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Cyclic voltammetry simulations with cellular automata

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ABSTRACT

Cyclic voltammetry is modeled using a probabilistic cellular automata (CA). The system is built up by simple evolution rules representing diffusion and electrochemical reactions. A connection between the CA model and electrochemistry is established using the electric charge of each cell and the chemical species that it represents. We studied two different kinetic regimes of electronic transfer at the electrode, which could be described by the Nernst and Butler–Volmer theories. In the evolution rules, we define probabilities that are directly related to the properties of the system and are described in terms of the electric potential. CA features are thus associated to macroscopic quantities and simulations are compared with experimental data from literature and validated with simulations using the standard finite element models (FEM). This work consolidates CA modeling as a quantitative approach for this domain of application and shows the capabilities of relatively cheap graphical processor units (GPU) on standard desktop workstation to model 3D complex systems.

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1. Introduction

Electrochemistry is the driving force for devices like batteries [1], fuel cells and electrochemical sensors like those used by diabetics to monitor blood glucose concentration [2–5]. All of them work through a charge transfer across an interface between an electroactive surface and an electrolyte. At the present time, the electrochemistry of this interaction is not fully understood and it is still an active field of academic research [6].

One popular method used for this kind of investigations is the cyclic voltammetry (CV) [7,8]. It consists of a linear potential scan on an electrode submerged in solution with electro-active species. Various electrochemical reactions occur for specific potentials thus, the concentration of species around the electrode changes during the scan. This method is mainly used to study the chemical reactivity of species but it is directly connected with mass transfer phenomena.

CV is considered a transient technique, where electrochemical kinetics are rarely linear. Therefore, analytical solutions are not always satisfactory and computer simulations are necessary to obtain a full description.

Randles [9] presented the first mathematical relations for CV in 1948. He faced the complexity of the diffusion equations by deriving a series of approximations for the current-potential curve in terms of the concentration of the electroactive species. Nicholson and Shain [10] contributed by solving the diffusion equation via Laplace Transforms and integrating numerically for different values of scanning rate and kinetic parameters in order to obtain standard curves to avoid tedious calculations. Feldberg and Auerbach [11] presented the first digital simulations using Fortran. They used a finite difference method (FDM) to solve the CV electrochemistry equations. This work led to the commercial program *DigiSim* [12] that is still used and on active stage of development. One particular point is its ability to fit experimental curves by the least squares method and find the respective kinetic parameters.

Even though, the FDM is not still fully adapted to the simulation of electrodes or substrates, which have regions of complex or fast changing geometry [13]. There are other alternative methods like the Boundary Element Method (BEM) that requires only the discretization of the surface boundaries, reducing the computation cost [14] and FEM, whose main interest is to deal with problems that involve fluid dynamics and/or complex geometries [15]. However, the discrete mesh should be carefully defined, especially in regions where there is a sharp change in nature of the boundary

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conditions. For instance, the change of the material on the surface of the electrode between the glass and metal as seen in other CA simulations [16].

In this work, a three-dimensional CA-based model is proposed. Great progress has been done on this type of modeling for the field of electrochemistry, more specifically in terms of corrosion [17], electrolysis [18,19] and passivation [20] phenomena. At this moment, most of the results from these models are qualitative, considering that they describe more a general tendency of the process than specific physical values. This versatile method is best adapted for cases where the electrode has low symmetry geometry or it has imperfections on the surface. The objective of this work is to expand the scope of CA modeling and demonstrate that it can be used also as a quantitative tool.

This method has a probabilistic nature that makes the distinction with the previously cited ones. This is adequate to represent stochastic phenomena such as corrosion or Brownian motion. Its simplicity represents an other advantage, where complex phenomena are described by simple local iterations, avoiding the resolution of differential equations or some other typical computational problems such as heterogeneous meshing or convergence of the system. On the other hand, it requires several simulations or time steps to limit probabilistic noise and obtain clean meaningful results, making this method slower compared to the other ones.

This paper is organized as follows. Section 2 presents a brief description of experimental CV, more detailed descriptions can be found in the literature [7,21–23], Section 3 describes the characteristics of our CA model and finally Section 4 includes the main results and discussions.

2. Cyclic voltammetry principles

A typical electrode reaction involves the transfer of charge between an electrode and species in solution. The electrode reaction usually referred to as electrolysis, typically involves three steps: the reactant moves to the interface, the electron transfer occurs and the product moves away from the electrode. The electron transfer produces electrochemical reaction of the type:

$$A + e \underset{[k_b]}{\overset{k_a}{\rightleftharpoons}} A^- \tag{1}$$

This reaction has a double arrow that represents reversibility. Species can give or take an electron, which corresponds respectively to oxidation and reduction processes. The net electron flow resulting from the reaction gives a direct access to its kinetics when the potential is changed. In this work, we consider linear ramps potential variations as shown in Fig. 1. Each direction of the reaction (1) contributes to opposite currents called anodic and cathodic. The net current is the difference between the two and it depends on reactivity and mass transfer rates. In general, the mass transfer mechanism is natural convection or diffusion for unstirred solutions.

