Problems of stability and electrochemical phase transitions at metal-electrolyte interfaces

Andrzej Sadkowski, Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland (E-mail:ansad@ichf.edu.pl)

ABSTRACT

There is distinct specificity of thermodynamics and kinetics of interfacial electrochemical processes in comparison with normal (not electrically qualified) physical and/or chemical transformations. This specificity consists in the role of electric variables i.e. electric potential (voltage) playing the role of the generalized "force" variable, the electric charge transferred playing the role of the generalized "shift" and the current - the "flux" variable. This is significant complication from the point of view of formal description, the more so, that the electrostatic potential can not be unequivocally separated from its chemical counterpart in definitions of interfacial energy, electrochemical potentials of charged components and other variables characterizing charged species and interfaces. Consequently, the conditions of electrochemical equilibrium have to be expressed in terms of electrochemical potentials of reacting species without explicit conditions being formulated in terms of its electrostatic and chemical components [1, 2]. On the other hand, the mere variations of electric potential at the electrochemical interface are done easily and these variations represent vital parameters of the control of equilibria and kinetics of electrochemical transformations.

Equations of equilibria and kinetics at charged interfaces include empirical, measurable variables: electrode potential (E) measured with respect to the suitable reference electrode and the electrode charge (q) measured with respect to the arbitrary state of zero charge. Their variations in most cases are directly related to those of thermodynamic variables (experimentally not accessed): electrical potential difference at the interface $_{Me}\varphi_s = \varphi^{Me} - \varphi^s = \Delta E$, and the charge $q = \int_{E_{pzc}}^{E} i_c \, dE$ where E_{pzc} is the "zero charge potential" and i_c is the current density [A.m^{-2}] consumed only for charging the interfacial capacitance and not for the electrochemical (Faradaic) reaction [2, 3]. Determination of E_{pzc} and of i_c is still challenging problem in electrochemistry.

In case of adsorption the surface concentration (activity) is controlled by the electrode potential and the dependence $q_{ads} - E$ (q_{ads} – charge equivalent to adsorbed species) presents the electrochemical adsorption isotherm [4-6]. In case of strong attractive interactions (of whatever origin) this isotherm may present non-monotonous dependence similar to e.g. van der Waals isotherm for real gases and it is usually described by Frumkin isotherm [7] corresponding to Fowler-Guggenheim adsorption isotherm of gaseous species [8, 9]. The part of the isotherm with negative slope $dq_{ads}/dE < 0$ represents instability and corresponds to the 1st order phase transformations in 2-D.

The prominent feature of electrochemical systems is the dependence of stability conditions on the way of the electrical control realized experimentally [10-12]. Specifically, there is the important difference between the potential control (by voltage source with zero output impedance) and the current control (by current source with infinite output impedance). In

most cases systems unstable under current control are stable under voltage control; opposite situations are also reported but seem to be exceptional [13].

The most comprehensive mean of electrochemical stability analysis is with electrochemical impedance spectroscopy (EIS) [14]. Analysis of EIS spectra using modern methods of complex non-linear least squares fits (CNLS) and Kramers-Kronig transformations (KKT) allows evaluation of zeros and poles of electrochemical impedance [15] and from this conclusions can be made on electrochemical stability under various conditions and on possible loss of stability leading to phase transitions at the interface. It is interesting to note that the zeros of electrochemical impedance are equal to eigen-values of the Jacobi matrices for electrode under control with current source and the poles are equivalent to these eigen-values under potential control [16].

Problems of stability and phase transformations are of crucial importance in various applications of electrochemical theory involving 2-D pattern formation: passivation and inhibition in corrosion engineering, local phenomena in electrocatalysis and electrochemical surface treatment and also in functional modification of metal and semiconductor surfaces [17-19].

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