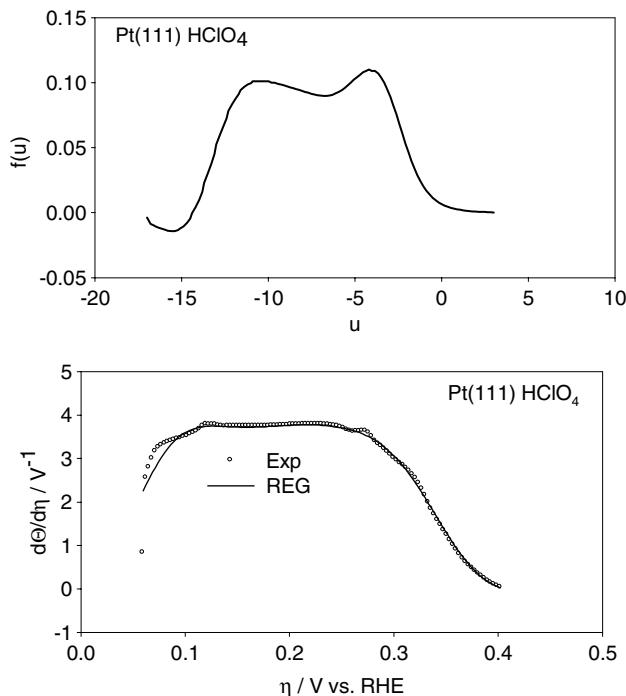


Fig. 1. Adsorption energy distribution function and experimental and reconstructed (using Eq. (5)) data of $d\Theta_H/d\eta$ vs. overpotential for Pt(111) in 0.1 M HClO_4 .

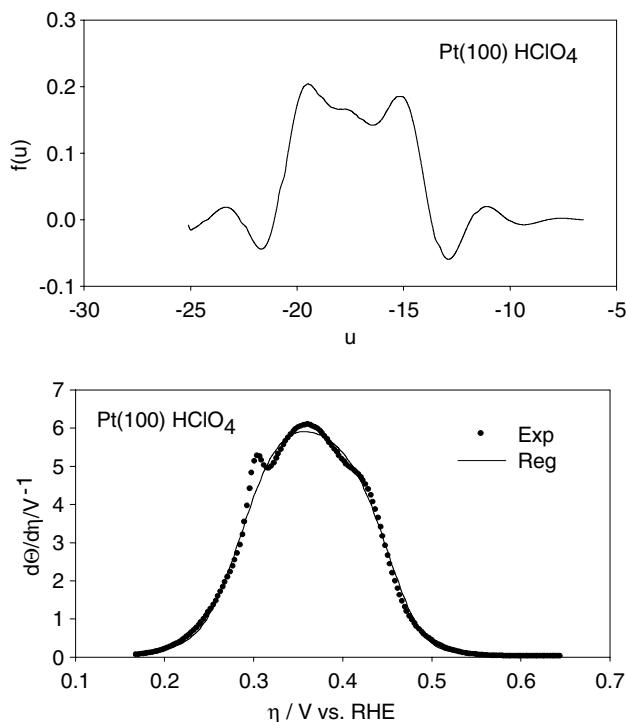


Fig. 2. Adsorption energy distribution function and experimental and reconstructed (using Eq. (5)) data of $d\Theta_H/d\eta$ vs. overpotential for Pt(100) in 0.1 M HClO_4 .

adsorption of oxides/hydroxides [1]. Figs. 1–5 present the experimental derivatives $d\Theta_H/d\eta$ on Pt(hkl).

