

ON THE COUPLING OF INTERFACIAL CHARGE TRANSFER AND BULK TRANSPORT
IN IONIC CRYSTALS*

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A mathematical model is presented for the coupled charge transport/electrode reaction processes recently proposed by Lányi to explain apparent incomplete blocking at the interfaces of a NaCl crystal with nominally inert porous electrodes. Analysis of the model elucidates the conditions under which Lányi's treatment of small-signal a.c. response may be valid and suggests a more general approach to the problem.

SEVERAL YEARS AGO S. Lányi [1] reported the rather surprising observation that a small but apparently steady direct current would flow through the solid system Pt|NaCl|Pt at approximately 400°C on the application of a few millivolts potential difference. He has since published similar results for the solid system C|NaCl|C [2]. In both cases results were reported for nominally pure and for Ca²⁺-doped NaCl. Lányi considers this current to be ionic in nature for a number of reasons [3, 4]. He has taken care to eliminate the possibility of surface conduction, and a quick calculation shows that the total amount of charge flowing during a typical long time measurement [2] is equal to that contained in some 100 planes of the NaCl lattice, thus ruling out an adsorption pseudocapacitance.

The flow of direct ionic current through a NaCl crystal for sufficiently long times would result in the electrolysis of the crystal, with the production of chlorine gas and sodium metal. Although such a process is, in principle, possible if the system is maintained at constant temperature and the electrolysis products are removed, it seems quite doubtful that a true electrolysis would occur at a detectable rate under small-signal conditions. On the time scale of Lányi's experiments, however, one can conceive of several more likely alternative processes which might permit a near-steady flow of electrode reaction products into the electrode, especially a porous electrode. The product atoms or molecules might, for instance, be adsorbed at active sites

within the pores or might react with adsorbed impurity molecules.

Lányi [4] has recently published a theoretical treatment of the exchange of ions between a crystal with Schottky defects, such as NaCl, and nominally inert electrodes. Central to his treatment is the recognition that while the flow of faradaic current through the crystal corresponds to the motion of the defects, faradaic current across the interface requires the motion of ions. Two possible sets of conditions might be assumed to occur at the electrodes: one may imagine that at each electrode both cations and anions are exchanged with the surface layers of the crystal, providing for the formation and annihilation of anion and cation vacancies at both electrodes, or one may believe that only anions are removed from the crystal at the anode and only cations are removed at the cathode. Which of these two possible situations actually occurs will depend on the structure of the electrode, the nature of the ambient, and the duration of the measurement. Lányi appears to favor the second possibility, and he notes that under such conditions a steady current can flow only if anion and cation vacancies can annihilate each other to form a new region of crystal surface. In the present communication we shall consider both alternatives, allowing for significant vacancy pair annihilation in each.

Lányi's analysis [4] differs from conventional treatments of small-signal electrical response [5–8] in that no explicit use is made of the differential equations governing charge transport and no specific rate laws are assumed for the electrode processes. Instead, Lányi writes for the fluxes of the charge carriers

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$$J_i = \frac{\epsilon_i I}{e} \quad (1)$$

where $i = 1$ for positive charge carriers (anion vacancies), $i = 2$ for negative charge carriers (cation vacancies), ϵ_i is the corresponding transference number, and I is the total current. Further, Lányi writes for the excess concentrations Δc_{iL} at the left-hand electrode and Δc_{iR} at the right-hand electrode,

$$\Delta c_{iL} = -\Delta c_{iR}. \quad (2)$$

(For conciseness we will let c_i denote the concentration of the (vacancy) charge carriers, c_{ie} its equilibrium value, and c_{iL} and c_{iR} , the values of the concentration at the left and right hand electrodes, respectively. Thus $\Delta c_{iL} = c_{iL} - c_{ie}$ and $\Delta c_{iR} = c_{iR} - c_{ie}$.) Lányi's essential conclusion is that the dimensionless ratios

$$\rho_{iL} = -J_i/D_i\Delta c_{iL}, \quad (3)$$

and

$$\rho_{iR} = J_i/D_i\Delta c_{iR}, \quad (4)$$

where D_i is the diffusion coefficient of the i th species, obey the relationship

$$\rho_{1L} = \rho_{2L} = \rho_{1R} = \rho_{2R}, \quad (5)$$

in the steady state. Since the boundary parameters employed in most small-signal a.c. response theories are defined by relations of the forms (3) and (4) [9], Lányi then states that these theories, which were originally derived for systems without pairwise charge carrier annihilation at the electrode/crystal interface, are applicable to his system, with equation (5) holding for both a.c. and d.c. conditions.

