Chaos, Solitons and Fractals 84 (2016) 81–87

Contents lists available at ScienceDirect

Chaos, Solitons and Fractals

Nonlinear Science, and Nonequilibrium and Complex Phenomena

journal homepage: www.elsevier.com/locate/chaos

Differential equation of a fractal electrode–electrolyte interface

Carmelo José Felice*, Gabriel Alfredo Ruiz

Laboratorio de Medios e Interfases, Departamento de Bioingeniería, UNT/CONICET, CC 327-Correo Central, 4000 Tucumán, Argentina

ARTICLE INFO

Article history:
Received 7 August 2015
Accepted 7 January 2016
Available online 3 February 2016

Keywords:
Electrodes
Electrochemistry
Impedance
Fractal
Differential

ABSTRACT

Understanding an electrode–electrolyte interface (EEI) behavior is a valuable tool in several areas of science. There are models based on discrete fractal structures, which explain the measurements of linear and non-linear impedance at fixed frequencies, or at determined ranges of high and low current densities. A level by level discrete calculation is needed to evaluate these models, or the use of *black-box* models, which affect the good understanding of the phenomenon. A continuous model based on a differential equation of an EEI is presented in this paper. It includes an electrical circuit similar to a long transmission line. It has been deduced from the discrete Liu model.

1. Introduction

Understanding an electrode–electrolyte interface (EEI) behavior is a valuable tool in several areas of science. For instance, when measuring pH or bacterial concentration [1–3], or when recording electrocardiogram (*ECG*), electroencephalogram (*EEG*) or electromyogram (*EMG*) [3]. Besides, it is essential to understand how it interferes with measurements when the interface is operating in the non-linear zone, such as the non-linear dielectric spectroscopy of biological suspensions [2].

In all cases, it is necessary to deeply understand the electrode behavior, mainly when it is in contact with a biological tissue or cells in suspension.

Physically, the electric current encounters Ohmic resistances in both media (metal and electrolyte), and a capacitance through the interface.

On the other hand, polished surfaces usually show scraping lines under magnification. These grooves have been modeled as distributed RC elements [4,5].

The cross section of the interface model is shown in Fig. 1a, where the electrolyte is depicted in black. The grooves in the electrode can be seen as projections on the electrolyte side. Each groove has a self-similar structure, that is, it is divided into two branches ($N=2$) and these are similar to the original groove (hence the name of self-similar) when magnified by a factor $\boldsymbol{a}$, with $\boldsymbol{a} > N \geq 2$ [13].

The reader would recognize this model as the Cantor-bar fractal structure.

The equivalent electric circuit is shown in Fig. 1b represented in 3D. In it, the electrolytic resistance (R) is increased by a factor a in each subdivision, since at this ratio the cross section is reduced. Z_p represents the impedance of the EEI (of the two side faces of the branches) and it is modeled as the double layer capacity C_{dl} in parallel with the charge transfer resistance R_{ct}. Z_p is the same at each fractal level. The common ground of the circuit is the electrode.

This model includes two electrochemical parameters (C_{dl} and R_{ct}) incorporated in the geometric structure of the electrode. The charge transfer resistance R_{ct} has been incorporated to take into account redox processes.

Since the circuit components of Fig. 1 have the same value, it can be assumed that there are equipotential points

* Corresponding author. Tel./fax: +54 381 4364120.
E-mail address: cfelice@herrera.unt.edu.ar (C.J. Felice).

http://dx.doi.org/10.1016/j.chaos.2016.01.003
0960-0779/

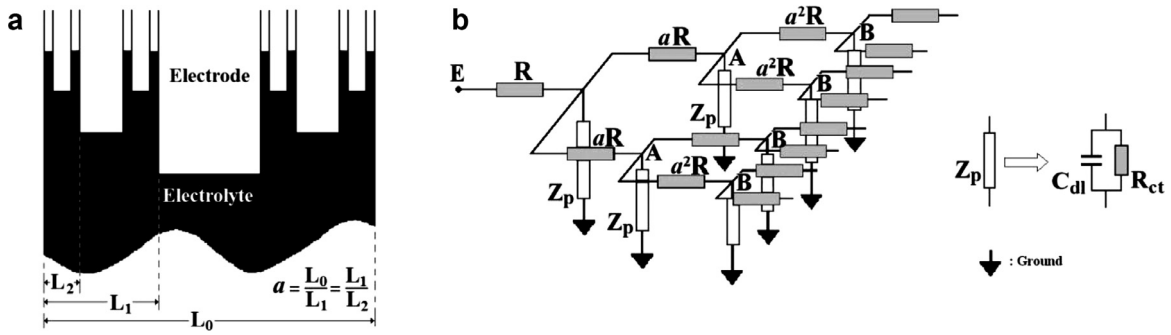

Fig. 1. (a) Cantor-bar fractal model of a rough-EEI, showing two grooves each with four fractal levels. The electrode is shown in white while the electrolyte in black. (b) Equivalent electric circuit for the fractal net of the rough-EEI in a three-dimensional way. *R*: electrolytic resistance, *a*: scale factor, R_{ct}: charge transfer resistance and the C_{dl} double layer capacity. A and B are equipotential points.