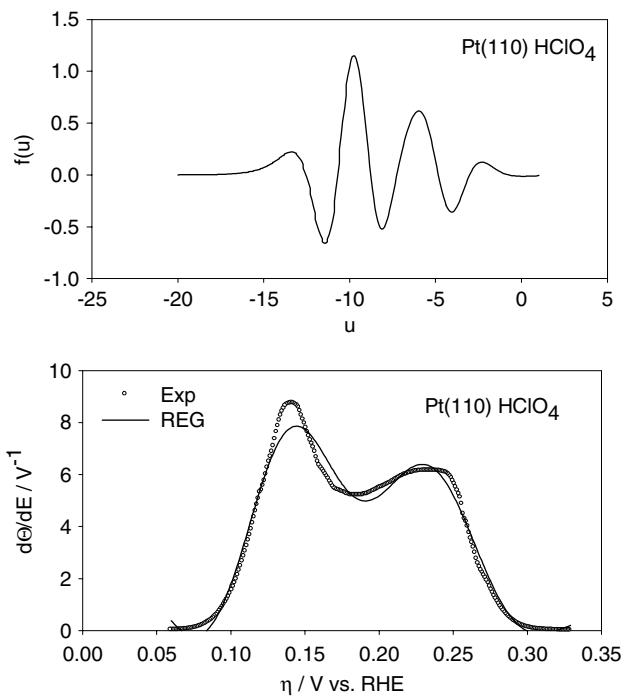


Fig. 3. Adsorption energy distribution function and experimental and reconstructed (using Eq. (5)) data of $d\Theta_H/d\eta$ vs. overpotential for Pt(110) in 0.1 M HClO_4 .

Application of the regularization procedure to the data for Pt(111) gives the distribution function shown in Fig. 1. For this electrode, a linear Frumkin isotherm was found earlier with a repulsion parameter g of 11.9 [1]. Analysis of the experimental derivative isotherm gave a relatively flat distribution in the energy range of u between -3 and -13 , corresponding to the adsorption energies between -7.4 and -32 kJ mol^{-1} . It has been shown earlier [6] that such a distribution function corresponds to a rectangular (see Fig. 4 in [6]) or Frumkin-like distribution function with a positive repulsion parameter. This distribution function may be used to obtain the experimental $d\Theta_H/d\eta$ dependence using Eq. (5). The result is shown in Fig. 1 and the distribution function obtained reconstructs the experimental derivative isotherm correctly. It should be added that the adsorption energies presented here are different from those determined in [1] because they were not corrected for the configuration entropic term $\ln[\Theta_H/(1 - \Theta_H)]$, that is u in the present paper corresponds to

$$\begin{aligned} u &= \Delta G_{\text{ads}}(\Theta_H)/RT \\ &= \Delta G_{\text{ads}}^{\text{a}}(\Theta_H)/RT + \ln[\Theta_H/(1 - \Theta_H)], \end{aligned}$$

where $\Delta G_{\text{ads}}^{\text{a}}(\Theta_H)$ is the surface coverage dependent adsorption Gibbs energy corrected for the configuration entropy used previously in the earlier paper [1]. Of course the configuration entropy term is intrinsically included in the kernel of the integral equation.

