



# Direct estimation of surface pressures by hydrogen adsorbates on platinum surfaces in perchloric acid

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## ABSTRACT

The surface pressure solely by hydrogen species at polycrystalline and single crystalline platinum is calculated from a modified Gibbs-Lippmann Equation taking the contributions of electrode potential and hydrogen coverage in perchloric acid. Hydrogen surface pressures at reference surface coverages are rather low for Pt(100) and Pt(110), i.e., 20–35  $\mu\text{N cm}^{-1}$ , but 5-fold larger for Pt(111) due the formation of long range water-hydrogen layers on trigonal sites. Surface tensions also follow the same tendencies. On polycrystalline platinum they are sensibly inferior to those obtained on single crystals but similar in magnitude for both types of hydrogens indicating that the presence of water in weakly bound hydrogen responds to a slight interaction (not bound to platinum atoms).

Free energy of adsorption for hydrogen ad-atoms on polycrystalline platinum is reported here at experimentally found reference coverages, i.e.  $-29$  and  $-14 \text{ kJ mol}^{-1}$  for both kinds of hydrogens in perchloric acid. The interaction/heterogeneity factor of the Frumkin/Temkin isotherm, which are similar (ca.  $11-12 \text{ kJ mol}^{-1}$ ) for both types of hydrogens, again verifies that water interaction is not straight to platinum atoms. On single crystalline surfaces, the most favorable value of adsorption energy was found on Pt(100) and the lowest on Pt(111). The three single crystals exhibit positive interaction/heterogeneity factors (from  $11$  to  $18 \text{ kJ mol}^{-1}$ ) being the greatest on Pt(110) as a consequence of being the most disordered surface.

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## 1. Introduction

The plastic deformation significantly influences the current intensity during hydrogen evolution on *pc* (polycrystalline) nickel and platinum electrodes. This is the consequence of pre-strained microstructures and dislocations leading to new hydrogen adsorption sites on stepped planes [1]. Elastic moduli for *pc* platinum and elastic stiffness constants ( $C_{ii}$ ) of platinum *sc* (single crystal) have been measured using a pulse-echo technique [2]. Elastic constant parameters for platinum are near  $0.08 \text{ mN cm}^{-2}$  for  $C_{44}$  and  $0.32 \text{ mN cm}^{-2}$  for  $C_{11}$  elastic moduli twice than palladium.

The surface tension,  $\gamma$ , of a solid can be regarded as supplementary information to characterize the energetics of the interface that enables the equilibrium between a bulk and a surface phase. Generally,  $\gamma$  is available in the literature for pure liquids or even for liquid/vapor interfaces [3,4] or molten salts [5] and liquid noble metals [6]. Nevertheless, the Butler–Sugimoto thermodynamic approach was applied for liquid metal/liquid interfaces with oxygen adsorption [7], Du–Noüy ring method to nanoparticle containing-liquids [8] or mathematically calculated using a Constrained Gibbs Energy Minimization model [9].

Uniform compression model with repulsive interactions between adsorbed species have been advanced for surface stress at gold *sc* by two or one-bending of the crystal in perchloric acid [10]. Also, non-quadratic  $\gamma$  dependences with electrode potential (ca. linear) were attributed to a surface stress–charge coefficient due to underlying microscopic interactions [11]. One of the most outstanding observations in experimental data is the parallelism between cyclic voltammograms and the derivation of surface stress,  $f$ , with electrode potential [12]. If the adsorbate could be homogeneously distributed to the surface, its contribution to  $f$  would equal its influence to  $\gamma$ , and would follow the electrocapillary equation. Since this situation is not observed the adsorption phenomena has to follow different laws and the peaking behaviour can only be attributed to adsorption at specific sites. Over the investigated range  $f$  varies much more strongly than  $\gamma$ , indicating that the surface excess by adsorbates,  $\Gamma$ , has a straight consequence on  $f$ , and not only an indirect effect through double-layer charging. The induced  $f$  can be described on well-defined *sc* surfaces [10] by an initially linear increase of  $f$  with  $\theta$  followed by an exponential growth at higher  $\theta$  values. The non-linear increase is first thought to be due to the repulsive interaction between adsorbates or defects disordered arrangements as Frumkin/Temkin behaviors.

