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Influence of hydrogen absorption on the potential dependence of the Faradaic impedance parameters of hydrogen evolution reaction

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ABSTRACT

The influence of hydrogen absorption reaction (HAR) proceeding through H_{ads} with kinetic or with diffusion control on the dependence of the elements R_1, R_2, C_2 of the equivalent electrical circuit for hydrogen evolution reaction (HER) on the electrode potential E has been considered. It has been shown that if HER proceeds through the Volmer–Heyrovsky mechanism, then the presence of HAR reduces the slope $d\log R_2/dE$ at all E and the slope $d\log C_2/dE$ at sufficiently high cathodic polarisations. In the case of the Volmer–Tafel mechanism the presence of HAR mainly affects the resistance R_2. The character of the dependences of R_1, R_2, C_2 on E is the same for both kinetic and diffusion control of HAR. An interpretation of the experimental impedance data for HER on $CoSi_2$ in 0.5 M H_2SO_4 has been presented.

1. Introduction

Previously [1] we suggested the diagnostic criteria for hydrogen evolution reaction (HER) mechanisms that are applicable within the framework of electrochemical impedance spectroscopy. These criteria are the derivatives of the values of the Faradaic impedance elements in equivalent electrical circuit with respect to the electrode potential (or overvoltage) and with respect to the concentration of hydrogen ions (in acidic solutions) or hydroxyl ions (in alkaline solutions). Theoretical development of the criteria is based on a number of assumptions: HER proceeds according to the Volmer–Tafel or Volmer–Heyrovsky mechanism; hydrogen atom adsorption obeys the Langmuir or Temkin isotherm; there is no influence of hydrogen ion diffusion towards the electrode and H_2 from the electrode and hydrogen absorption by the electrode material; transfer coefficients of the Volmer and Heyrovsky steps do not depend on the overvoltage; electrode surface is smooth and clean (there are no oxides, organic adsorbates, etc.). It is assumed implicitly that the current and potential distributions over the working electrode surface are uniform.

Thus, an idealised situation was analysed in [1]. In practice, we can expect different kinds of deviations from simple relations corresponding to this idealised situation. One can mention some reasons that will lead to more or less significant deviations of this kind: adsorption phenomena (water chemisorption, the presence of different forms of adsorbed hydrogen, the difference of the adsorption isotherm from the Langmuir or Temkin isotherm); hydrogen entry into the electrode; the presence of oxide films or chemisorbed oxygen on the electrode surface; different types of surface heterogeneities on solid electrodes; dependence of the transfer coefficients of HER steps on the overvoltage, etc. Some of these effects can change the structure of equivalent electrical circuit.

One of the most common factors that can affect the dependences of equivalent circuit elements on the electrode potential E is the absorption of atomic hydrogen by electrode material that can occur simultaneously with HER. The entry of hydrogen into the solid phase is typical for transition metals, alloys, and intermetallic compounds [2–4].

The influence of hydrogen absorption reaction (HAR) on the impedance of the hydrogen electrode was discussed in many studies [5–23]. Many theoretical and experimental results on the HAR impedance are summarised in [24–26]. The main attention in [5–23] was focused on the analysis of frequency dependence of the impedance, the derivation of expressions for the Faradaic admittance, the determination of the equivalent circuit structure, the experimental tests of obtained relationships (using, in most cases, palladium or its alloys [5–9,16,18–22]).

In these works two mechanisms of hydrogen absorption – direct (one-step) [7,8,11,12,15,16,23] and indirect (two-step) [5,7–9,13,17,19,23] absorption – were considered, and two types of boundary conditions – permeable [7,8,10,12,19] and impermeable [9,10,12–14,18,19] boundary conditions – were used. In some cases the evolution of molecular hydrogen was not taken into account at the analysis of impedance spectra [5,9,12,13,15]. In the mentioned

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works [5–23] the influence of HAR on the potential dependence of Faradaic impedance elements associated with HER was studied insufficiently. In some papers [6,8,9,17,18,20,22] one gives only the estimated or experimental dependences of the charge transfer resistance R_{ct} on E. Gabrielli et al. [18] presented the dependences of all equivalent circuit elements (including 3 parameters of HER impedance) on E. However, in all these cases there was no analysis of the relationship between HER mechanism (in the presence of HAR) and the character of the dependence of HER impedance parameters on the electrode potential.

The purpose of this work is to estimate the changes in the values of diagnostic criteria [1] for HER mechanisms due to the occurrence of HAR in parallel with HER.

2. Background

Assume that HER in acid solution may include the following steps:

$$\text{Volmer reaction: } H^+ + e^- + M \rightarrow MH_{ads} \tag{1}$$

$$\text{Heyrovsky reaction: } H^+ + MH_{ads} + e^- \rightarrow M + H_2 \tag{2}$$

$$\text{Tafel reaction: } MH_{ads} + MH_{ads} \rightarrow 2M + H_2 \tag{3}$$

The expressions for the rates v_i of these steps can be represented respectively by [25]:

$$\begin{aligned} v_1 &= k_1(1-\theta)\exp(-\alpha_1 F\eta/RT) - k_{-1}\theta\exp((1-\alpha_1)F\eta/RT) \\ &= k_1{}'(1-\theta) - k_{-1}{}'\theta \end{aligned} \tag{4}$$

$$\begin{aligned} v_2 &= k_2\theta\exp(-\alpha_2 F\eta/RT) - k_{-2}(1-\theta)\exp((1-\alpha_2)F\eta/RT) \\ &= k_2{}'\theta - k_{-2}{}'(1-\theta) \end{aligned} \tag{5}$$

