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Electrochemistry Communications 2 (2000) 371-375



The transmission line equivalent circuit model in solid-state electrochemistry

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Received 17 January 2000; received in revised form 25 February 2000; accepted 28 February 2000

Abstract

This note presents a generalization of the small-signal ac transport description of systems with electronic and ionic charges. To be specific, hole polarons and counterions in a conjugated polymer are considered. The derivation of the transmission line equivalent circuit is in principle close to the one of Sah (1969–1970) for solid-state electronics. It is shown (i) that in non-equilibrium current generators have to be added to the Barker/Brumleve/Buck circuit; (ii) in addition, traps for both the hole polarons and the ions are taken into account; (iii) the reduction to the lf limit is discussed; (iv) the principle extension to a porous two-phase system is presented. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Equivalent circuit; Transmission line; Conjugated polymers; Polarons; Counterions; Traps

1. Introduction

The large number of publications on transmission line equivalent circuits (TLECs) for the electrochemical impedance of (non-porous) systems with electrons (or holes) and ions as mobile charge carriers culminated recently in a paper by Buck and Mundt [1] on finite transmission lines of the Barker/Brumleve/Buck type for exact representations of transport by the Nernst-Planck equations for each charge carrier. Simplified treatments are given, e.g., in Refs. [2–4]. Actually, the transmission line equivalent circuit description of the transport in such systems has been developed about 30 years ago by Sah [5-7] for solid-state electronics (here electrons and holes are the carriers). Most important for obtaining a complete description is to carry out a careful small-signal analysis of the Poisson and continuity equations. In contrast, in Ref. [1] and in the previous publications on electrochemical systems, the current generators derived in Ref. [7] for non-equilibrium conditions are missing. Furthermore, there is, e.g., in conjugated polymers clear evidence for the existence of traps for the polarons [8,9]. In a disordered system one should also expect that energetically strongly favored sites will occur causing trapping/detrapping of counterions.

Therefore, in this note a generalization of the ac smallsignal description and the corresponding TLEC for systems

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with electronic and ionic mobile charge carriers are presented and discussed. In this first step non-equilibrium conditions and traps for both types of charge carrier are taken into account. Depending on the experimental conditions, different boundary conditions have to be used at both ends of the transmission line. Further processes will be taken into account in a subsequent publication. The analysis applies to systems with two types of charge carriers obeying non-degenerate statistics and Einstein relations. These are the assumptions made, e.g., by Vorotyntsev et al. [4] to describe transport in conducting polymers. Of course, especially electrochemically deposited polymers are porous, as also assumed in former publications of the author [10–12]. Modifications needed to describe the two-phase system will be discussed shortly.

2. Basic assumptions and equations

A system with positive (p) and negative (c) mobile charges is considered. As an example, in a conducting polymer one has hole polarons and stable counterions. The concentrations of the two species are c_p and c_c , respectively. Under the same conditions as considered in Ref. [1], the two diffusion coefficients D_p and D_c are related to the mobilities μ_p and μ_c by the simple non-degenerate Einstein relations $\mu_p = D_p(F/RT)$ and $\mu_c = D_c(F/RT)$, respectively. *F* and *RT*

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have their usual meaning. The electrical current densities (in A cm⁻²) are then given as in [1] by the drift and the diffusion currents, or they are completely driven by the gradients of the respective electrochemical potentials, which are here expressed in units of V as $\phi_{\rm Fp}$ and $\phi_{\rm Fc}$ (quasi-Fermi potentials in the notation of solid-state electronics). Thus, the current densities are given by

$$\vec{j_{\rm p}} = \sigma_{\rm p}(-\nabla\phi) + D_{\rm p}F(-\nabla c_{\rm p}) = \sigma_{\rm p}(-\nabla\phi_{\rm Fp})$$
(1)

$$\vec{j_c} = \sigma_c (-\nabla \phi) - D_c F(-\nabla c_c) = \sigma_c (-\nabla \sigma_{Fc})$$
(2)

where the electric field $\vec{E} = -\nabla \phi$ is connected with the electric potential ϕ caused by the deviation from neutrality and by boundary conditions. The specific conductivities are defined as usual by

$$\sigma_{\rm p} = \frac{F^2}{RT} D_{\rm p} c_{\rm p}, \quad \sigma_{\rm c} = \frac{F^2}{RT} D_{\rm c} c_{\rm c} \tag{3}$$

