A generalized Warburg impedance for a nonvanishing relaxation process

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For an electrochemical system with a nonvanishing relaxation time we obtain a generalized Warburg impedance from a hyperbolic diffusion equation. The generalized Warburg impedance determined in this way presents a slight positive curvature in the complex plane with smaller imaginary value at high frequencies. © 1996 American Institute of Physics.

I. INTRODUCTION

Some systems with mobile ions, electrochemical systems, and for a gradient of ionic concentration show a diffusion flux and an electric impedance known as the Warburg impedance. This impedance is a $\omega^{-1/2}$ function, where $\omega$ is the angular frequency of the external electric field.

The Warburg impedance can be calculated from the Fick diffusion equation for a semi-infinite diffusion. The classic diffusion equation as the Maxwell–Cattaneo–Vernotte for the process in systems with constant specific heat and constant fluxes. This is an usual approximation on the linear irreversible thermodynamics that leads to a vanishing relaxation time for the dissipative flux, as the ions diffusion in solids.3

The aim of this paper, is to determine the Warburg impedance for a diffusion flux with a nonvanishing relaxation time. In the framework of extended irreversible thermodynamics (EIT), a generalized diffusion equation is used.4 The phenomenological description of the behavior of a system in a nonequilibrium state is the goal of irreversible thermodynamics. In the classical approach, the entropy is only a function of extensive variables but there are a large number of systems that cannot be described by a classical formalism. Therefore, it is necessary to go beyond the classical theory of irreversible thermodynamics. There are different ways to extend the classical theory.5,6 One is to make an extension of the local equilibrium hypothesis.7 This method needs the entropy to be not only a function of the variables at equilibrium, but also of the dissipative fluxes.8 A nonvanishing relaxation time for dissipative fluxes implies very important restrictions in the linear transformation of fluxes and forces9,10. On the other hand, if we consider a quasilinear process in systems with constant specific heat and constant transport coefficients, we can obtain a hyperbolic constitutive equation as the Maxwell–Cattaneo–Vernotte11 for the heat propagation with a finite velocity.

II. GENERALIZED DIFFUSION EQUATION

The starting point of the EIT framework is the assumption that the entropy is a function of classical variables and independent dissipative fluxes. We assume that the enlargement of the space of the states, (whose set of variables shall be denoted by $\mathbf{G}$), is done by adding to the local specific variables $(\mathbf{c}_k, \mathbf{u}_k)$, denoted by $\mathbf{C}$, other "nonconserved" quantities, $\mathbf{N}$. Thus, $\mathbf{G} = \mathbf{C} \cup \mathbf{N}$; in practice, these quantities are the dissipative fluxes or nonconservative variables $(\mathbf{J}_k)$, since they appear in the balance equations which describe the evolution of conservative variables. EIT also assumes the existence of a function defined in $\mathbf{G}$, the generalized entropy, from which a generalized Gibbs relation can be obtained. Here, the time derivative of the $\mathbf{N}$ variables appears unknown, so for a quasilinear regime the entropy balance equation can be expressed as

$$
\frac{dS}{dt} = \sum_{k=1}^{m} \left( \frac{\partial S}{\partial u_k} \right)_{c_k, \mathbf{J}_k} \frac{du_k}{dt} + \sum_{i=1}^{n-1} \left( \frac{\partial S}{\partial c_k} \right)_{u_k, c_k, \mathbf{J}_i} \frac{dc_k}{dt},
$$

(1)

$$
\frac{\partial S}{\partial c_k} = \theta^{-1}(u, c_k, \mathbf{J}_i),
$$

(2)

$$
\frac{\partial S}{\partial u_k} = -\theta^{-1} \eta,
$$

(3)

where $u$ is the specific internal energy, $c_k$ the mass fraction of the $k$th component, and $\mathbf{J}_i$ the $i$th independent dissipative flux, respect to the reference framework. Equations (2) and (3) are the first order state equations, where $\theta(u, c_k, \mathbf{J}_i)$ and $\eta(u, c_k, \mathbf{J}_i)$ are the nonequilibrium generalized temperature and chemical potential respectively.12 The state equations up to second order are

$$
\sum_{k=1}^{m} \gamma_{ik} \mathbf{J}_k = T^{-1} \nu \sum_{k} \mathbf{J}_k.
$$

(4)

in which $\nu$ is the specific volume and $\gamma_{ik}$ is a function of temperature, phenomenological coefficient and relaxation time.13