In order to clarify the physical content of Lányi's treatment, we have examined in detail the steady-state small-signal behavior of an electrode/material/electrode system in which the fluxes of the positive and negative charge carriers are governed by the Nernst-Planck equations,

$$J_i = (-1)^i \mu_i c_i E - D_i (dc_i/dx), \quad (6)$$

and for which the electrode reaction kinetics are governed by the simple but plausible relations

$$J_{iL} = -k_{iL}(c_{iL} - c_{ie}) - k_r(c_{iL}c_{2L} - c_{ie}c_{2e}) \quad (7)$$

and

$$J_{iR} = k_{iR}(c_{iR} - c_{ie}) + k_r(c_{1R}c_{2R} - c_{1e}c_{2e}). \quad (8)$$

Here k_{iL} and k_{iR} are reaction rate constants for the exchange of cations and anions between the crystal surface and the electrode and k_r is a rate constant for the annihilation of anion and cation vacancies at the interface. We assume the Einstein relation, $D_i = (\mu_i kT/e)$, to

be valid throughout our treatment. We have considered both the symmetric case of identical electrodes ($k_{iL} = k_{iR} \equiv k_i$) and the asymmetric case proposed by Lányi ($k_{1L}, k_{2R} > 0, k_{2L} = k_{1R} = 0$), and for each case obtained closed form expressions for the fluxes J_i and the excess concentrations Δc_i .

The expressions obtained are quite complicated and are presented in the appendix. We note that in general the results for the symmetric case are consistent with equation (2) but not with equation (1), while in the asymmetric case neither equation (1) nor equation (2) is valid in general. Therefore the treatment of Lányi is not always justified, even under steady-state conditions. We are however, able to obtain the behavior assumed by Lányi and described in equations (1) and (2) of this communication in certain limiting symmetrical cases. For the symmetrical situation it is found that when $k_r c_{1e}$ and $k_r c_{2e}$ are much greater than both k_1 and k_2 , and L , the distance between the electrodes, is greater than both $D_1 k_2$ and $D_2 k_1$, the assumptions made by Lányi are justified. For asymmetric systems it is found that when $k_r c_{ie} L > D_2$ and $k_r c_{2e} L > D_1$, equation (1) is valid, but even in this limit equation (2) is not justified. In physical terms the conditions which allow the symmetrical case to be described by equation (1) and (2) specify that vacancy pair annihilation occurs sufficiently rapidly compared to transport or electrode reaction that quasi-equilibrium conditions are maintained at the electrodes. Under these possible but by no means universal conditions the Lányi treatment appears justified at zero frequency and probably over a finite frequency range. A more general treatment, however, would take into account the dynamics of the electrode reaction products as well as charge transfer and vacancy annihilation at the interface. In the remainder of this communication we present the outline of one such more general approach, and explicitly consider not only the steady state, but general small-signal a.c. conditions.

For definiteness we consider the right-hand electrode. Let b_{1R} denote the concentration of anions in the surface plane of the crystal, b_{2R} the concentration of cations, and let b_{1E} denote the corresponding concentrations of electrode reaction products in the surface of the electrode. The fluxes of anions and cations out of the crystal surface may then be taken as

$$J_{bi} = k_{i7} b_{iR} - k_{ib} b_{iE}. \quad (9)$$

The fluxes of anion and cation vacancies from the bulk towards the crystal surface are given by the negative of these quantities plus the recombination flux

$$J_r = k_r(c_{1R}c_{2R} - c_{1e}c_{2e}). \quad (10)$$

For a planar crystal surface $c_i + b_i$ must be a constant and one may thus set $\Delta c_{iR} = -\Delta b_{iR}$. (Some

modification of this assumption may be required in a more realistic treatment.) The fluxes, J_{iR} , of the charge carrying vacancies at the crystal surface may then be taken as

$$J_{iR} = k_{if}\Delta c_{iR} + k_{ib}\Delta b_{iR} + k_r(c_{2e}\Delta c_{iR} + c_{ie}\Delta c_{2R}), \quad (11)$$

and this relation may be employed as a boundary condition for the small-signal equations of charge transport [compare equation (4)].

If one further assumes that the product species diffuse independently into the electrode, one may eliminate Δb_{iE} from the equations by solving the diffusion equations for the electrode reaction products subject to the boundary conditions (11) to obtain a relationship between Δb_{iE} and Δc_{iR} [10]. In the simplest case, that of electrodes of semi-infinite length, one then obtains

$$J_{iR} = k_{i1}\Delta c_{1R} + k_{i2}\Delta c_{2R}, \quad (12)$$

where

$$k_{11} = \frac{k_{1f}\sqrt{i\omega D_{1e}}}{k_{1b} + \sqrt{i\omega D_{1e}}} + k_r c_{2e}, \quad (13)$$

$$k_{22} = \frac{k_{2f}\sqrt{i\omega D_{2e}}}{k_{2b} + \sqrt{i\omega D_{2e}}} + k_r c_{1e}, \quad (14)$$

$$k_{12} = k_r c_{1e}, \quad (15)$$

and

$$k_{21} = k_r c_{2e}, \quad (16)$$

where D_{1e} and D_{2e} are diffusion constants for the atoms within the electrode. From these equations it can be seen that as $\omega D_{ie} \rightarrow 0$ the fluxes are given by

$$J_{1R} = k_r(c_{2e}\Delta c_{1R} + c_{1e}\Delta c_{2R}) = J_{2R}, \quad (17)$$

a relation which can only be satisfied in a logically consistent way when $\Delta c_{1R}/\Delta c_{2R} = -c_{1e}/c_{2e}$, so that $J_{1R} = J_{2R} = 0$ as $\omega \rightarrow 0$. It should thus be noted that surface recombination alone is not sufficient to allow the flow of steady direct current in the limit of semi-infinite electrodes. This conclusion remains true for electrodes of finite thickness and other forms of diffusion as long as the products of the electrode reaction are not able to leave the electrode.