Hydrogen electroadsorption on well-defined *sc* platinum surfaces has been the most studied subject in the last four decades [13–15]. The process depends on the surface arrangement and crystalline orientation of

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platinum surfaces [16–19]. The presence of misfits or defects on platinum and anions specific adsorption is revealed by abrupt changes in elastic and plastic deformations as a function of the electrode potential. The surface energy in distinct elasto-plastic states will only depend on surface pressures,  $\Pi$ , if the state of strain of the solid surface remains constant [20,21]. The role of  $f$  in reconstruction phenomena has become a matter of considerable interest in the electrochemical surface science. At first evidence for the importance of  $f$  upon reconstruction of either clean or adsorbate-covered surfaces came from spectroscopic techniques curves [22].

### 1.1. On the Gibbs-Lippman Equation at electrochemical interfaces

Adsorption thermodynamics for hydrogen ad-atoms on smooth  $pc$  surfaces are generally described by Langmuirian models [23], but at  $pc$  platinum, surface heterogeneity and lateral interactions are required for a proper description of the interface [24–27]. We propose here a dual Frumkin/Temkin-type isotherm, as in other Reviews [15], to consider both effects [28].

The integration of Gibbs' adsorption equation gives rise to  $\Pi_H$  by H-adatoms on platinum [29,30], by deduction in Appendix A [31,32]:

$$\Pi_H = \theta_H \sigma_{H,m} \left[ (E - E_{\theta=0}) - \frac{RT}{F} \ln(1 - \theta_H) + \frac{g\theta_H}{F} + \frac{\Delta G_{ads,\theta=0}^0}{F} \right]. \quad (1)$$

The symbols and terms are defined in the Nomenclature.

Hydrogen by itself produces a change in  $\Pi_H$  so the existence of adsorbable anions can lead to mistakes. Most of the evidence obtained at a platinum  $sc$  is run out in bisulphate/sulphate ions-containing electrolytes, because of their sharp defined voltammetric peaks [33]. Little information is given using perchlorate anion as base electrolyte because of chloride free ions interference as trace impurities ( $< 10^{-7}$  M) [34] and electrochemical reduction of perchlorate during potentiodynamic runs in the hydrogen ad-atom region [35].

There are no direct experimental methods to determine the absolute values of surface tensions at a solid/liquid interface, and when it is possible (changes in the elastic deformation at different electrode potentials) the accuracy of the data is very low [36]. Thus, we conduct here the double integration of the voltammetric responses through a simple calculation to obtain the values of  $\Pi_H$  using Eq. (1). We will also present thermodynamic data ( $\Delta G_{ads,\theta_{ref}}^0$  at reference state  $\theta_{H,ref}$  and  $g$  factor) for H-adatoms only using cyclic voltammograms at medium scan rates.

## 2. Experimental section

Electrochemical experiments were carried out at room temperature using a micro flux three-electrode cell and the glassware cleaned firstly by boiling in a 1:1 mixture of concentrated nitric and sulfuric acid and finally by repeated boiling with ultra-pure water. Platinum wires 0.5 mm wide and 1 cm length, and discs (99.999% purity polished on one side to 1  $\mu\text{m}$ , from Goodfellow Co.) with 0.1 cm depth and 1 cm of diameter, were used as  $pc$  and  $sc$  electrodes, respectively. Each platinum  $sc$  was again polished using standard metallurgical procedures to a mirror-like finishing with alumina  $< 0.05 \mu\text{m}$ , finalising with sonication for several hours with ultrapure water. Before each experiment the  $sc$  electrodes were annealed in a nitrogen flame for about 15 s, cooled down to 90–100  $^{\circ}\text{C}$  in a nitrogen- 5% hydrogen stream for 5 min and protected by a droplet of ultrapure deaerated water from contact with air to transfer into the solution. In this way the temperature shock which induces strains in the crystal while quenching directly by ultrapure water (from Merck), was avoided. The contact of the electrode with the electrolyte solution was made always under potential control in the double layer region, i.e. 0.40 V and the first sweep was conducted starting from this potential in the negative direction to 0.05 V and then upwards. The sweeping potential was 0.10  $\text{V s}^{-1}$  for  $pc$  while 0.05  $\text{V s}^{-1}$

for  $sc$  platinum, while upper potential limits were selected according to the chosen platinum crystalline orientation.