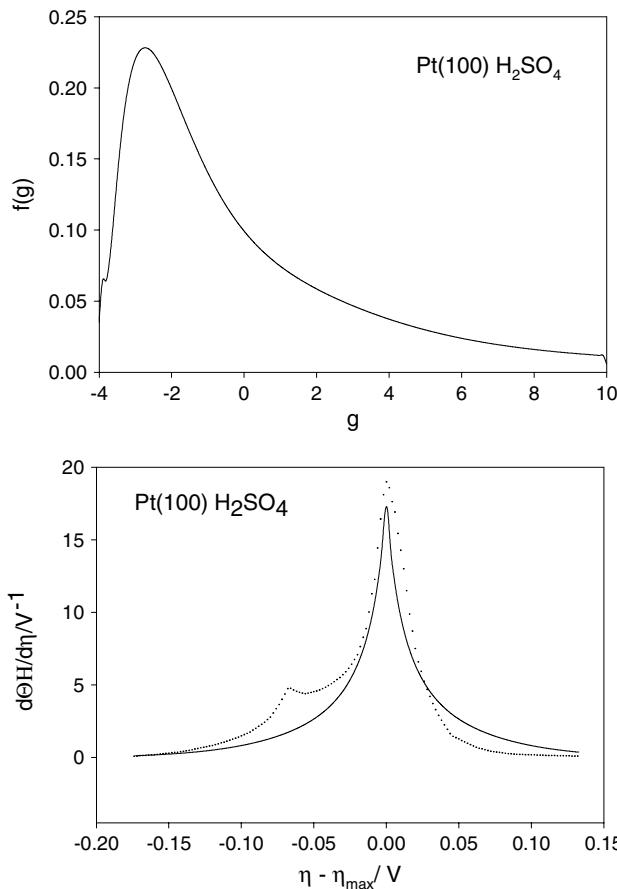


Fig. 4. Interaction parameter g (from Frumkin isotherm) distribution function and experimental and reconstructed (using Eq. (8)) data $d\Theta_H/d\eta$ for Pt(100) in 0.5 M H_2SO_4 .

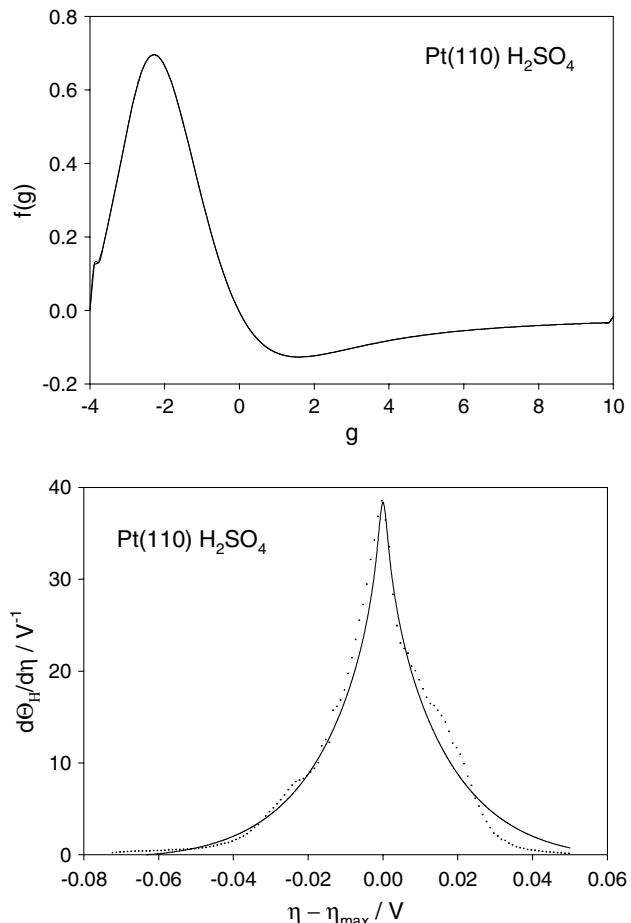


Fig. 5. Interaction parameter g (from Frumkin isotherm) distribution function and experimental and reconstructed (using Eq. (8)) data $d\Theta_H/d\eta$ for Pt(110) in 0.5 M H_2SO_4 .

3.1.2. Pt(100)

Another plane for which a Frumkin-type isotherm was found earlier is Pt(100) [1]. The experimental curve was corrected for anionic adsorption and the most positive peak was removed (see Lasia [1], Fig. 4). In this case the charge under the experimental curve, $206 \mu C cm^{-2}$, was similar to that predicted theoretically, $208 \mu C cm^{-2}$ [1]. The distribution function obtained is shown in Fig. 3; it also shows that the distribution function is flat between u values of -14 and -19 , corresponding to adsorption energies between -37 and -50 kJ mol $^{-1}$. Reconstruction of the initial curve of $d\Theta_H/d\eta$ from the distribution function is good, Fig. 2, although the small peak at $\eta = 0.3$ V could not be approximated. It is well known that because of the nature of the numerical regularization algorithm used to solve Eq. (5), small details of the experimental curve cannot be reproduced.

