

Thermodynamics of Hydrogen Adsorption on Pt(111), Pt(100) and Pt(110) Electrodes

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A wealth of information on the behavior of platinum monocrystalline electrodes has been gathered since the 80's by means of electrochemical and non-electrochemical methods. Structural aspects and catalytic activity of such electrodes have been dealt with many times. However, only a number of studies have appeared on the determination of thermodynamic quantities for electroadsorption processes. Among them and unsurprisingly, the adsorption process studied more thoroughly to date is the adsorption of hydrogen on Pt(111) [1,2]. In fact, the electrochemical behavior (including electrocatalysis) of platinum is dominated on many occasions by the adsorption of hydrogen.

We present a detailed study on the thermodynamics of hydrogen adsorption on Pt(111), Pt(100) and Pt(110) electrodes in contact with 0.1 M HClO₄ solutions. The experiments consist basically in obtaining voltammograms at different temperatures (using a RHE at the temperature of the working solution). Figs. 1 and 2 show the sets of voltammograms obtained for Pt(111) and Pt(100) electrodes, respectively.

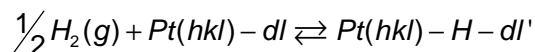
Before doing any proper calculation we must separate the voltammetric contribution due to hydrogen adsorption from the contribution linked to the adsorption of oxygenated species. This is straightforward in the case of Pt(111) but poses problems for the other two basal planes. A well-founded deconvolution of the adsorption processes does not seem feasible in the case of the Pt(110) electrode but is possible for Pt(100) electrodes. We may correlate the voltammogram with the total charge vs potential curve and also assume a Frumkin isotherm for the OH adsorption. Fig. 3 shows how the voltammogram for T=293 K is deconvoluted.

The treatment of the data is analogous to that presented in refs. 1 and 2 although a few modifications are done, aiming at providing a physical interpretation to the values of the different thermodynamic quantities, especially to that of entropy. We take advantage of the fact that the potential scale is directly a scale of free energy of adsorption for hydrogen. The configurational term is separated out of the total free energy of adsorption and the generalized isotherm used in previous studies is deduced:

$$\frac{q_{H_{UPD}}}{1 - q_{H_{UPD}}} = f_{H_2}^{1/2} \exp\left(\frac{-E_{RHE} \cdot F}{RT}\right) \exp\left(\frac{-\Delta G_{ads}^0(H_{UPD})}{RT}\right)$$

where f_{H_2} corresponds to the fugacity of hydrogen and E_{RHE} to the potential of hydrogen adsorption measured vs a reference hydrogen electrode.

It is important to recognize that the process under scope is:



where dl and dl' stand for the structure of the double layer prior and after hydrogen adsorption. The fact that double layer may rearrange upon hydrogen adsorption should be taken into account when interpreting the values obtained for the thermodynamic functions.

It is found that all the adsorption thermodynamic values depend on the surface crystallographic orientation. Values for the adsorption enthalpy are similar to those found in UHV, which puts forward that the energetic effect of the dl rearrangement is negligible. Values obtained for the entropy of adsorption point to the fact that the H adlayer does not possess an important degree of mobility.

References

1. A. Zolfaghari, G. Jerkiewicz, J. Electroanal. Chem., 467 (1999) 177.
2. N.M Markovic, T.J. Schmidt, B.N. Grgur, H.A. Gasteiger, R.J. Behm, P.N. Ross, J. Phys. Chem.. B, 103 (1999) 8568

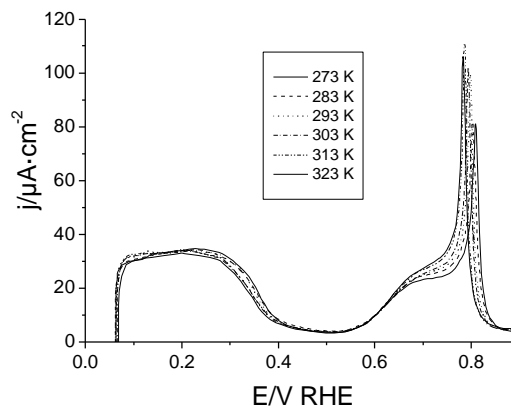


Figure 1. Positive-going voltammograms for Pt(111) electrodes in contact with 0.1 M HClO₄ at different temperatures. Scan rate: 50 mV/s.

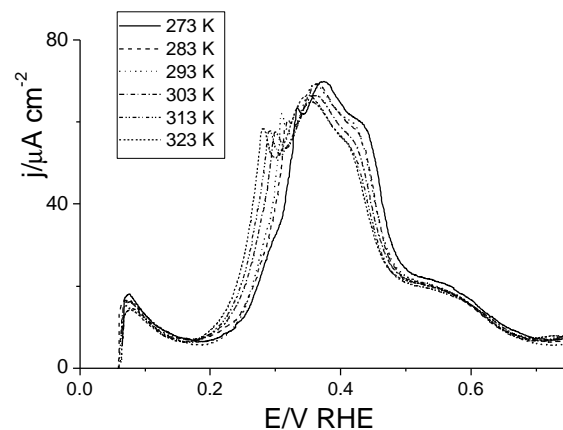


Figure 2. As in fig. 1 for Pt(100) electrodes

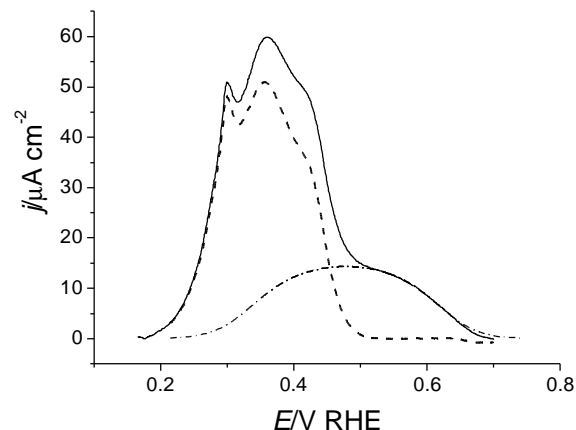


Figure 3. Deconvolution proposed for voltammogram corresponding to the Pt(100) electrode. Dotted-Dashed line: OH adsorption contribution (Frumkin isotherm). Dashed line: H adsorption contribution.