It should be emphasized that these equations do not depend on the type of the transport mechanism ¹. It is only assumed that the transport is linear with the gradient of the quasi-Fermi potential and, as mentioned, that non-degenerate or Maxwell– Boltzmann statistics apply. Therefore, from Eqs. (1) and (2) it follows also that one has

$$\frac{F}{RT}(\phi_{\rm Fp} - \phi) = \ln\left(\frac{c_{\rm p}}{c_{\rm p0}}\right) \tag{4}$$

$$\frac{F}{RT}(\phi - \phi_{\rm Fc}) = \ln\left(\frac{c_{\rm c}}{c_{\rm c0}}\right) \tag{5}$$

which is important for the derivation of the small-signal equations. Eq. (4) is valid for polarons in a conducting polymer [13] and Eq. (5) holds for stable counterions due to the existence of the membrane potential. The reference concentrations c_{p0} and c_{c0} are connected with the choice of the zero for the scale of the common electric potential ϕ . The transport is then determined by the two continuity equations and by the Maxwell equation for the displacement field $\vec{D} = \varepsilon \varepsilon_0 (-\nabla \phi)$, or the Poisson equation for the electric potential ϕ :

$$\nabla \varepsilon \varepsilon_0 (-\nabla \phi) = F(c_p - c_c) + F(c_{td} - c_{ta})$$
(6)

$$\nabla \sigma_{\rm p}(-\nabla \phi_{\rm Fp}) = -F \frac{\partial}{\partial t} c_{\rm p} - F U_{\rm p} \tag{7}$$

$$\nabla \sigma_{\rm c}(-\nabla \phi_{\rm Fc}) = +F \frac{\partial}{\partial t} c_{\rm c} + F U_{\rm c} \tag{8}$$

Here, in addition to the transport description common in electrochemistry [1] possible traps for both kinds of carriers have been taken into account. The concentrations of positively and negatively charged traps are denoted by $c_{\rm td}$ and $c_{\rm ta}$, respectively, and $U_{\rm p}$ and $U_{\rm c}$ are the respective net trapping

rates. The requirement of a vanishing divergence of the total current density, $\nabla(\vec{j_p} + \vec{j_c} + \vec{D}) = 0$, leads with Eqs. (6)–(8) to the total trap rate equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}(c_{\mathrm{td}} - c_{\mathrm{ta}}) = U_{\mathrm{p}} - U_{\mathrm{c}} \tag{9}$$

In general, the system of Eqs. (6)-(8), together with the rate equations for all traps, and with the appropriate boundary conditions can be solved only numerically even in the one-dimensional case.

3. Small-signal equations and the equivalent circuit model

Eqs. (6)-(9) with Eq. (3) contain as variables the electric potential, two electrochemical potentials which are connected to the concentrations by Eqs. (4) and (5), and the trap concentrations. To obtain the small-signal ac equations in the one-dimensional case each of these quantities is expressed as $A = A^{s}(x) + a(x) \exp(i\omega t)$ with the dc steady-state solution $A^{s}(x)$ and a complex small-signal amplitude a(x). The smallsignal amplitudes for $\phi_{\rm Fp}$, $\phi_{\rm Fc}$ and ϕ are denoted in the following by $\varphi_{\rm Fp}$, $\varphi_{\rm Fc}$ and φ , respectively. In contrast to the small-signal analysis by Sah [7] the ac case is considered here. Furthermore, here the use of an additional quasi-Fermi potential for the traps is avoided. Both lead to a more convenient formulation. In the following only traps for both types of carriers are taken into account but the inclusion of the mutual polaron-counterion capture and release (which is in principle of the Langevin type) is postponed to later work. Linearization of the system of equations, including the trap rate equations, leads to

$$\frac{d}{dx} \varepsilon \varepsilon_0 \left(-\frac{d}{dx} \varphi \right) = \left(C_p + \frac{G_{tp}}{i\omega + 1/\tau_{tp}} \right) (\varphi_{Fp} - \varphi)$$

$$+ \left(C_c + \frac{G_{tc}}{i\omega + 1/\tau_{tc}} \right) (\varphi_{Fc} - \varphi)$$

$$\frac{d}{dx} \left\{ \sigma_p \left(-\frac{d}{dx} \varphi_{Fp} \right) + G_p (\varphi_{Fp} - \varphi) \right\}$$

$$= -i\omega \left(C_p + \frac{G_{tp}}{i\omega + 1/\tau_{tp}} \right) (\varphi_{Fp} - \varphi)$$

$$(11)$$

$$\frac{\mathrm{d}}{\mathrm{d}x} \left\{ \sigma_{\mathrm{c}} \left(-\frac{\mathrm{d}}{\mathrm{d}x} \varphi_{\mathrm{Fc}} \right) - G_{\mathrm{c}} \left(\varphi_{\mathrm{Fc}} - \varphi \right) \right\}$$

$$= -\mathrm{i}\omega \left(C_{\mathrm{c}} + \frac{G_{\mathrm{tc}}}{\mathrm{i}\omega + 1/\tau_{\mathrm{tc}}} \right) \left(\varphi_{\mathrm{Fc}} - \varphi \right)$$
(12)

