Electrochimica Acta 160 (2015) 313–322

Contents lists available at ScienceDirect

Electrochimica Acta

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

Mathematical solutions of comprehensive variations of a transmission-line model of the theoretical impedance of porous electrodes

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ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 17 November 2014
Accepted 7 February 2015
Available online 9 February 2015

Keywords:
impedance
porous electrode
transmission-line model
mathematical solution

ABSTRACT

Mathematical solutions were obtained for the impedance of one-dimensional transmission-line (TML) models with all possible variations of the boundary conditions and connections to an external circuit. First, three types of connection (Z-type, T-type, and E-type) were considered. A more generalized connection that includes the characteristics of both Z-type and T-type (universal-type) was also considered. All four of the resulting general solutions were versatile, but quite complicated. Next, comprehensive variations of the general solutions depending on specific boundary conditions, which are generally simpler, were also considered. Finally, an equivalent transform from a three-terminal TML model to a simple Y-circuit was calculated. This enables calculation of the serial connection of multiple TML models with different parameters, which represents a multi-layered electrode.

1. Introduction

Transmission-line (TML) models are generally used to describe the electrochemical impedance response of a system with an electrode | electrolyte interface that is distributed not only in the vertical direction with respect to the electric current, but also in the parallel direction, such as a porous electrode [1–7] or an electrode with a lateral ionic current in a thin electrolyte film covering the electrode [8]. In such a case, the actual potential difference at the electrode | electrolyte interface is not uniform, and this is due to the different degrees of the contribution of ionic and/or electronic resistance depending on the position.

A TML model is usually represented using a drawing of a discretized ladder-like circuit (e.g., Fig. 1). However, if the material is macroscopically uniform and the values of the component elements (R_i, R_e, C_{dl}, and R_{ct} in the example shown in Fig. 1) do not depend on the position, the material is considered to be a continuous medium, which can be understood as a ladder with an infinite number of infinitesimal component elements. In such a case, the impedance can be obtained analytically as a differential equation problem, which is the main issue of this work. On the other hand, if the values of the component elements depend on the position (a typical case would be a porous electrode under DC generation with varied charge-transfer resistance), it is difficult or impossible to obtain an analytical solution. In such a case, we must consider a discretized, ladder-like circuit as in Fig. 1, in which some finite elements have different values [9]. It is desirable to assume a circuit with as many ladder steps as possible, since in this case the model approaches a continuous condition. The actual number of ladder steps used for the calculation may depend on the balance between the complication of the calculation and the desired accuracy. For the calculation of a ladder-like circuit with finite steps, a technique that involves the use of two theoretically interchangeable circuits, known as a Y–Δ transform (Fig. 2) [10], can be a useful tool. The application of this transform reduces the number of steps by one (Fig. 3), and thus a recurrence formula can be made to determine the overall impedance, which is represented by the final Y-circuit.

In the case of a macroscopically uniform material, although mathematical solutions for uniform and one-dimensional TML models have been developed and are widely used [1–8,11–17], their boundary conditions are generally simple, and the solutions are neither generalized nor comprehensive. In actual devices, boundary conditions of porous electrodes are often not ideal. For example, in the positive electrode of a lithium-ion battery, there is some electronic resistance (contact resistance) between the

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http://dx.doi.org/10.1016/j.electacta.2015.02.065
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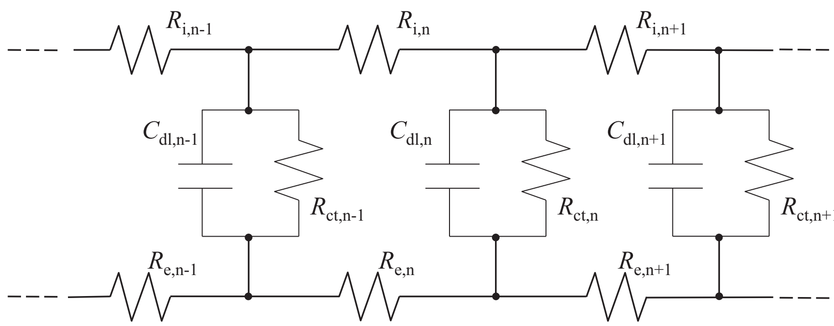

Fig. 1. Typical circuit with a ladder-like structure, where $R_{i,\,x}$,$R_{e,\,x}$, $C_{dl,\,x}$, and $R_{ct,\,x}$ represent the ionic resistance, electronic resistance, double-layer capacitance, and charge-transfer resistance at each position, respectively.

