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State estimation in Volmer–Heyrovsky reactions coupled with sorption processes: Application to the hydrogen reaction

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Abstract

In this work, a procedure to estimate variables of electrochemical systems involving adsorption and absorption of intermediate species coupled to diffusion is presented. The method is model-based and needs potential and current measurements. Since the system is linear and time variant, the well known Kalman's filter theory is used to estimate the variables. An analysis of theoretical observability shows the procedure success even in the case of constant potential/current. The error estimation converge asymptotically to zero for slow time variations. The procedure is useful to estimate H concentrations in metallic substrates during H evolution and insertion. To illustrate the proposed procedure, state observations of the hydrogen concentration on steel and metal hydride electrode are presented. In the last case, the procedure is used to estimate the state of charge of the electrode.

Keywords: State of charge; Observability; Metal hydride; Hydrogen reaction; Kalman filter

1. Introduction

The study of hydrogen evolution, sorption, and diffusion on metals and alloys has been the subject of numerous scientific publications. These processes are related to the operation of hydrogen storage materials in rechargeable batteries such as Ni/metal hydride (MH) [1–3]. They are also related to the ingress of H into ferrous alloys, which is a major cause of embrittlement and damage coupled to metallic corrosion in many technological processes [4]. In both cases, the mechanism for hydrogen evolution and adsorption may be described by the Volmer–Heyrovsky–Tafel scheme coupled to subsequent absorption and diffusion of H atoms into the metallic substrate [5–7]. For both systems, the determination of H concentration dependence with respect to position and time is important. In the case of metal hydride electrodes, the H concentration profile is directly related to the state of charge (SOC) of the electrode. In the case of systems undergoing corrosion processes, the hydrogen content is related to the failure of the material. Typically the SOC of the battery is desired to be kept within appropriate limits, for example $20\% \leqslant \text{SOC} \leqslant 95\%$, so the estimation of the SOC is essential for the battery to operate within these safe limits.

In this work we study the modeling and state observation of hydrogen evolution and absorption reactions coupled to H diffusion. The reactions shall be described in terms of the mechanism associated with absorption and diffusion processes. Using spatial discretization of the metallic substrate, the diffusion differential equations are approximated by ordinary linear differential equations with constant parameters. In this way, having previous knowledge of initial and boundary conditions, the state variables such as surface concentration of intermediate species and bulk concentration of H may be well predicted. However, even when knowing the initial conditions, the presence of

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disturbances may produce differences between predicted and real values. In a more realistic scenario where initial conditions and disturbances are unknown, state estimation by direct model simulation is imprecise. Instead, using the model and filtering theory, it is possible to estimate the state evolution by just measuring output variables like current and voltage [8,9]. In this paper the state observation problem is solved by using the Kalman's filter for non-stationary systems [10]. For this purpose, the model was written as a lineal time/dependent set of equations.

The paper is organized as follows: in Section 2, electrochemical mechanisms are mathematically modeled as a set of nonlinear differential equations in terms of mass and charge balances. Subsequently, the model equations are spatially discretized and represented as ordinary nonlinear differential equations with time varying parameters. Afterward, reformulation using the measured current allow us to set up the model as linear and time-varying, which is used properly in the Kalman's filter. In Section 3, the observability condition is analyzed in the context of the Kalman's filter. In Section 4, the state estimation procedure is performed in two different electrochemical systems by using model-based simulations of real electrodes whose parameters were reported in the literature. The first one deals with H_2 evolution on an AISI 1045 planar steel electrode in 0.1 M NaOH [11], and the second one, with potentiostatic variations of a metal hydride electrode constituted by $MmNi_{3.6}Co_{0.8}Mn_{0.4}Al_{0.3}$ quasi-spherical alloy particles, in 6 M KOH [12]. Finally, conclusions are presented in Section 5.