In this work, the initial solution has only one electroactive species and the initial potential is such that no reaction occurs when the electrode is turned on. This is indicated on point 1 of Fig. 2. The x and y axis have been adapted to present international electrochemical conventions (IUPAC) different from the ones used in [22]. As the potential sweeps, the cathodic current first remains constant and then rapidly increases until the concentration of A at the electrode surface is substantially diminished, causing a peak of current, indicated on point 2 of Fig. 2. Then the current decreases and gradually reaches a steady state due to the diffusion limited rate of arriving species at the electrode. The potential scan direction is then reversed as shown in point 3 of Fig. 2. The potential is still sufficiently negative to reduce A, so cathodic current continues. When the electrode reaches a sufficiently oxidant potential, A^- can now

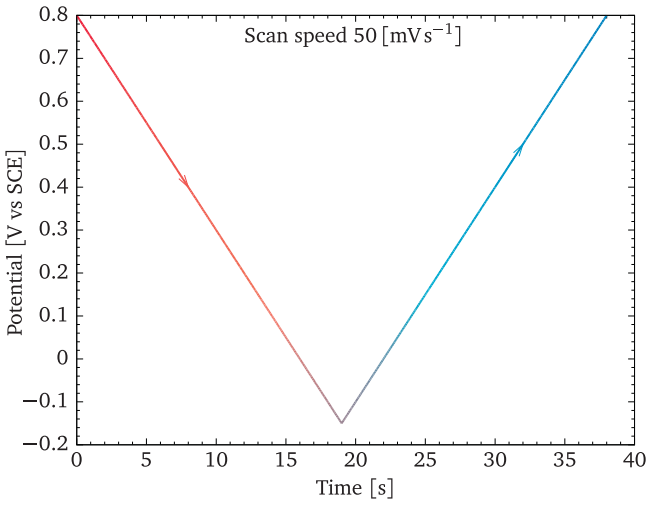

Fig. 1. Variation of the electrode potential with time.

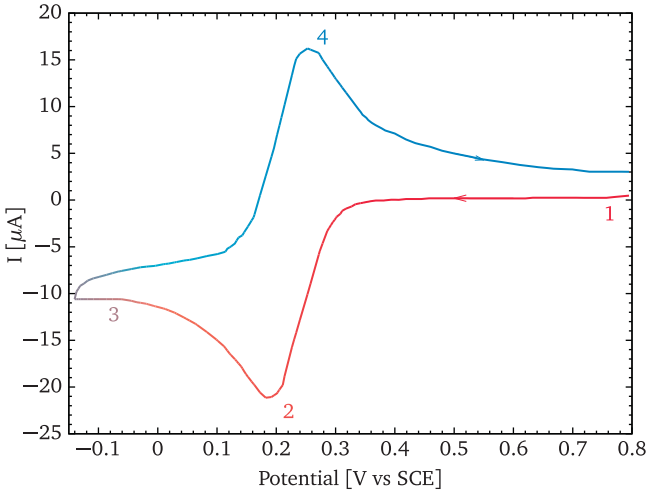

Fig. 2. Typical cyclic voltammetry curve [22].

be oxidized by the backward reaction in Eq. (1). The current slowly varies as a combination of the anodic and cathodic current. Then the anodic current rapidly increases and the surface is depleted of A^- species, causing the current to peak as shown in point 4 of Fig. 2. The current then decays as the solution surrounding the electrode is free of A^- species. The cycle is completed when the potential reaches the initial value. Electron transfer rate (k_a and k_b in reaction (1)) determines the system. Rapid electron transfer indicate that following the application of an applied potential, equilibrium between A and A^- will be re-established quickly. These systems are called reversible and are determined by a local form of the Nernst equation. The only process that limits the current is diffusion. In these systems, the position of the current peaks on the potential axis is independent of the potential scan rate and concentration.

When the electron transfer rate is finite and below a certain scan speed, the equilibrium conditions cannot be maintained as the potential changes. Irreversibility manifests itself with current peak separation varying with the scan speed. Quasi-reversible reactions (when k_a and k_b have the same order of magnitude) are described by the Butler–Volmer equation.

The nature of the electrode plays an important role in the behavior of the system. Most electrodes used are made of graphite or platinum because of their inertness (no corrosion), but each of them has different catalytic properties.

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