3.1.3. Pt(110)

In this case the experimental curve was also corrected [1]; however, the total experimental charge,

$173 \mu C cm^{-2}$, is larger than that predicted theoretically, $148 \mu C cm^{-2}$. This effect may be due to the surface reconstruction or the influence of ionic adsorption [8]. In the former case the proposed method will give correct results. The adsorption energy distribution function for Pt(110) is shown in Fig. 3. The solution obtained is characterized by strong oscillations (positive and negative values). There are two maxima at $u = -6.0$ and -9.8 corresponding to -15 and -24 kJ mol $^{-1}$ and the original $d\Theta_H/d\eta$ is well reproduced although the sharper peak at 0.14 V is slightly attenuated. Similar double peaks were observed for Pt(531) where a similar distribution function was found [6].

3.2. H_2SO_4

Because of the overlapping of the ionic adsorption and hydrogen upd, the Pt(111) electrode was not analyzed in H_2SO_4 . However, hydrogen adsorption in both acids at more negative potentials seems to be identical [1].

The adsorption peaks in the presence of H_2SO_4 on Pt(100) and Pt(110) are very narrow implying the influence of the ionic adsorption (sulfate/bisulfate). Such narrow adsorption peaks cannot be explained assuming a Langmuir adsorption isotherm. It should be stressed that the distribution of adsorption sites with a Langmuir local isotherm always leads to peaks larger than those predicted by a simple Langmuir isotherm. Only for negative values of the interaction parameter g do the peaks on the plots of $d\theta_H/d\eta$ vs. η become narrower. To explain such a behavior the Frumkin isotherm centered at $\theta_H = 0.5$ [6], was used

$$\frac{\theta_H}{1 - \theta_H} \exp(g(\theta_H - 0.5)) = \exp(-u - F\eta/RT), \quad (6)$$

where g is the interaction parameter. As it is impossible to find a distribution of two parameters from one experiment in this method, the adsorption energy, corresponding to the maximum of the adsorption peak, was assumed constant (u_{\max}) and only the distribution of the interaction parameter was taken into account. This means that interactions between adsorbed H atoms depend on their distance on the surface, while the standard adsorption energy, that is the interaction between isolated hydrogen atoms and the Pt surface was assumed constant. Of course the presence of interactions between neighboring adsorbed atoms modifies the total adsorption energy. In such a case the kernel of the integral equation is a derivative $d\theta_H/d\eta$ determined from Eq. (6) and is given by

$$K(g, \theta_H) = \frac{d\theta_H}{d\eta} = \frac{F}{RT} \frac{\theta_H(1 - \theta_H)}{1 + g\theta_H(1 - \theta_H)}. \quad (7)$$

This is incorporated in Eq. (8) assuming the distribution of the interaction parameter

$$\frac{d\theta_H(\eta)}{d\eta} = \int_{g_{\min}}^{g_{\max}} K(g, \eta) f(g) dg. \quad (8)$$

Because Eq. (6) describing the dependence of the surface coverage on overpotential is nonlinear, it was solved numerically for each overpotential and g value. The results for Pt(100) and Pt(110) are shown in Figs. 4 and 5. It should be stressed that the minimal value of the interaction parameter g is -4 ; at lower values, the solution of the nonlinear Eq. (6) becomes unstable (three values of θ_H are possible for the same value of the overpotential, see e.g. Fig. 31 in [9]).

3.2.1. Pt(100)

The hydrogen upd adsorption peak appears at $\eta_{\max} = 0.376$ V corresponding to $u_{\max} = -14.6$ or $\Delta G_{\text{ads}} = -36$ kJ mol $^{-1}$. The isotherm was centered on this value, and that the potentials were expressed as $\eta - \eta_{\max}$ and u was assumed as equal to zero at η_{\max} . The distribution function of the interaction parameter g is shown in Fig. 4. It represents an asymmetric peak with

the maximum at $g = -2.72$ and a tail at higher values of the interaction parameter. The reproduction of the experimental curve using this distribution function and using Eq. (8) is also shown in Fig. 4. Although the general shape of the peak was recovered, some deviations exist on both sides of the peak. There are probably more adsorption energies in the system; however, the analysis cannot be performed without deconvolution of the experimental curve into different contributions and there is no theoretical model permitting such a deconvolution to be carried out.