For a system not far from equilibrium, the balance entropy equation can be written as

$$
\frac{dS}{dt} = \text{div} \mathbf{J}_s + \sigma_s
$$

(5)

here, $\mathbf{J}_s$ is the generalized entropy flux and $\sigma_s$ is the entropy production that is a bilinear form $\sigma_s = \mathbf{J}_s \cdot \mathbf{X}_s$ where $\mathbf{X}_s$ is the generalized force.
\[ X_C = X_c + T^{-1} \gamma \dot{J}. \]

For a dilute binary solution (\( c_1 \) as the solute concentration), \( c_2 \approx 1 \) and \( c_1 \ll 1 \), the equation state of second order, for an isothermic diffusion, is now
\[
\left( \frac{\partial S}{\partial J_1} \right)_{u.c.} = -\nu T^{-1} \gamma J_1,
\]
with \( \gamma = -T \tau \dot{\phi}^{-1} \). \( \tau \) is the direct phenomenological coefficient between the diffusion flux and its associated direct force \( \{ -\nabla \mu_i \}/T \); the entropy production can be now expressed as
\[
\sigma_s = J_1 \left( -\frac{1}{T} \nabla \mu_1 + \frac{1}{\tau} \gamma \dot{J_1} \right),
\]
and
\[
\dot{J_1} = \frac{T}{\gamma} \left( \frac{1}{T} \nabla \mu_1 + \dot{\phi}^{-1} J_1 \right),
\]
where \( \dot{\phi} = -T \tau \dot{\phi}^{-1} \).

From Eqs. (7) and (8) we obtain
\[
\nabla \mu_1 = -\frac{T}{\mathcal{D}} (J_1 + \tau \dot{J_1}),
\]
and for the solute concentration, we get
\[
\nabla c_1 = -\frac{1}{\mathcal{D}} (J_1 + \tau \dot{J_1}),
\]
where \( \mathcal{D} \) is the diffusion coefficient
\[
\mathcal{D} = \frac{T}{\tau} \frac{\partial \mu_1}{\partial c_1}.
\]

If we apply the operator \( \nabla \) step by step, and taking into account the conservation mass equation, a hyperbolic equation for the temporary variation \( c_1 \) is obtained:
\[
\nabla^2 c_1 = \frac{\tau}{\mathcal{D}} \frac{\partial^2 c_1}{\partial t^2} + \frac{1}{\mathcal{D}} \frac{\partial c_1}{\partial t},
\]
the diffusion velocity being
\[
v = \sqrt{\mathcal{D}/\tau}.
\]
Equation (12) is analogous to the Maxwell–Cattaneo equation\(^4\) which is obtained for thermic wave propagation.

### III. GENERALIZED WARBURG IMPEDANCE

The generalized Warburg impedance can be obtained from Eq. (12). First we apply the Laplace transform\(^1\) obtaining an equation in the frequency space that leads to the generalized Warburg impedance.

We can write Eq. (12) in a general form:
\[
\nabla^2 c = a^2 \frac{\partial c}{\partial t} + \frac{1}{v^2} \frac{\partial^2 c}{\partial t^2},
\]
where \( a = \sqrt{\mathcal{D}/\tau} \) and \( v = \sqrt{\mathcal{D}/\tau} \).
\( \mathcal{E}(x,p) = \{c\} \) denotes the Laplace transform of \( c(x,t) \), where \( p = \sigma + j \omega \). Then the Laplace transform of Eq. (14) is
\[
\frac{\partial^2}{\partial x^2} - \left( a^2 p + \frac{p^2}{v^2} \right) \mathcal{E}(x,p)
= \left( -a^2 - \frac{p}{v^2} \right) c(x,0) - \frac{1}{v^2} \frac{\partial c}{\partial t} (x,0) = F(x).
\]

On the other hand, the Laplace transform of the excess concentration, \( \Delta c(x,t) = c(x,t) - c(x,0) \), which is defined in every point of the system, is given by
\[
\Delta c = \{c\} - c(x,0) \{1\} = \mathcal{E}(x,p) - c(x,0) \frac{1}{p},
\]
and from Eqs. (15) and (16) we get
\[
\frac{\partial^2 \{\Delta c\}}{\partial x^2} - \left( a^2 p + \frac{p^2}{v^2} \right) \{\Delta c\}
= -\frac{1}{p} \frac{\partial^2}{\partial x^2} c(x,0) - \frac{1}{v^2} \frac{\partial c}{\partial t} (x,0) = G(x).
\]

Next, we consider the following initial conditions for a transmitter system:
\[
c(x,0) = 0, \quad \frac{\partial c(x,0)}{\partial t} = 0,
\]
for boundary condition, we consider the case of semi-infinite diffusion
\[
x \to \infty \quad c(x,t) \text{ bounded},
\]
and at \( x = 0 \) (the electrode–electrolyte interface)
\[
\left[ \frac{d \Delta c}{dx} \right]_{x=0} = -\frac{1}{Z \mathcal{F}} (\Delta I),
\]
where \( \Delta I \) is ac current, \( Z \) the charge number, and \( \mathcal{F} \) the Faraday constant.