2. Model formulation

Hydrogen evolution coupled to insertion in metallic substrates constitutes an electrochemical intercalation process involving charge transfer steps, adsorption and absorption of electroactive species, and mass transfer. The process can be modeled as follows [5,7]: in the first step, water reacts with a surface metal atom (M) producing an adsorbed intermediate (MH_{ad}) on the surface. This electroreduction step is described by the Volmer reaction and can be represented by the following electron-transfer equation:

$$H_2O + M + e^- \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} MH_{ad} + OH^-, \tag{1}$$

where $k_i = k_i^0 e^{-b\alpha_i\eta(t)}$ and $k_{-i} = k_{-i}^0 e^{b(1-\alpha_i)\eta(t)}$ with $b = F/RT$, α_i the symmetry factor – being a number in the interval $[0,1]$, $\eta(t) = E(t) - E_{eq}$ is the overpotential – E_{eq} is the Hydrogen reaction equilibrium potential. In a second electroreduction step, adsorbed species react with water producing hydrogen evolution (Heyrovsky's reaction) which can be described as

$$MH_{ad} + H_2O + e^- \underset{k_{-2}}{\overset{k_2}{\Longleftrightarrow}} M + H_2 + OH^-. \tag{2}$$

The equilibrium kinetic constants related to Volmer and Heyrovsky steps are related in terms of [17]

$$\frac{k_1^0 k_2^0}{k_{-1}^0 k_{-2}^0} = 1. \tag{3}$$

In a third step, the hydrogen adatoms, MH_{ad}, are transferred to a free interstitial site in the metal (S) just beneath the metal surface. This process is parallel to the Heyrovsky's step. Calling (SH_{ab}) the absorbed atom of hydrogen, the absorption reaction may be written as follows:

$$MH_{ad} + S \underset{k_{-3}^0}{\overset{k_3^0}{\Longleftrightarrow}} M + SH_{ab} \quad \text{H sorption reaction}, \tag{4}$$

where k_3^0, k_{-3}^0 are both potential-independent rate constants. Then, the equations for mass and charge balances representing the kinetics of the system are the following:

$$\frac{d\theta}{dt} = k_1\tilde{\theta} - k_{-1}\theta - k_2\theta + k_{-2}\tilde{\theta} - \frac{J(0,t)}{\Gamma}, \tag{5}$$

$$J(0,t) = \Gamma(k_3^0\theta\tilde{x} - k_{-3}^0 x\tilde{\theta}), \tag{6}$$

$$I_f = -FA\Gamma(k_1\tilde{\theta} - k_{-1}\theta + k_2\theta - k_{-2}\tilde{\theta}), \tag{7}$$

followed by diffusion of MH_{ad}. $J(0,t)$ is the flux of hydrogen diffusing from the surface to the interior of the metal. Let us assume that $\theta(t) \in [0,1]$ is the surface coverage of the intermediate species MH_{ad} and $\tilde{\theta}(t) = 1 - \theta(t)$ the corresponding free metal surface. Let us call $x(z,t)$ the fractional concentration of SH_{ab} species, being $x(z,t) = c(z,t)/\bar{c}$, where $\bar{c}$ is the maximum SH_{ab} concentration, being z the spatial position and t, the time. $x(z,t)$ is expressed adimensionally in the interval $[0,1]$. The complementary concentration is given by $\tilde{x}(z,t) = 1 - x(z,t)$, which represents the fractional concentration of available vacant sites for H in the bulk; $J(z,t)$ is the flux of hydrogen diffusing from the surface to the interior of the metal at spatial position z and time t; Γ is the MH_{ad} maximum surface concentration; I_f is the faradaic current; F is the Faraday constant; and A is the active electrode area.

To complete the model given by Eqs. (5)–(7) we need to include the equations describing hydrogen diffusional transport in the metal substrate. This may be expressed by Fick's first and second laws, which in the case of spherical geometry corresponds to [13]

$$J(z,t) = -D\bar{c}\frac{\partial x(z,t)}{\partial z}, \tag{8}$$

$$\frac{\partial x(z,t)}{\partial t} = D\left(\frac{\partial^2 x(z,t)}{\partial z^2} + \frac{2}{z}\frac{\partial x(z,t)}{\partial z}\right), \tag{9}$$

where D is the diffusion coefficient. Using Eq. (8) in (9) we get

$$\frac{\partial x(z,t)}{\partial t} = -\frac{1}{\bar{c}z^2}\frac{(\partial z^2 J(z,t))}{\partial z}. \tag{10}$$

The analytical solution of Eq. (10) is complex [13]. Then, in order to simplify, it can be approximated into a set of ordinary differential equations by using a spatial discretization. Spatial discretization is a very well known method to approximate partial differential equations in ordinary differential equations, for details see [6,7]. Eq. (10) can be