

A model for electrode effects based on adsorption theory



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ARTICLE INFO

Article history:

Received 27 April 2015

Received in revised form 7 July 2015

Accepted 8 July 2015

Available online 29 July 2015

Keywords:

Electrode effects

Electrolytic plasma

Electrode coverage

Percolation theory

Gas-evolving vertical electrodes

ABSTRACT

A model to describe the electrode effects based on the adsorption theory is proposed. We assume that the coverage (i.e. by gas bubbles, electrodeposition of compounds, etc) of the electrodes is governed by a kinetics equation where the adsorption term is proportional to the bulk current density, and the desorption term to the actual coverage. The adsorption can take place only on the uncovered part of the electrode. We show that the coverage is responsible for a variation of the interface properties of the electrode. The time dependence of the electric response of the cell, submitted to an external voltage, is determined by solving the differential equation for the coverage. We show that two regimes are expected. One, in the limit of small time, controlled by the charging of the surface interface, and one related to the coverage. The theoretical predictions are in reasonable agreement with the experimental data concerning the time dependence of the current and the current-voltage characteristics of a home-made photo-electrolyzer constituted by a BiVO_4 photoanode and a Pt cathode. Moreover, a normalized current-voltage curve was obtained, which fit also literature data based on (i) electrolysis on cylindrical stainless-steel electrodes in NaOH electrolyte and (ii) electrolytic plasma nitrocarburizing of AISI 1020 steel discs in an Urea-based aqueous solution, demonstrating the versatility and broad range of application of the here proposed model.

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1. Introduction

Electrode effects have been observed and theoretically analyzed by several authors [1–3]. Starting from the pioneeristic work of Kellogg [4] it has been observed that at a certain value of voltage between two electrodes in an aqueous electrolyte, there is significant deviation from the standard electrolytic regime: the gas formed at the electrodes, for a critical value of the potential, coalesces, forming a unique continuous gas, which acts as an envelope around the electrodes, giving a sudden drop down in the current at the electrodes, normally followed by a luminous discharge (glow discharge plasma [5,6]). This process called also electrolytic plasma process has been widely used for practical purpose as surface treatment process for generating oxide coatings on metals, in a similar way to anodizing, but in this case the resulting plasma modifies the structure of the oxide layer [7,8].

To our knowledge an analytic model describing all this process is still missing. Good reviews on the electrochemical discharges, relevant to its discovery and recent applications, have been published

by Gupta et al. [9] and by Wuthrich and Bleuler [10]. In a previous paper Wuthrich and Bleuler proposed also an interesting model for the electrode effects based on the percolation theory [11]. In the same way, our group recently used a percolation approach in order to study the time variation of the photoelectric process during bubbles generation [12]. The goal of the present work is to develop a model for the same effect based on the adsorption phenomenon. The adsorption phenomenon is supposed to be well described by a kinetic equation similar to Langmuir's isotherm, valid in the limit of small adsorption [13]. We assume that the electrical response of the working cell can be described by an electrical circuit formed by a bulk resistance in series with a surface layer characterized by a resistance and a capacitance [14]. Due to the adsorption phenomenon, the surface resistance and capacitance are the parallel of the covered and uncovered parts [15]. In this framework we show that the time dependence of the current contains two characteristics time: one short, related to the charging of the surface layer, and one long related to the kinetics of the coverage. The predictions of the model are validated with experimental data concerning the time dependence of the current and the current-voltage characteristics of a photo-electrolyzer, which is constituted by a BiVO_4 photoanode and a Pt cathode assembled in a home-designed cell. In addition, a normalized current-voltage curve is compared with

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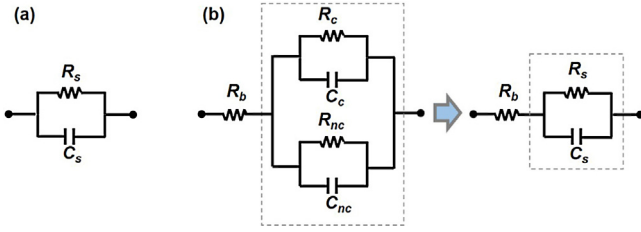


Fig. 1. The electrolytic cell is modeled as a parallel formed by a resistance and a capacitance only (a). In order to take into account the coverage effect of the electrode due to the bubbles formation in the electric response of the cell to an electric applied voltage, also the bulk resistance of the cell has to be considered, and the circuit has been modified as reported in the subplot (b)

literature data based on another electrolytic applications, in order to assess the versatility of the developed model.

This paper is organized as follows. In Sect. 2 the electrical response of a simple circuit is considered, to show the divergence of the electric current in an ideal electrochemical cell modeled as a parallel formed by a resistance and a capacitance only. The presence of a bulk resistance on the time dependence of the current is discussed in Sect. 3, whereas the analysis of an electric circuit simulating a real cell is reported in Sect. 4. The influence of the adsorption on the covering effect is considered in Sect. 5, where the kinetic equation used in the analysis is introduced. In that section a simple expression for the time dependence of the covering ratio, valid when the bulk resistance of the cell is negligible with respect to that of the naked interface layer is deduced. The comparison of the theoretical predictions with the experimental data, along with the best obtained fit, is presented in Sect. 6. The final Sect. 7 is devoted to the conclusions.