The conductances, capacitances and relaxation times in these equations are defined in Table 1 (there the quantities K_p^s and K_c^s are the capture rates of the traps under steady-state conditions and Γ_p and Γ_c are the emission rates). It should be mentioned that all parameters in these equations are deter-

¹ Especially in the case of hopping, the macroscopic diffusion coefficient depends on the (equilibrium) concentration.

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Table 1

Definition of the parameters of the small-signal ac Eqs.	(10)-(12) and of	the corresponding equivalent of	circuit depicted in Fig. 1
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Specific conductivity	$\sigma_{\rm p} = \frac{F^2}{RT} D_{\rm p} c_{\rm p}^{\rm s}$	$\sigma_{\rm c} = \frac{F^2}{RT} D_{\rm c} c_{\rm c}^{\rm s}$	$\mathrm{S}~\mathrm{cm}^{-1}$
Dielectric constant	$\mathcal{E}\mathcal{E}_0$		F cm ⁻¹
Current generator conductance	$G_{\rm p} = \frac{F}{RT} j_{\rm p}^{\rm s}$	$G_{\rm c} = \frac{F}{RT} j_{\rm c}^{\rm s}$	${\rm S~cm^{-2}}$
Charging capacitance	$C_{\rm p} = \frac{F^2}{RT} c_{\rm p}^{\rm s}$	$C_{\rm c} = \frac{F^2}{RT} c_{\rm c}^{\rm s}$	$\mathrm{F}\mathrm{cm}^{-3}$
Trap conductance	$G_{\rm tp} = \frac{F^2}{RT} K_{\rm p}^{\rm s} c_{\rm tp}^{\rm s}$	$G_{\rm tc} = \frac{F^2}{RT} K_{\rm c}^{\rm s} c_{\rm tc}^{\rm s}$	S cm ⁻³
Trap relaxation time	$\tau_{\rm tp} = (K_{\rm p}^{\rm s} + \Gamma_{\rm p})^{-1}$	$\tau_{\rm tc} = (K_{\rm c}^{\rm s} + \Gamma_{\rm c})^{-1}$	s
Trap capacitance	$C_{\rm tp} = \tau_{\rm tp} G_{\rm tp}$	$C_{\rm tc} = \tau_{\rm tc} G_{\rm tc}$	$\mathrm{F}\mathrm{cm}^{-3}$

mined in general by the steady-state solutions of the general Eqs. (6)-(8).

The capacitances C_p and C_c have been discussed extensively in previous work [1–3]. The coupling of the system of equations (apart from traps and current generators) is expressed mainly by the following relations of the parameters with the dielectric relaxation times:

$$\tau_{\rm p} = \frac{\varepsilon \varepsilon_0}{\sigma_{\rm p}}, \quad \tau_{\rm c} = \frac{\varepsilon \varepsilon_0}{\sigma_{\rm c}} \tag{13}$$

the diffusion coefficients:

$$D_{\rm p} = \frac{\sigma_{\rm p}}{C_{\rm p}}, \quad D_{\rm c} = \frac{\sigma_{\rm c}}{C_{\rm c}} \tag{14}$$

and the screening or diffusion lengths:

$$\left(\frac{\varepsilon\varepsilon_0}{C_p}\right)^{1/2} = (D_p\tau_p)^{1/2} = L_p$$

$$\left(\frac{\varepsilon\varepsilon_0}{C_c}\right)^{1/2} = (D_c\tau_c)^{1/2} = L_c$$
(15)

As seen from Eqs. (10)–(12) the traps give essentially additive complex contributions to the capacitances C_p and C_c modifying in this way the diffusion coefficients and the diffusion lengths. Further characteristic quantities do occur for non-zero values of G_p and G_c .

The contributions $G_p(\varphi_{Fp} - \varphi)$ and $-G_c(\varphi_{Fc} - \varphi)$ in Eqs. (11) and (12) are current generators which are well known in solid-state electronics [7]. As seen from the definitions for the conductances G_p and G_c in Table 1 they are independent from the existence of the traps. They result from the small-signal expansion and they occur only if one has steady-state conduction currents j_c^s and/or j_p^s . They have been overlooked in previous electrochemical transmission lines, probably because one does not normally have steady-state currents in electrochemical systems. But they are possible, at least in membrane systems. Thus, in a system (electrolyte|film of

conducting polymer electrolyte) there can be a steady-state current of counterions.