The Warburg impedance is defined as
\[
W_{\phi}^\rho(p) = \left[ \frac{\Delta \Phi}{\Delta I} \right]_{x=0},
\]
in which \( \Delta \Phi \) is the ac component of the voltage. For small perturbations around equilibrium, we may write \( \Delta \Phi/\Delta c = d\Phi/dc \) and for \( \sigma=0 \ (p=j \omega) \), we obtain
\[
W_{\phi}^\rho(p) = \left[ \frac{d \Phi}{dc} \right]_{x=0} \frac{1}{Z \mathcal{F} \sqrt{\mathcal{D}}} (\omega^2 \tau^2 + \omega^2)^{-1/4}
\times \left\{ \cos \left[ \tan^{-1} \left( -\frac{1}{\omega \tau} \right) \right] \right\}
- j \sin \left[ \tan^{-1} \left( -\frac{1}{\omega \tau} \right) \right].
\]
This is the generalized Warburg impedance for a system with a dissipative isothermic diffusion flux with a nonvanishing...
relaxation time. Note, that we can obtain the usual Warburg impedance from Eq. (22) for a vanishing relaxation time ($\tau = 0$).

IV. EQUIVALENT CIRCUIT

The equivalent circuit for the generalized Warburg impedance is similar to the usual Warburg impedance, i.e., a semi-infinite transmission line composed only by resistor and capacitor; however, in this case, we must consider a finite propagation velocity.

For a system with an electric potential gradient and without gradient of charge carrier concentration, we can obtain from Eq. (9)

$$\nabla \Phi = - \frac{T}{\mathcal{D}_{e}} (\mathbf{J}_{e} + \tau \mathbf{J}_{e}),$$

(23)

where $\mathcal{D}_{e}$ is now the phenomenological coefficient between $\mathbf{J}_{e}$, charge flux density, and its associated direct force $[(\nabla \Phi)/T]$, i.e.,

$$\mathcal{D}_{e} = \frac{T}{q_{e}} \sigma_{e},$$

(24)

Here, $q_{e}$ is the carrier charge and $\sigma_{e}$ is the electrical conductivity; now Eq. (23) can be expressed as

$$\nabla \Phi = - \frac{q_{e}}{\sigma_{e}} (\mathbf{J}_{e} + \tau \mathbf{J}_{e}).$$

(25)

If $\rho$ is the resistance per unit length and $\varepsilon$ is the capacitance per unit length, then

$$I = - \frac{1}{\rho} \left( \frac{\partial \Phi}{\partial x} \right),$$

(26)

$$\frac{\partial \Phi}{\partial t} = - \frac{1}{\varepsilon} \left( \frac{\partial I}{\partial x} \right),$$

(27)

where $I$ is the electrical flux intensity ($I = q_{e} \mathbf{J}_{e}$); if we apply the operator $\nabla$ step by step, and take into account Eqs. (26) and (27), a hyperbolic equation for $\Phi$ is obtained

$$\nabla^{2} \Phi = \rho \frac{\partial \Phi}{\partial t} + \varepsilon \tau \frac{\partial^{2} \Phi}{\partial t^{2}}.$$  

(28)

In the complex plane, the usual Warburg impedance is a straight line at an angle of $\pi/4$ respect to the real axis; but the generalized Warburg impedance presents a slight positive curvature (Fig. 1). Therefore, both curves show similar behavior for low frequencies although the generalized Warburg impedance presents a smaller imaginary value at high frequencies.

V. CONCLUSIONS

A nonvanishing relaxation time implies some very important modifications in the phenomenological description of the behavior of a system in a nonequilibrium state; hence, the EIT framework leads to a hyperbolic equation with a finite diffusion velocity for the diffusion flux with a nonvanishing relaxation time. For an electrochemical system, the hyperbolic equation for diffusion flux implies an important modification in the Warburg impedance. This is a frequency function and presents a slight positive curvature in the complex plane with smaller imaginary values at high frequencies.

1 E. Warburg, Annu. Phys. Chem. 67, 493 (1899).
13 C. Cattaneo, Atti dei Seminario Matematico e Fisico della Università di Modena 3, 83 (1948).