INVESTIGATION OF INTERFACIAL PARAMETERS WITH Pt SINGLE CRYSTAL ELECTRODES

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The study of the electrochemical interphase is of paramount importance for the understanding of electrocatalytic phenomena. Most of the electrochemical reactions of technological interest (oxygen reduction, hydrogen evolution and oxidation, oxidation of organic fuels, CO_2 reduction…) exhibit a strong influence of the interfacial parameters on both selectivity and reaction rate. Among the most important phenomena that characterise the electrochemical interphase, the charge separation is what really marks the difference between electrochemical and other heterogeneous or surface processes. Still, in electrochemistry, most of the time, charge is not directly controlled. For this reason, it is very important to establish a quantitative relationship between charge and potential. In this regard, a key parameter is the potential of zero charge. Moreover, the very notion of electrode charge is obscured by the existence of adsorption processes. In this case, it is necessary to distinguish between the concept of total and free charge [1].

In this communication, we will show what methodologies are available for the characterization of the electrochemical interphase with emphasis on the properties of platinum single crystal electrodes. Total charges for platinum electrodes can be measured using the CO charge displacement method [2]. Such charge curves can be analyzed on the basis of the electrocapillary equation to determine the thermodynamic properties that characterize the interphase. Study of the interphase as a function of the temperature allows determination of additional thermodynamic properties, such as the entropy of formation of the interphase [3]. The influence of crystallographic orientation on properties such as the potential of zero charge, potential of maximum entropy and anion adsorption will be investigated with different techniques and methodologies. Such methodologies will be extended to investigate also the interphase between platinum single crystal and novel solvents of the family of ionic liquids.

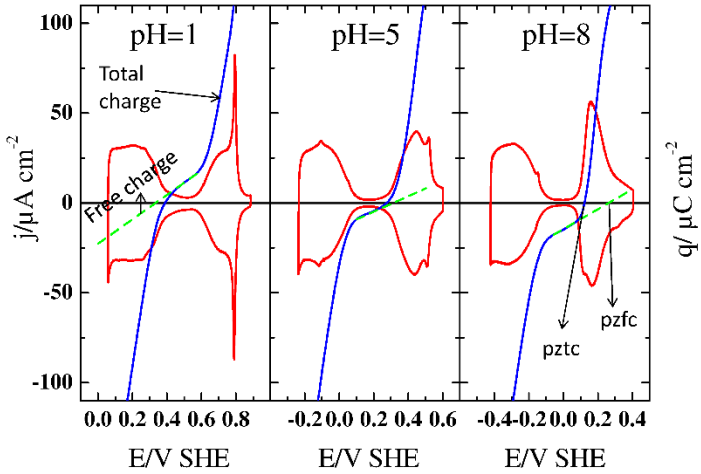

Figure 1: cyclic voltammograms and total and free charge curves, as a function of potential, for a Pt(111) electrode in solutions of different pH, in the absence of specific anion adsorption. Scan rate: 50 mV/s.

[1] A.N. Frumkin, O.A. Petrii, Electrochim. Acta, 20 (1975) 347-359.
[2] V. Climent, R. Gómez, J.M. Feliu, Electrochim. Acta, 45 (1999) 629-637.
[3] N. Garcia-Araez, V. Climent, J. Feliu, J. Phys. Chem. C, 113 (2009) 19913-19925.