Due to the formulation of Eqs. (10)-(12) in terms of conductances and capacitances one can represent them directly by an equivalent circuit. The basic element of the resulting transmission line (for a sufficiently thin slab of thickness Δx) for the two conduction currents and the displacement current (denoted as 'Poisson string' in [1]) is shown in Fig. 1. In addition to the model considered so far as the general model (in the case of two types of mobile charge carriers, see Fig. 1(b) in Ref. [1]) one has now at first the contributions from the traps with their respective conductances (G_{tp} and G_{tc}) and capacitances (C_{tp} and C_{tc}) for both types of carriers. Also, independently from the existence of traps, for situations with non-zero steady-state con-



Fig. 1. The transmission line equivalent circuit. In addition to the established electrochemical model [1] it contains trap conductances (G_{tp} and G_{tc}) and capacitances (C_{tp} and C_{tc}) and, in the non-equilibrium steady-state case, also the current generators ($G_p(\varphi_{Fp} - \varphi)$ and $-G_c(\varphi_{Fc} - \varphi)$). In the low-frequency limit the displacement current ('Poisson string') disappears.

duction currents $(j_p^s \text{ and/or } j_c^s)$, current generators do occur which are determined by their conductances $(G_p \text{ and } G_c)$.

4. The low-frequency limit

For zero steady-state current and without traps the lowfrequency (lf) limit has been compared in detail with the full solution in Ref. [1]. The general equivalent circuit is reduced in the lf limit by omitting the 'Poisson string'. Formally this is obtained from the roots of the characteristic equation of the system of Eqs. (10)–(12). They give the possible complex wavelengths λ_i (*i*=1, ..., 4) for special solutions proportional to $\exp(x/\lambda)$. For low frequencies, $\omega \tau_p \ll 1$, $\omega \tau_c \ll 1$, one obtains

$$\lambda_{1,2}^{2} = \frac{L_{p}^{2}L_{c}^{2}}{i\omega(\tau_{p} + \tau_{c})} \left(\frac{1}{L_{p}^{2}} + \frac{1}{L_{c}^{2}}\right)$$

$$= \frac{1}{\frac{1}{1 + \frac{C_{p} + C_{c}}{C_{p} + C_{c}}}} = \frac{D^{*}}{D^{*}}$$
(16)

$$i\omega(\rho_{\rm p} + \rho_{\rm c}) \quad C_{\rm p}C_{\rm c} \qquad i\omega$$

$$\frac{1}{\lambda_{3,4}^2} = \left(\frac{1}{L_{\rm p}^2} + \frac{1}{L_{\rm c}^2}\right) - \frac{1}{\lambda_{1,2}^2} \tag{17}$$

with the ambipolar diffusion coefficient (for the reformulations see Eqs. (13)-(15)):

$$D^{*} = \frac{\frac{c_{\rm p}^{\rm s} + c_{\rm c}^{\rm s}}{D_{\rm c}}}{\frac{c_{\rm p}^{\rm s}}{D_{\rm c}} + \frac{c_{\rm c}^{\rm s}}{D_{\rm p}}}$$
(18)

Since the solutions (Eq. (17)) decay (increase) exponentially in a thick layer (compared to L_p , L_c) the solutions (Eq. (16)) dominate. The second equation in Eq. (16) gives immediately the connection with the reduced equivalent circuit. As seen from Eqs. (10)–(12) and Table 1 the trap influence is included by simply replacing the capacitances in Eq. (16) by

$$C_{\rm p} \rightarrow \left(C_{\rm p} + \frac{C_{\rm tp}}{1 + i\omega\tau_{\rm tp}} \right), \quad C_{\rm c} \rightarrow \left(C_{\rm c} + \frac{C_{\rm tc}}{1 + i\omega\tau_{\rm tc}} \right)$$
(19)

Therefore, if the trap relaxation times are smaller than the dielectric relaxation times, the trap capacitances are already included in the lf limit; in the reverse case, the trap capacitances are switched on only for $i\omega \ll \tau_{tp}^{-1}$, τ_{tc}^{-1} . This switching of one kind of trap, according to trap kinetics, will be observable if the equilibrium electrochemical potential is near to the corresponding trap level.

