

Towards understanding the role played by surface discontinuities on electrocatalytic activity

A.C. Chialvo, M.R. Gennero de Chialvo

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, (3000) Santa Fe, Argentina
 achialvo@fiq.unl.edu.ar

Electrocatalytic reactions can involve particular surface sites for each type of adsorbed reaction intermediates. Thus, the reactivity of such active sites depends strongly on their location and environment. Although the electrode surface is usually considered chemically and morphologically homogeneous, in numerous cases it exhibits discontinuities that can affect significantly the kinetics of an electrode reaction. These discontinuities can be due to chemically different materials or to changes in the surface atomic order. In the first type, two or more different electrocatalytic materials, e.g. two metals M_1 and M_2 , create a discontinuity in the interface M_1/M_2 (Fig. 1). Thus, when a reaction is taking place on this electrode, the reaction rate on the boundary region could be different to that on the rest of the electrode surface, involving the possibility of spillover of reaction intermediates from one phase to the other or, in the case of two or more intermediates, the feasibility of an elementary reaction between adsorbed species on both sides of the intermetallic boundary.

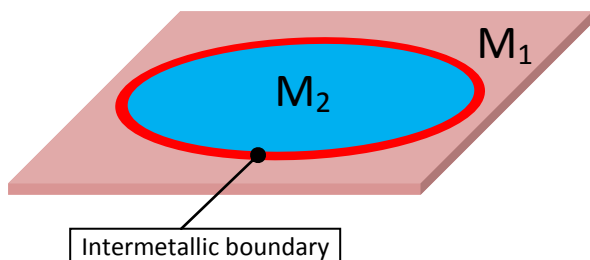


Figure 1: Chemical discontinuity

The second type corresponds to discontinuities in the surface atomic order, without changes in the chemical nature of the electrode surface. Examples of this type are steps in a single crystal surface (Fig. 2a) and edges in a nanoparticle (Fig. 2b). In this case active sites located on steps or edges are different than those situated on basal planes or on nanoparticle faces.

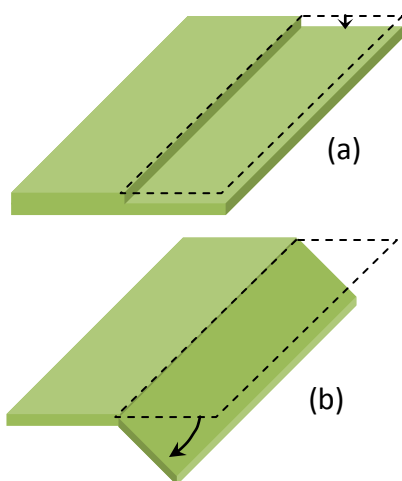


Figure 2: Surface order discontinuity. (a) Step; (b) Edge.

In both types of discontinuities, it should be important to evaluate their specific contributions to the reaction rate of a given electrocatalytic reaction, particularly when the number of surface sites involved on them is significant.

It has been found in the ethanol electrooxidation reaction on carbon supported Pt-Sn nanoparticles that the electrocatalytic activity of a biphasic catalyst is significantly higher than the alloy [1,2]. This behavior was explained on the basis of the intermetallic region Pt/Sn, although without a direct evidence of the processes involved [3]. Thus, it should be of interest to determine the contribution of this particular region to the overall response obtained experimentally.

In these context, it is proposed to evaluate the 'excess current', defined as the difference between the current drained by the electrode with surface discontinuities and the current obtained in model electrodes without such discontinuities, in identical experimental conditions. On this basis and taking into account the corresponding real electrode areas, the excess current density can be calculated. This new electrochemical variable, applied to the analysis of an electrocatalytic reaction, will be a measure of the corresponding contribution of the surface discontinuities to the electrocatalytic activity. This concept is applied to different reactions of technological interest, such as the CO electrooxidation on Pt/Ru [4,5], the ethanol electrooxidation on Pt/Sn, etc.

It is concluded that this tool is useful for the study of the role of chemical or morphological discontinuities on electrode processes and contributes to the comprehension of the phenomena involved on it.

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