



Diffusion impedance of electroactive materials, electrolytic solutions and porous electrodes: Warburg impedance and beyond

Jun Huang

College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China



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ABSTRACT

The diffusion coefficient is a key property of materials. Electrochemical impedance spectroscopy (EIS) is a routine tool to determine the diffusion coefficient. Albeit being versatile for varied electrochemical systems and powerful in distinguishing multiple processes in a wide frequency spectrum, the EIS method usually needs a physical model in data analysis; misuse of models leads researchers to provide unwarranted interpretation of EIS data. Regarding diffusion, the simple and elegant formula developed by Warburg has been serving as the canonical model for more than a century. The classical Warburg model has very strict assumptions, however, it is used in a wide range of scenarios where assumptions may not be satisfied. It is the main purpose of the present article to define the boundary of applicability of the Warburg model and develop alternative models for cases beyond the boundary. In so doing, the Warburg model is revisited and its limitations and assumptions are scrutinized. Afterwards, new impedance models for more complicated and realistic scenarios are developed. The present article features: (1) generalization of the boundary condition when treating diffusion in bounded space and geometrical variants; (2) diffusion impedance in porous electrodes and fractals; (3) the effect of electrostatic interactions and coupling between diffusion and migration on the diffusion impedance in electrolytic solutions; (4) introduction of homotopy perturbation method to treat the convective diffusion; (5) physical interpretations of diffusion impedance behaviors.

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1. Introduction

The diffusion coefficient is a key transport property of electroactive materials and electrolytic solutions. Electrochemical impedance spectroscopy (EIS) has been serving as a powerful and routine tool in estimating the diffusion coefficient [1–17], and characterizing electrochemical devices in a wider scope [18–21], due to its advantage of separating the diffusion processes from other physico-chemical processes in a wide frequency spectrum. In so doing, an EIS model is necessary. In most cases, the conventional wisdom, Warburg impedance [22], is adopted. This practice is, on one hand, prompted by the observation of an oblique line with an angle close to 45° in the low frequency range. On the other hand, the simplicity and elegance of the Warburg impedance also underpin its popularity. While it is nowadays customary to link a 45° line in the EIS plot with diffusion, there are caveats on this.

The assumptions of the classical Warburg impedance are very

strict, that is, semi-infinite, planar, purely concentration-gradient-driven, Fickian diffusion of neutral species in the dilute limit. In reality, we are, however, frequently encountered with 'non-ideal' diffusion processes, including but not limited to, diffusion in bounded or irregular space [23–37], diffusion of charged species which is coupled with migration [38–43] and/or convection [44–54], and multi-scale and multi-phase diffusion in porous electrodes [55–58]. In consequence, it shall not be surprising that non-idealities of the diffusion impedance, including but not limited to oblique lines deviating from a 45° line and even arced curves, are frequently observed in experiments. Non-idealities are also encountered in other cases, e.g. the constant phase element phenomenon [59].

There is a long history of recognizing the limitations of the classical Warburg impedance model, and many derivative models have been developed in the literature [26,30,40,41,60–68]. This study presents a systematic extension of the classical Warburg impedance model in two dimensions: new structures and new physics, and intends to develop new models for the aforementioned 'non-ideal' cases. For the purpose of completeness, existing

E-mail address: jhuangelectrochem@qq.com.

efforts in the literature are reproduced, while they are modified to ensure the uniformity of nomenclature, and generalized in a new framework in this work. In addition, this study also presents several original contributions, including a unified expression for the bounded diffusion with different boundary conditions and new resultant features observed on the EIS plot, consideration of the coupling between diffusion and migration of charged species in electrolytic solutions, introduction of the homotopy perturbation method to treat the diffusion-convection impedance, discussion on the double layer effect on the diffusion impedance, models for diffusion in fractals, discussion on diffusion in porous electrodes, and new physical interpretations of diffusion impedance phenomena. As this article stands in between a review paper and an original paper, it is important for us to give enough credits to original sources.

The reminder of this article is organized as follows. First, derivation, assumptions and limitations of the classical Warburg impedance are presented and discussed. Second, the classical Warburg impedance is extended to different structures, including the bounded planar space, other geometrical variants (cylinders and spheres), and porous electrodes. Third, the classical Warburg impedance is extended to incorporate new physics, including transport in electrolytic solutions in which diffusion and migration are strongly coupled, the convection effect, the double layer effect, non-Fickian diffusion and diffusion in fractals. This article is intended to help researchers in choosing an appropriate model for interpreting their data. As a result, implications of theoretical analysis for experimentalists are discussed in the penultimate section.