$$v_3 = k_3\theta^2 - k_{-3}(1-\theta)^2 \tag{6}$$

where η is the overvoltage, k_i and k_{-i} are the rate constants of steps at $\eta = 0$ in forward and backward direction respectively, $k_i{}'$ and $k_{-i}{}'$ are the rate constants at given overvoltage, α_i are the transfer coefficients, θ is the electrode surface coverage by adsorbed hydrogen. The concentration of hydrogen ions is included into the rate constants. Thus, it is assumed that the Langmuir isotherm is fulfilled, the rate constants for the Volmer and Heyrovsky steps are exponential functions of the overvoltage, and the rate constant for the Tafel step does not depend on η. In this work we discuss the Volmer–Heyrovsky and Volmer–Tafel mechanisms, both in combination with the HAR.

Although the direct absorption of hydrogen is discussed in many works on impedance of HER + HAR [7,8,11,12,15,16,23], a more likely mechanism is the entry of H into the metal through a common with HER intermediate H_{ads} [2,3,27]. In [28] it is assumed that hydrogen passes consecutively through two adsorbed states (weakly bonded H_{ads} in the on-top sites and strongly bonded H_{ads} in the hollow surface sites) during the absorption by transition metals at cathodic overvoltages. In the present work we assume that HAR proceeds through H_{ads} and this intermediate is identical to the intermediate in HER. In this case we can express the reaction of transition of adsorbed hydrogen atoms across the interface as [17]

$$MH_{ads} + S \leftrightarrow M + SH_{abs} \tag{7}$$

where M is a surface metal atom, S is a free subsurface site. The HAR rate can be expressed as [17,24,29]

$$v_a = k_a\theta(1 - X_0) - k_d(1-\theta)X_0 \tag{8}$$

where k_a and k_d are the rate constants for the steps of absorption and desorption respectively, $X = C_H/C_{H,max}$, C_H is the hydrogen concentration in metal, $C_{H,max}$ is the maximal value of C_H; index 0 in (8) indicates the concentration of hydrogen at the metal surface ($x = 0$). In assumption of low θ and X_0, expression (8) is simplified to

$$v_a = k_a\theta - k_d X_0 \tag{9}$$

In some works [6,27] equation (9) is expressed as

$$v_a = k_a\theta - k_d C_s \tag{10}$$

where C_s is the hydrogen concentration at $x = 0$.

There are few data on the values of k_a and k_d. For Fe electrode the values k_a from 3.5 s^{-1} in alkaline solutions [30] up to 14.75 s^{-1} in acidic chloride solutions [31] were obtained. The rate constant k_a in units of s^{-1} is used when the amount of adsorbed hydrogen is expressed in mol cm^{-2} and not in fractions of the surface covered by H_{ads}. In order to compare the values of k_a with the values of rate constants for the steps of HER let us express k_a in mol cm^{-2} s^{-1} by multiplying by the maximal adsorption of atomic hydrogen $\Gamma_m = q_1/F$ where q_1 is the charge required for the formation of adsorbed hydrogen monolayer. The typical value of Γ_m is equal to 2×10^{-9} mol cm^{-2}, so the above values of k_a will be from 7×10^{-9} up to 3×10^{-8} mol cm^{-2} s^{-1}. The value $k_a = 2 \times 10^{-10}$ mol cm^{-2} s^{-1} is reported for Fe in sulphuric acid solution [32]. Thus, the probable range of variation of k_a can be 10^{-10}–10^{-7} mol cm^{-2} s^{-1}, though it was estimated by a limited amount of experimental data.

The step of absorption of hydrogen atoms is followed by hydrogen diffusion into the bulk of electrode. Generally it is assumed that Reaction (7) is in quasi-equilibrium and the rate of hydrogen uptake in metal is limited by the bulk diffusion of H [2,28]. But in some cases the hydrogen absorption process may proceed with the kinetic control [3,21,27]. For example, the hydrogen diffusivity in pure iron is rather high (nearly 10^{-4} cm^2 s^{-1} at ambient temperature [33,34]) and in film Fe electrode the diffusion process is very rapid as compared with the surface processes [23]. The transition to the kinetic control of HAR is facilitated, e.g. by decreasing foil thickness when using membrane electrodes [27]. In this paper we consider both cases – kinetic as well as diffusion control of HAR.

In general, the properties of the surface change as a result of absorption of hydrogen by the metal [35], the energy of hydrogen adsorption $E_{M\text{-}H}$ on the metal surface decreases [36] which, in turn, will affect the kinetics of HER. This factor acts in addition to the change of θ as a result of H absorption. Decrease in $E_{M\text{-}H}$ is probably due to the indirect electronic interaction mediated by the substrate [37]. It may be noted that in many cases, including transition metals that tend to absorb hydrogen, the regularities of HER that are based on the Langmuir adsorption isotherm for H_{ads} are observed [38–42]. The Langmuir isotherm is fulfilled on a homogeneous surface with no interaction between adsorbate atoms and in this case $E_{M\text{-}H}$ = const. The interactions between adsorbed hydrogen atoms and the interactions between H_{ads} and subsurface hydrogen atoms H_{abs} may have the same nature being indirect interactions through the electronic system of the substrate. The realisation of the Langmuir isotherm means that we can neglect the interaction between the surface hydrogen atoms, and between surface and subsurface hydrogen. Therefore, we do not take into account the effect of reducing $E_{M\text{-}H}$ during hydrogen absorption but, generally speaking, it should be kept in mind.