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A detailed look at electrical equivalents of uniform electrochemical diffusion using nonuniform resistance–capacitance ladders ☆

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ABSTRACT

This paper discusses equivalent-circuit modeling of the electrochemical impedance corresponding to one-dimensional diffusion in a uniform medium. It argues that, of the several equivalent circuits in use for such modeling, one – namely the nonuniform resistance–capacitance ladder – has attractive properties that are not shared by any other equivalent circuit. Explicit, analytical expressions are derived for the efficient development of this ladder equivalent, which provide advantages compared to computer optimization. Although the context of this work is battery modeling, the results presented can be of value in other fields where diffusion is studied and modeled.

1. Introduction

The modeling of the electrochemical impedance corresponding to one-dimensional diffusion in a uniform medium [1–7] using electrical circuit analogs has been discussed extensively in the literature [2–5,7–20]. A significant number of alternative equivalent circuits has been presented for this purpose, including Voight (Foster) circuits, Maxwell circuits, and equal-*R*, equal-*C* ladder structures [9,20]. This paper argues that nonuniform ladder equivalents have certain unique properties not shared by other circuits. In contrast to the common practice of determining the element values of such circuits by computer optimization [21,22], this paper develops analytical methods for doing so, and discusses several advantages that can be had by using such an approach. These include the ability to model internal time-domain behavior (as opposed to only external frequency-domain behavior represented by the electrochemical impedance), predictive capability, and efficient computation. These and other advantages, discussed later in this section, make the model suitable for an important emerging application: the computer simulation of mixed electrochemical/electrical systems, such as systems involving both energy storage devices and power electronics. The need for efficient simulation of such systems arises during their design, as well as in their deployment in the field, where on-site, real-time computation can be an important aid in maximizing the performance of the energy storage devices involved. The attributes of the model presented make it attractive for inclusion in more extensive models, containing additional elements that model phenomena not addressed in this paper.

In order to prepare for the arguments to be made in this paper, we consider the diffusion-electrical circuit correspondence, shown in Fig. 1, in some detail. Diffusion is assumed within the structure of Fig. 1a, with volume density $\rho(x,t)$ and flux (number of particles per unit of cross-sectional area, per unit time) $j(x,t)$, where x is position and t is time. This structure is characterized by the continuity equation:

$$\frac{\partial \rho}{\partial t} = -\frac{\partial j}{\partial x} \tag{1}$$

Assuming a constant diffusion coefficient D, Fick's first law is:

$$j = -D\frac{\partial \rho}{\partial x} \tag{2}$$

Inserting (2) into (1) we obtain Fick's second law (the "diffusion equation"):

$$\frac{\partial \rho}{\vartheta t} = D\frac{\vartheta^2 \rho}{\vartheta x^2} \tag{3}$$

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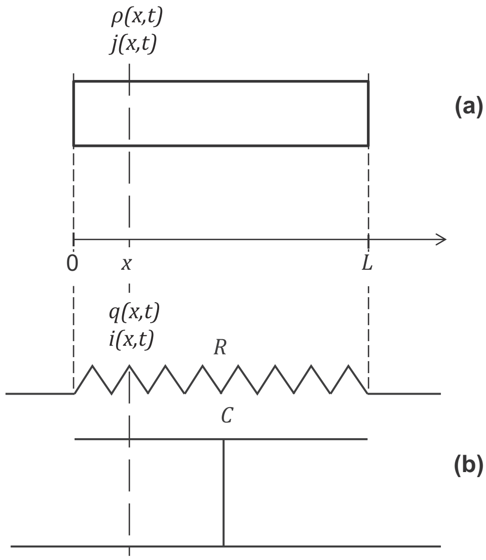

Fig. 1. (a) One-dimensional diffusion and (b) corresponding one-dimensional distributed *RC* circuit. The structures have the same length, *L*.