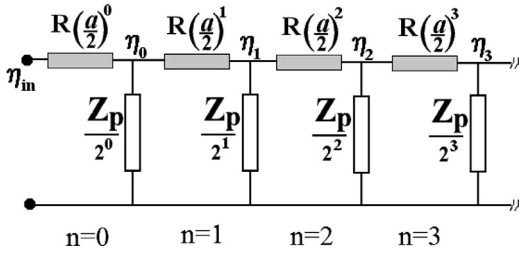

Fig. 2. Simplified fractal net showing the first four levels. *R*, Z_p and *a* idem Fig. 1, $\eta_{0,1,2,3}$ overpotential at different fractal levels ($n=0$ correspond to a flat electrode, $n=1$ to first fractal level, and so on).

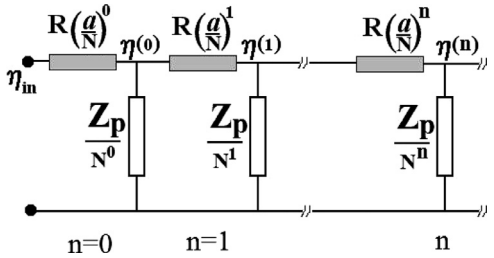

Fig. 3. Generalized discrete model of Fig. 2 considering *N* bifurcations by level and $\eta(n)=\eta_n$; $n=0,1,2\ldots$.

at every level [6], i.e., A corresponds to the first level, B to the second, and so on. Due to this equipotentiality, the circuit can be simplified as shown in Fig. 2.

It is possible to generalize the discrete model of Fig. 2, if N branches or bifurcations are considered by level for each level, instead of two (see Fig. 3).

Thus, a low value of N indicates a high roughness surface, because the grooves need more fractal levels to reach the molecular size. In the case where it is desired to calculate the voltage in every stage, the model has to be developed up to the desired stage. In the reviewed literature, the number of fractal levels of a surface has been modeled by a discrete variable [4,5,7–9].

In this paper we present a non homogeneous second order differential equation with constant coefficients to describe the behavior of an electrode–electrolyte interface. It has been obtained by replacing a discrete fractal model [4,5], by a quadrupole based model similar to a long transmission line. An analytic solution for a simplified version of the differential equation is presented.

The proposed continuous model predicts the potential's changes depending on the distance to the electrode arising from the roughness of the material, but does not report on what happens inside the double layer.

2. The model

It can start from the model of an EEI described by Ruiz et al. [4,5] and shown in Fig. 3. On it, the discrete variable n indicates the fractal level considered ($n=0$ correspond to a flat electrode, $n=1$ to first fractal level, and so on), *a* is the value that divides the channel width of a level to move on to the next one, and N is the number of branches or bifurcations considered by level.

The value of the parallel impedance for each fractal level ($n=0,1,2$, etc.) is:

$$Z_p = \frac{-jX\ R_{ct}}{R_{ct} - jX} \tag{1}$$

where $X = \frac{1}{2\pi f C_{dl}}$: reactance of the double layer capacitance, *f*: frequency, C_{dl}: double layer capacitance, and R_{ct}: charge transfer resistance. R_{ct} is evaluated as the inverse of the derivative of the current density through it respect overpotential falling upon it. The relationship between the current density and the overpotential is known as the Butler–Volmer equation. Z_p is a function of the applied overpotential because R_{ct} depends on the applied overpotential.

The components of the circuit in Fig. 3 have discrete values which depend on the "*n*" step number.

In order to obtain a continuous circuit, we assume that each level is a stage of a distributed parameter model, just like a long transmission line, and the discrete variable "*n*" is replaced by the continuous variable "*x*".

The x relative variable indicates the distance from the double layer charge, without including it, to infinity which in practice corresponds to a point within the solution but away from the electrode. The characteristics of the new continuous model shown in Fig. 4 are:where $R_e(x) = \frac{a^x R}{N^x}$: series electrolytic resistance, $Z_{pi}(x) = \frac{Z_p}{N^x}$: parallel impedance at each fractal level, Z_0: net impedance at $x=0$, $Z(x)$: partial right impedance for each fractal level,