substrate sheet and active material layer [18], and there is a double-layer capacitance between the substrate and electrolyte. And for another example, in the catalyst layer of a polymer electrolyte fuel cell, especially in a case of using different kinds of polymer for the membrane and ionomer in the catalyst layer, ionic resistance between the membrane | ionomer interface (a kind of contact resistance) might not be negligible [19,20], and simultaneously, faradaic impedance at the electrode | membrane interface at the outermost of the catalyst layer might be different from that at the catalyst | ionomer interface in the catalyst layer. In such cases, a simple solution seen in literature can not be directly used to analyze the impedance results. This work presents several mathematical solutions with generalized boundary conditions for use with as many problems as possible. Furthermore, since the obtained solutions are quite complicated, many simplified variations depending on the boundary conditions are also presented for use by researchers as tools.

2. Theory

2.1. Differential equations and general solutions

The general solutions of a TML model are derived as described in the literature [16], and as briefly explained below.

The model consists of an “upper line” and a “bottom line”, as shown in Fig. 4. For electrochemical systems, these represent the ionic current and electronic current, respectively. The current and potential are governed by two differential equations:

$$\frac{dI}{dx} = -\frac{E}{z_B} \tag{1}$$

$$\frac{dE}{dx} = -z_A I + z_C(I_T - I) \tag{2}$$

Their general solutions of them are:

$$I = C_1 \cosh\sqrt{\frac{z_A + z_C}{z_B}}x + C_2 \sinh\sqrt{\frac{z_A + z_C}{z_B}}x + \frac{z_C I_T}{z_A + z_C} \tag{3}$$

$$E = -C_2\sqrt{z_B(z_A + z_C)}\cosh\sqrt{\frac{z_A + z_C}{z_B}}x - C_1\sqrt{z_B(z_A + z_C)}\sinh\sqrt{\frac{z_A + z_C}{z_B}}x, \tag{4}$$

where C_1 and C_2 are integral constants, which depend on the boundary conditions.

2.2. Types of connection to an external circuit

Fig. 5(a)–(c) shows three possible connections to an external circuit that can be by selecting two of the four terminals of a TML model. Here, we refer to these connections as “Z-type”, “T-type”, and “E-type”, respectively. Although in this report we mainly discuss these three types and their variations, a more general type, the “universal-type” shown in Fig. 5(d), is also discussed. The universal-type is equivalent to Z-type when Z_V and Z_Y are zero, and to T-type when Z_V and Z_X are zero. In the models shown in Fig. 5, additional elements (Z_P, Z_Q, $Z_V \sim Z_Y$) are introduced to cope with any possible boundary conditions. These are macroscopic elements with [Ω] dimension, put out of the arrays of infinitesimal elements. To avoid confusion, in the following figures, an array of infinitesimal elements is represented by a gray area, and the values of the component elements are represented by lowercase

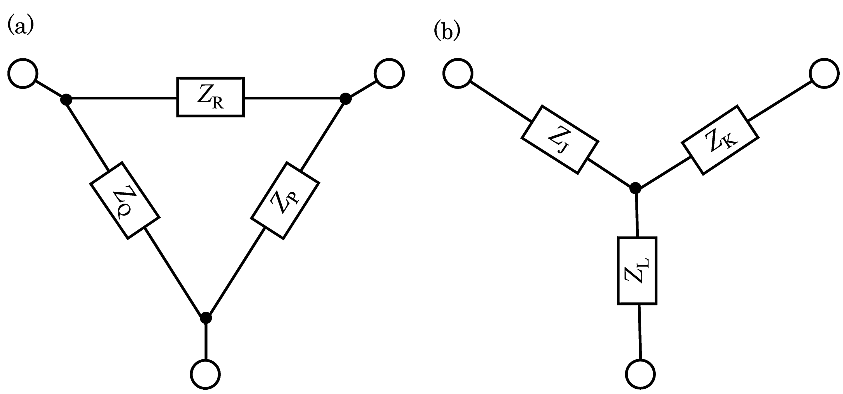

Fig. 2. Y–Δ transform. (a) A Δ-circuit and (b) a Y-circuit are equivalent when $Z_J = Z_Q \cdot Z_R/(Z_P \cdot Z_Q \cdot Z_R)$, $Z_K = Z_R \cdot Z_P/(Z_P \cdot Z_Q \cdot Z_R)$, and $Z_L = Z_P \cdot Z_Q/(Z_P \cdot Z_Q \cdot Z_R)$.