2. Electrical response of a simple circuit

Let us consider a simple cell whose electrical response to an external excitation can be simulated by an electrical resistance R_s in parallel with a capacitance C_s . When the circuit is submitted to a voltage $V_0(t)$, due to an external power supply, the electric current in the circuit is $i(t) = i_R(t) + i_C(t)$. In this relation $i_R(t)$ is the conduction current in R_s and $i_C(t)$ the displacement current in C_s (see Fig. 1a). By means of simple considerations we get $i_R(t) = V_0(t)/R_s$ and $i_C = C_s dV_0(t)/dt$, and the total current in the circuit is

$$i(t) = \frac{V_0(t)}{R_s} + C_s \frac{dV_0(t)}{dt}. \quad (1)$$

In the particular case in which $V_0(t) = V_0 u(t)$, where $u(t)$ is the step function such that $u(t < 0) = 0$ and $u(t > 0) = 1$, taking into account that $\delta(t) = du(t)/dt$, where $\delta(t)$ is Dirac's function, from Eq. (1) we obtain

$$i(t) = \frac{V_0}{R_s} u(t) + C_s V_0 \delta(t). \quad (2)$$

From Eq. (2) it follows that the $i(t)$ diverges at $t=0$ and tends to a constant value V_0/R_s , as expected.

3. Real Cell

In a real cell, in the presence of the electrode effect, the electrode is partially covered by bubbles coming from the bulk. In this case, the electrical response of the cell can be simulated by the circuit shown in Fig. 1b: the series of a bulk resistance R_b and a surface layer whose resistance, R_s , and capacitance, C_s , are given by

$$R_s = \frac{R_c R_{nc}}{R_c + R_{nc}}, \quad \text{and} \quad C_s = C_c + C_{nc}, \quad (3)$$

where the subscripts c and nc refer to the covered and uncovered part of the electrode. According to (3) the effective resistance and capacitance of the surface layer are the parallel of the surface resistances and capacitances of the covered and uncovered parts [15]. We indicate by λ the thickness of the surface layer, ρ_c and ρ_{nc} the resistivity and by ε_c and ε_{nc} the dielectric constant of the covered and uncovered parts. Indicating by S_c and S_{nc} the surface of the covered and uncovered parts we have

$$R_c = \rho_c \frac{\lambda}{S_c}, \quad \text{and} \quad R_{nc} = \rho_{nc} \frac{\lambda}{S_{nc}}, \quad (4)$$

for the resistances, and

$$C_c = \varepsilon_c \frac{S_c}{\lambda}, \quad \text{and} \quad C_{nc} = \varepsilon_{nc} \frac{S_{nc}}{\lambda}, \quad (5)$$

for the capacitances. If S is the total surface of the electrode, we have the obvious relation $S = S_c + S_{nc}$. If $\beta = S_c/S$ is the coverage of the electrode due to the deposition of the bubbles on it we have $S_c = \beta S$ and $S_{nc} = (1 - \beta)S$, and Eq.s (3) can be rewritten as

$$R_s = \frac{R_0}{(1 - \beta)[1 + m\beta/(1 - \beta)]}, \quad (6)$$

$$C_s = C_0[(1 - \beta) + n\beta], \quad (7)$$

where $R_0 = \rho_{nc}(\lambda/S)$ and $C_0 = \varepsilon_{nc}(S/\lambda)$ are the surface resistance and capacitance of the naked electrode. The parameters m and n are defined by $m = \rho_{nc}/\rho_c$ and $n = \varepsilon_c/\varepsilon_{nc}$. Since the presence of the bubbles makes the electrode blocking, $\rho_c \rightarrow \infty$, and hence $m \rightarrow 0$. Moreover, since $\varepsilon_{nc} \sim 80 \times \varepsilon_0$, whereas $\varepsilon_c \sim \varepsilon_0$, $n \sim 1/80$, and can be neglected too. Consequently, from Eq.s (6, 7) we get

$$R_s = \frac{R_0}{1 - \beta}, \quad \text{and} \quad C_s = (1 - \beta)C_0. \quad (8)$$

It follows that the time constant of the surface layer, defined by $\tau_s = R_s C_s = R_0 C_0$, is a constant, independent of the coverage β . We observe that in a working cell β depends on time t , and is regulated by a kinetic equation, as discussed in the following. However, τ_s is time independent.

4. Analysis of the electric circuit simulating a real cell

From the discussion reported above for what concerns the electric response the cell can be simulated by the series of R_b with the parallel (R_s , C_s). When the cell is subjected to an external voltage $V_0(t)$ we have

$$V_0(t) = R_b i(t) + R_s i_R(t), \quad (9)$$

where, as above, $i_R(t)$ is the conduction current across R_s . Furthermore, since R_s and C_s are in parallel we have $R_s i_R(t) = Q/C_s$, where Q is the electrical charge on C_s . From this condition we get $Q = R_s C_s i_R$. The total current in the circuit is then $i(t) = i_R + dQ/dt$, and Eq. (9) can be rewritten, for the discussion reported above about τ_s , as

$$V_0(t) = \left(R_b + \frac{R_0}{1 - \beta(t)} \right) i_R(t) + R_b \tau_s \frac{di_R}{dt}. \quad (10)$$

Supposing again that $V_0(t) = V_0 u(t)$, where $u(t)$ is the step function, the solution of Eq. (10), satisfying the initial condition $i_R(0) = 0$ is

$$i_R(t) = \frac{V_0}{R_0 + R_b} \left(1 - e^{-t/\tau} \right), \quad (11)$$

where the effective time constant of the circuit is

$$\tau = \frac{R_b}{R_0 + R_b} \tau_s < \tau_s. \quad (12)$$

We observe that for $t \gg \tau$, but small with respect to the characteristic time related to the covering effect, $i_R \sim V_0/(R_0 + R_b)$.

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