3.2.2. Pt(110)

The hydrogen upd adsorption peak is observed experimentally at $\eta_{\max} = 0.147$ V corresponding to $u_{\max} = 5.7$ or $\Delta G_{\text{ads}} = -14$ kJ mol $^{-1}$. There is one quite symmetrical peak in the distribution function of the g parameter, with a maximum at $g = -2.28$, Fig. 5. The approximation of the original $d\theta_H/d\eta$ curve using this distribution function is good, Fig. 5.

4. Discussion/conclusions

Upd adsorption of hydrogen on Pt(hkl) was modeled using distribution of sites. Even on a monocrystalline surfaces there are different adsorption sites or surface defects/irregularities and adsorption of the near or further neighbors influences the adsorption energy through the interaction via the metal. Two types of distribution functions were used; in HClO_4 the Langmuir local isotherm was assumed and the distribution of adsorption energy was determined, while in H_2SO_4 , the Frumkin local isotherm with constant adsorption energy, but with the distribution of the interaction parameter g , was used. It should be stressed that these methods do not need any assumptions about the distribution functions except that they are normalized, that is

$$\int_{-\infty}^{\infty} f(u) du = 1.$$

Assuming a distribution of the local Langmuir isotherm leads to derivative peaks that are larger than those predicted by a simple Langmuirian isotherm. It has been shown [6] that the Frumkin adsorption isotherm with a positive value of the interaction parameter may also be represented by the Langmuir isotherm with a distribution of adsorption energies. On Pt(111) and (100), flat distribution functions, between certain adsorption energies, were obtained, in agreement with the predictions for the Frumkin-type isotherms with a positive interaction parameter [1,6]. These Frumkin-like isotherms correspond to repulsive interactions between adsorbed hydrogen atoms. These interactions seem to behave isotropically, without differences between specific adsorption sites. On Pt(110) two peaks exist on

the derivative isotherm and two peaks were also found on the distribution function. These indicate two different adsorption sites with repulsive interactions. However, in this case, the approximation is the poorest, as the experimental derivative isotherm is quite narrow at the peak and wide at the bottom, which makes it impossible to be well approximated by the distributed Langmuir isotherm. However, other regularization procedures give similar values of the peak adsorption energies indicating that two sites contribute most significantly to the total isotherm. Similar examples with two or three peaks were found earlier on polycrystalline Pt and Pt(531) [6], although the origin of these peaks is different.

In the presence of H_2SO_4 the observed experimental peaks are very narrow and cannot be explained by the model used in HClO_4 . Such narrow peaks may arise from the Frumkin isotherm with a negative interaction parameter. However, the observed peaks cannot be explained by one interaction parameter because the peak is very sharp while the base of the peak is large. We have proposed using the Frumkin local isotherm with one adsorption energy, corresponding to the peak of $d\theta_{\text{H}}/d\eta$, and the distributed g values. Although the general shape of the experimental curve was well reproduced, some deviations were observed on Pt(100). It seems that, in this case, there are contributions from sites having other adsorption energies, however; it is impossible to deconvolute the experimental curve into two (or more) contributions, as the nature of the isotherm is not known.

Of course, in the presence of H_2SO_4 there is an overlap of ionic (sulfate/bisulfate) and hydrogen adsorption and only global behavior is known [1]. Desorption of bisulfate causes a fast hydrogen upd reaction leading to a narrow isotherm. However, the detailed contributions of H and ionic adsorption (detailed enough to carry out mathematical modeling) are not known. Nevertheless, our analysis characterizes the global behavior observed in sulfuric acid and explains the experimental behavior in terms of one adsorption energy and a distributed interaction parameter. The results obtained indicate that the adsorption energy is similar everywhere on the surface, while the formal interactions between adsorbed species depend on the lateral distance between adsorbed atoms.