The electrochemical set-up was completed using a large-area-platinum counter electrode (ca. 10  $\text{cm}^2$ ) and a reversible hydrogen reference electrode (RHE). 0.5 M perchloric acid supporting electrolyte was prepared from TraceSELECT reagent (72%, chloride  $< 0.1 \text{ mg/kg}$ ) with Millipore-MilliQ plus treated water (18.2  $\text{M}\Omega \text{ cm}$  resistivity) and purified by long-time pulsed electrolysis using large area platinum electrodes (previously cleaned with standard procedures). The cell solution was purged for 15 min and later the atmosphere was slowly and continuously deaerated with pre-saturated water vapor high purity nitrogen (99.998%) from Linde. The cleanliness of the entire electrochemical system was tested by a detailed study of the platinum cyclic voltammograms after a potential holding in the double layer region for 10 min under unstirred and stirring conditions [37]. The electrochemical fingerprints of the interfaces were collected for the freshly prepared electrodes by cycling in the low potential region to verify their quality as well as the cleanliness of the surface.

The real surface area of  $pc$  and  $sc$  electrodes were calculated from the integration of the H- adatom voltammetric profile after double layer correction using the right value of maximum charge density by hydrogen adsorbates,  $\sigma_{H,m}$ . All potentials in the text are referred to the RHE scale. The values of  $\theta_H$ , or simply surface charge densities,  $\sigma_H$ , were found after integration of the hydrogen ad-atom current intensities of potentiodynamic profiles (with double layer correction) after potential window experiments and graphical deconvolutions, plotted against  $E$ . In the case of “weakly” and “strongly” adsorbed hydrogen at  $pc$  platinum, they were calculated by only cycling between, 0.45 and 0.20 V, and 0.18 to 0.04 V, respectively. From the isotherms,  $\Delta G_{ads}^0$  was calculated as a function of  $\theta_H$  and then, the value(s) of  $g$  were obtained from its slope within linear ranges. After then, the value of  $\theta_H$  at the reference state,  $\theta_{H,ref}$ , was gained from the  $\ln(\theta_H/(1 - \theta_H)) + g\theta_H$  vs.  $\theta_H$  plot at zero ordinates. At this  $\theta_{H,ref}$  the right figure for  $\Delta G_{ads,\theta_{ref}}^0$  was acquired. Finally, from a second integration of voltammetric data we found  $\gamma_H$  values, from which,  $\Pi_H$  was calculated using from Eq. (1) and plotted against  $E$  to get the values at reference state,  $\Pi_{H,ref}$ .

## 3. Results and analysis

### 3.1. Electrochemical profiles and adsorption behaviour of hydrogen atoms on $pc$ platinum in perchloric acid

A precise distinction between hydrogen electroadsorption/absorption as underpotential or overpotential deposited ensembles was presented by Jerkiewicz [38]. The assignment to the so-called “weakly” and “strongly” adsorbed hydrogens was advanced not only by the potential region where the peaks appeared. However, many papers consider this possibility [39], while others took the entire hydrogen adsorption region as one [40] to easily obtain the properties of the two thermodynamically distinguishable species. Though, it is possible to study the current decay after a certain potential far beyond the peaking value and the starting of the new hydrogen adsorbate.

Fig. 1 (A) shows the cyclic voltammetric profile of  $pc$  platinum in 0.5 M perchloric acid run at 0.10  $\text{V s}^{-1}$  within each hydrogen adsorption region and up to the solvent stability upper potential. No signs of chloride ions either from trace impurities or electrochemical transformation of perchlorate with strongly hydrogen adsorption region can be seen. Correspondingly, there are no changes in the cyclic voltammograms after holding the potential near the  $E_{pzc}$  of the interface, by recording the electrochemical profile in the hydrogen adsorption/desorption region. The cycling upon “weakly” and “strongly” hydrogen adatoms regions is also presented and superimposed in the same Figure.

The graphical deconvolution of the voltammetric current intensities (using theoretical adsorption kinetics) between 0.45–0.22 V and 0.18–0.04 V leads, after integration,  $\sigma_H$  as a function of  $E$ . The process exhibits saturation,  $\sigma_{H,m}$ , 115 and 110  $\mu\text{C cm}^{-2}$  at 0.055 and 0.250 V for the first

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