5. Porosity and double-layer capacity

In the case of conducting polymers, porosity can be important but it depends strongly on the preparation. Since the basis work of de Levie [14,15] porous systems are usually described by two-phase models. In such models, at any position averaged quantities of both phases are supposed to exist. This requires an *averaging* over regions large compared to the pore dimensions [10,16]. Then, the concentrations are modified by the respective volume fractions and one has to use effective conductivities [16,17]. Variables are then the averages $\bar{\varphi}_{Fp}$, $\bar{\varphi}_{Fc}$, and of course only *one* averaged electrical potential $\bar{\varphi}$. With the areal double-layer capacitance $C_{\rm dl}$ and with the specific pore area $S(\text{cm}^2\text{cm}^{-3})$ one has the doublelayer capacitance per volume $C_{dl}S$. Averaging over regions large compared to the pore dimensions leads to a zero net double-layer charge in the Poisson equation (Eq. (10)). However, in the (small-signal) continuity Eqs. (11) and (12), double-layer charging leads to contributions $\mp C_{\rm dl}S(\bar{\varphi}_{\rm Fp}-\bar{\varphi}_{\rm Fc})$ in the right-hand side of these equations. In the TLEC shown in Fig. 1 this leads to the additional capacitance $C_{dl}S$ connecting directly the two conduction currents. For an inhomogeneously oxidized polymer layer a distributed charge-transfer resistance with hindrance [10] by diffusion also has to be taken into account.

6. Conclusions

In this note transmission line equivalent circuits often used in solid-state electrochemistry have been extended. At first, under steady-state conditions additional current generators do occur and, secondly, traps for the different types of carriers have been taken into account. Especially the trap influence is discussed in the lf limit. The generalization for more than two types of carriers is trivial. The extension to a two-phase description is also given. For a concrete system, processes at the interfaces have to be added as boundary conditions.

In principle, the solution of the whole system of equations is only possible numerically and, indeed, the transmission line model is nothing more than a discretization of the smallsignal ac equations. Since, in general, the parameters (conductances, capacitances, conductivities, time constants) depend on the inhomogeneous steady-state solution, the practical importance of such transmission lines is limited insofar as the small-signal ac solutions can be obtained from the steady-state solutions with an S³A (small-signal sinoidal analysis) method. However, the TLEC is of principal importance as it allows us to derive lumped equivalent circuits for special conditions. This approach has not yet been developed in connection with electrochemical applications.

Acknowledgements

The author thanks Dr Susanne Scheinert for drawing his attention to the early work of Sah. Stimulating discussions with her and with Dr Phuong Hoa Nguyen, Professor Boris Michailovich Grafov, Dr Lothar Dunsch and Dr Andreas Petr are gratefully acknowledged.

References

- [1] R.P. Buck, C. Mundt, Electrochim. Acta 44 (1999) 1999.
- [2] W.J. Albery, A.R. Mount, J. Chem. Soc., Faraday Trans. 89 (1993) 327.
- [3] W.J. Albery, A.R. Mount, J. Chem. Soc., Faraday Trans. 90 (1994) 1115.
- [4] M.A. Vorotyntsev, L.I. Daikin, M.D. Levi, J. Electroanal. Chem. 364 (1994) 37.
- [5] C.-T. Sah, Proc. IEEE 55 (1967) 654.
- [6] C.-T. Sah, Proc. IEEE 55 (1967) 672.
- [7] C.-T. Sah, Solid-State Electron. 13 (1970) 1547.
- [8] J.-H. Xu, J. Shen, J. Appl. Phys. 83 (1998) 2646.

- [9] H.L. Gomes, P. Stallinga, H. Rost, A.B. Holmes, M.G. Harrison, R.H. Friend, Appl. Phys. Lett. 74 (1999) 1144.
- [10] G. Paasch, K. Micka, P. Gersdorf, Electrochim. Acta 38 (1993) 2653.
- [11] K. Roßberg, G. Paasch, L. Dunsch, S. Ludwig, J. Electroanal. Chem. 443 (1998) 49.
- [12] P.H. Nguyen, G. Paasch, J. Electroanal. Chem. 460 (1999) 63.
- [13] G. Paasch, P.H. Nguyen, S.-L. Drechsler, Synth. Met. 97 (1998) 255.
- [14] R. de Levie, Electrochim. Acta 8 (1963) 751.
- [15] R. de Levie, Electrochim. Acta 9 (1964) 1231.
- [16] I. Rousar, K. Micka, A. Kimla, Electrochemical Engineering, vol. 2, Elsevier, Amsterdam, 1986.
- [17] K. Micka, M. Svata, J. Power Sources 3 (1978) 167.