To be more precise, one should consider two different adsorption isotherms, one for the hydrogen

$$\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}} - \theta_{\text{A}}} \exp(g_{\text{HH}}\theta_{\text{H}} + g_{\text{HA}}\theta_{\text{A}}) = K_{0,\text{H}} \exp(-f\eta) \quad (9)$$

and the other for the anions A

$$\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}} - \theta_{\text{A}}} \exp(g_{\text{AA}}\theta_{\text{A}} + g_{\text{HA}}\theta_{\text{A}}) = K_{0,\text{A}} \exp(-f\eta) \quad (10)$$

with three lateral interaction terms corresponding to the interactions between H–H, A–A and H–A. However, analysis of the above equations is much more complex and demands very high quality data of θ_{H} and θ_{A} vs. potential, but the necessary experimental data to do this are not available. Of course experimental curves cannot be described by one Frumkin isotherm, as their shape is very peculiar; they are very sharp at the peak and wide at the bottom. It should be mentioned that the Monte-Carlo simulations of the voltammograms at the stepped Pt surfaces indicate that the interaction parameters of adsorbed hydrogen have different signs on steps and terraces [10].

In the present paper we have modeled these curves assuming a distribution of the interaction parameter g , which has a maximum at negative values but may extend to more positive values. Such an approach has never been undertaken before. This approach can give us information about the formal nature of the isotherm but of course the approach given above (which is currently impossible) should be used to evaluate adsorption of all the participating species.

The alternative approach to the analysis of adsorption is deconvolution of the observed isotherms into a series of Langmuir or rather Frumkin isotherms, which could be done only if the experimental data correspond to the hydrogen adsorption only. Such a task for H upd on Pt(hkl) is relatively difficult. For the cases analyzed in this paper one should use a superposition of n “fractional” Frumkin isotherms, each characterized by three parameters: $\theta_{\text{m},i}$, g_i and u_i

$$\frac{d\theta_i}{d\eta} = \frac{F}{RT} \frac{\theta_i(\theta_{\text{m},i} - \theta_i)}{\theta_{\text{m},i} + g_i\theta_i(\theta_{\text{m},i} - \theta_i)} \quad \text{subject to} \\ \frac{\theta_i}{(\theta_{\text{m},i} - \theta_i)} \exp(g_i(\theta_i - \theta_{\text{m},i}/2)) = \exp(-u_i - F\eta/RT) \quad (11)$$

with $\frac{d\theta_{\text{H}}}{d\eta} = \sum_{i=1}^n \frac{d\theta_i}{d\eta}$ and $\sum_{i=1}^n \theta_{\text{m},i} = 1$, where $\theta_{\text{m},i}$ is the maximal coverage for the isotherm i and, for each point, n nonlinear equations must be solved to determine the partial surface coverages from the Frumkin isotherms. This operation corresponds to the replacement of the continuous distribution function $f(u)$ by a series of discrete functions, each characterized by three parameters. Brief analysis shows that the number of individual functions must be quite large (≥ 5 , therefore number of parameters ≥ 15) to approximate the experimental curve. In fact, Arvia et al. [11] separated the experimental isotherms for Pt in H_2SO_4 into five contributions corresponding to five Frumkin adsorption isotherms with different adsorption energies and the distributed parameters g . However, the shape of the individual contributions was not shown and only the distribution functions of the g parameter were presented. On the other hand the regularization method gives a continuous

distribution of one parameter only; this is a much simpler task and the results obtained are acceptable.

It can be added that, in the case of Pt electrodes in H_2SO_4 , another approximation is also possible, assuming one Frumkin isotherm with a fixed sufficiently negative value of the interaction parameter and finding the distribution of the adsorption energies. This approach is identical to that shown for Pt in HClO_4 with the Frumkin instead of the Langmuir isotherm. Very good approximations may be obtained in such cases but the physical significance of such approximations is doubtful as sufficiently narrow approximating isotherms (sufficiently negative g) lead to very sharp derivative isotherms, which could approximate any experimental isotherm (also corresponding to a positive value of g).

The methods presented above give a new insight into the upd of hydrogen on well-defined surfaces and may lead to the development of a mathematical model describing this process. The methods presented are general, and do not need any a priori assumption on the character of the distribution function. It should be added that the analysis would be only as good as the experimental data. However, further interpretation of the results obtained must be based on detailed knowledge of the possible adsorption sites.

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