The structure in Fig. 1b is a linear uniformly-distributed *RC* structure of the same length *L* as the top structure, characterized by total resistance *R* and total capacitance *C*, corresponding to resistance per unit length $r = R/L$ and capacitance per unit length $c = C/L$, respectively. The current at position *x* is denoted by $i(x,t)$, and the charge per unit length stored at position *x* is denoted by $q(x,t)$. Fig. 2 shows corresponding incremental elements of the structures in Fig. 1. In Fig. 2b, the net increase in the charge in time Δt is $i\Delta t - (i+\Delta i)\Delta t = -\Delta i \Delta t$, which corresponds to a charge increase per unit length of $\Delta q = -\Delta i \Delta t/\Delta x$. Allowing finite differences to approach 0, we obtain:

$$\frac{\partial q}{\partial t} = -\frac{\partial i}{\partial x} \tag{4}$$

From Ohm's law we have $i = -\Delta v/(r\Delta x)$; the changes in v and q over the length Δx are related by $\Delta v = \Delta q/c$. Combining these two equations we obtain $i = -\Delta q/(rc\Delta x)$. Allowing finite differences to approach 0, we obtain:

$$i = -\frac{1}{rc}\frac{\partial q}{\partial x} \tag{5}$$

Inserting (5) into (4) we obtain:

$$\frac{\partial q}{\vartheta t} = \frac{1}{rc}\frac{\vartheta^2 q}{\vartheta x^2} \tag{6}$$

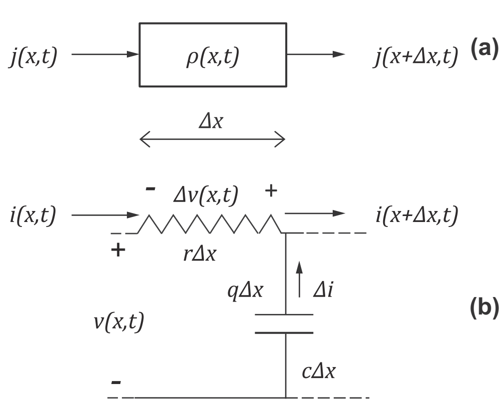

Fig. 2. Incremental elements of the structures in Fig. 1.

Table 1
Correspondence between quantities in diffusion problem and in electrical analog.

Diffusion problem – Fig. 1a	Electrical analog – Fig. 1b
Volume density, ρ	Charge per unit length, q
Diffusion flux, j	Electric current, i
Diffusion coefficient, D	$1/rc$

The correspondence of the two structures in Fig. 1 is now apparent, with (4)–(6) corresponding to (1)–(3) respectively, if the analogies shown in Table 1 are made.

For the structure in Fig. 1b, the equation for the current, $i(x,t)$, has the same form as (6), with q replaced by i [23], and the voltage can be found from:

$$v = \frac{q}{c} \tag{7}$$

The correspondence of physical variables in Table 1 is not only qualitative, but also quantitative. Thus, the charge in the structure of Fig. 1b is numerically equal to the volume density in Fig. 1a, at the same position and the same time, if one chooses $1/rc = D$ and analogous excitation. Thus the analogy does not only hold for the external behavior across, say, the port on the left, but rather holds throughout the structure. This detailed analogy can be crucial, as discussed below.

1.1. Need for equivalent circuits

Electrical equivalent circuits for the structure of Fig. 1a have been used for a long time. Such circuits allow for efficient computer simulation of this structure by highly-developed electrical circuit simulators, such as Spice [24,25], not only for the small-signal electrochemical impedance (which, after all, could also be computed analytically), but also for transient response to a variety of excitations.

In recent years, another reason for using electrical equivalents has emerged. Electrochemical devices, such as batteries and supercapacitors, are increasingly incorporated into sophisticated electronic systems. The resulting hybrid (electrochemical/electronic) systems need to be analyzed as a whole; for example, a designer of power conversion circuits needs to analyze complicated circuits that interface directly with a battery. In order to be able to use circuit analysis computer aids, such as Spice, for the simulation of the hybrid systems mentioned above, one needs to model batteries and supercapacitors in terms of equivalent electrical circuits. Such equivalent circuits, besides modeling other phenomena [3,9–13], need also to include structures such as the one shown in Fig. 1b to model diffusion.

Most circuit simulators have been developed for lumped-element circuits described by nodal equations, and have difficulties handling distributed elements, for which nodal equations cannot, in principle, be written. In various versions of the popular Spice simulator, one may consider using the available transmission-line elements, with an appropriate definition of their parameters, to model a distributed structure. However, such use is plagued by numerical issues; for example, calculating the real part of electrochemical impedance at very low frequencies can result in very large errors (and even result in negative values). Transmission line models are also known to have numerical problems in transient simulations, which are essential in some electrochemical device work (e.g., battery system simulation). Finally, known transmission line models in circuit simulators are inherently linear elements, and one cannot introduce nonlinearities in them.