2. Warburg impedance

We begin with the canonical scenario considered by E. Warburg in 1899 [22], as schematically shown in Fig. 1. The species in the solution diffuse away or towards an electrode-electrolyte interface (EEI). At the EEI, $x = 0$, the following redox reaction takes place,



The current-potential relation of the reaction in Eq. (1) is written in a general form,

$$E = f(i, c_{\text{Ox}}, c_{\text{Re}}), \tag{2}$$

where i is the current density, E the potential across the EEI, c_{Ox} , c_{Re} the concentration of oxidant and reductant, respectively.

In the electrolyte solution, the species flux is exclusively driven by the concentration gradient, which is described by the Fick's law. The mass conservation law gives,

$$\frac{\partial c_i(x, t)}{\partial t} = D_i \frac{\partial^2 c_i(x, t)}{\partial x^2}, \tag{3}$$

where D_i is the diffusion coefficient of oxidant ($i = \text{Ox}$) or reductant ($i = \text{Re}$).

We take the bulk electrolyte at infinite distance, $x = \infty$, where c_i has its bulk value,

$$c_i = c_i^0. \tag{4}$$

At the EEI, the reactant/product is consumed/formed in the charge transfer reaction. The consumption/formation rate is related to the reaction rate, which is usually measured by the current density, i . As a result, the diffusion process is linked with the charge transfer reaction at the EEI,

$$D_i \frac{\partial c_i}{\partial x} = \pm \frac{i}{nF}, \tag{5}$$

where ‘-’ is for the oxidant and ‘+’ is for the reductant and i is positive for oxidation, F is Faraday constant and n is the number of transferred electrons in Eq. (1).

There are two widely adopted methods to solve for the impedance response from Eq. (3): a time-domain method and a frequency-domain method. In the time-domain method, as employed in the original study of E. Warburg [22], the voltage response to a sinusoidal perturbation of the current density, $\tilde{i} = A_i \sin(\omega t)$ (A_i the amplitude, ω the frequency), is obtained, which is expressed as, $\tilde{V} = A_V \sin(\omega t + \psi)$. As a result, the impedance response is given by, $Z = A_V/A_i \cdot \exp(i\psi)$ with A_V/A_i being the amplitude and ψ the phase angle. The frequency-domain method is comparatively more concise; it first transforms Eq. (3) to,

$$j\omega \tilde{c}_i = D_i \frac{\partial^2 \tilde{c}_i}{\partial x^2}, \tag{6}$$

in the frequency-domain via Fourier transformation, where \tilde{c}_i is the perturbation in the concentration of species i . Through this paper, variables marked with an over-tilde represent the perturbed quantity.

Accordingly, Eq. (4) is transformed to,

$$\tilde{c}_i = 0. \tag{7}$$

because the bulk concentration is invariant.

Eq. (5) in the frequency domain is rephrased as,

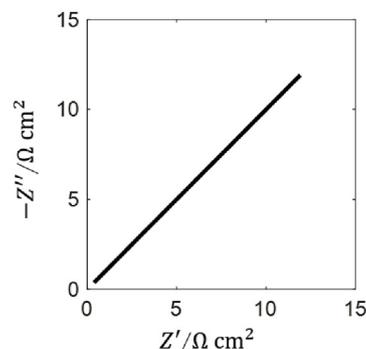
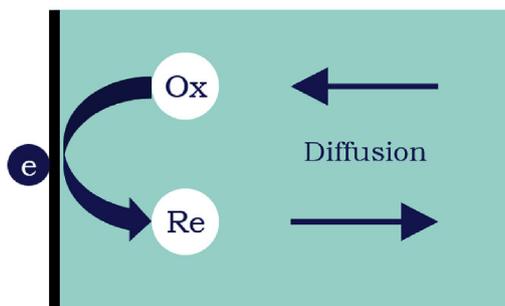


Fig. 1. Semi-infinite diffusion coupled with charge transfer reaction at the electrode-electrolyte interface and the representative diffusion impedance in the frequency range of $1 \sim 10^{-3}$ Hz with $n = 1, \bar{c}_{\text{Ox}} = \bar{c}_{\text{Re}} = 1\text{M}, D_{\text{Ox}} = D_{\text{Re}} = 10^{-10}\text{m}^2\text{s}^{-1}$

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