Considerable caution is appropriate when dealing with experimental data at very low frequencies or for the "steady state" [11]. An absolute steady state measurement is, of course, not feasible, and measurements on very long time scales may bring into play mechanisms which are otherwise unimportant in characterizing the system. One notes from equations

(12)–(16) that for finite ω and sufficiently large D_{1e} and D_{2e} , $k_{11} \approx k_{1f}$, $k_{22} \approx k_{2f}$ and $k_{11}, k_{22} \gg k_{12}, k_{21}$. Under these conditions equation (12) reduces to the form of equation (4), but without any predetermined relation between ρ_{1R} and ρ_{2R} . Thus even if vacancy pair annihilation is significant at very low ω , a good fit to the existing small-signal a.c. theory may be possible, if this frequency range is excluded.

It is of interest to ask whether the experimental observations reported by Lányi could be described by the theory presented here for diffusion of the reaction products into the electrode. In the absence of vacancy pair annihilation and for $c_{2e} \gg c_{1e}$, the interfacial admittance corresponding to equation (7) is $Y(\omega) \cong (k_{22}c_{2e}e^2/kT)$, and from the Laplace transform of $s^{-1}Y(s)$, where s the Laplace transform complex frequency variable, we find that the current transient corresponding to a step function potential difference $V_a/2$ applied to the interface is

$$i(t) = \frac{V_a e^2 c_{2e} k_{2f}}{2kT} \exp(k_{2b}^2 t/D_{2e}) \operatorname{Erfc}(k_{2b} t^{1/2}/\sqrt{D_{2e}}). \quad (18)$$

Although the decay is not exponential, this sets a time scale. If the Lányi "steady state" results are to be explicable by the present version of the Lányi mechanism, then we must require that this current fall perhaps only five percent or less in value during the time of the measurement, e.g. 218 hours for Lányi's study of $\text{C}|\text{NaCl}|\text{C}$ [2]. This will be so provided that

$$(k_{2b}/\sqrt{D_{2e}})(218 \text{ hr} \cdot 3600 \text{ sec/hr})^{1/2} \leq 0.0454. \quad (19)$$

A rough estimate of $k_{2f} \approx 10^{-8} \text{ cm sec}^{-1}$ can be obtained from Lányi's expression for the interfacial conductance of a graphite|NaCl (200 ppm Ca^{2+}) interface. Assuming one-tenth of this value for k_{2b} , one then has from equation (19) $D_{2e} \sim 4 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$, a perhaps reasonable value, and one that might suggest that the assumption of a semi-infinite electrode does not introduce major errors into the analysis.

Whether the mechanism proposed by Lányi is indeed found applicable or not by further studies, the extension of the small-signal a.c. theory to encompass surface generation/recombination reactions is probably desirable. Such reactions are known to occur in electronic semiconductors [12] and undoubtedly occur in Schottky and Frenkel defect materials. The development of the appropriate theory, using boundary conditions of the form (11), is being undertaken by the authors.

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APPENDIX: SOLUTIONS OF SMALL-SIGNAL
STEADY-STATE EQUATIONS

For the symmetrical case ($k_{iL} = k_{iR} \equiv k_i$) we obtain

$$J_i = \frac{(-1)^{i+1}I}{e} \left\{ \frac{2D_1D_2k_i c_{ie} + D_i c_{ie} LK}{2D_1D_2(k_1c_{1e} + k_2c_{2e}) + (D_1c_{1e} + D_2c_{2e})LK} \right\} \quad (A1)$$

where I is the steady state current through the system and

$$K \equiv k_1k_2 + k_r(k_1c_{1e} + k_2c_{2e}). \quad (A2)$$

Further we find $\Delta c_{iR} = -\Delta c_{iL} \equiv \Delta c_i$, with

$$\Delta c_i = \frac{(-1)^{i+1}Ic_{ie}}{2e} \times \left\{ \frac{2D_i k_i' c_{i'e} L(k_i' - k_i) + (D_1c_{1e} + D_2c_{2e})LK + 2D_1D_2(k_1c_{1e} + k_2c_{2e})}{(k_1c_{1e} + k_2c_{2e})[2D_1D_2(k_1c_{1e} + k_2c_{2e}) + (D_1c_{1e} + D_2c_{2e})LK]} \right\} \quad (A3)$$

where $i' = 2$ for $i = 1$, and $i' = 1$ for $i = 2$.

For the asymmetric case ($k_{2L} = k_{1R} = 0$, $k_{1L} = k_1$, $k_{2R} = k_2$), we find

$$J_i = \frac{(-1)^{i+1}I}{e} \left\{ \frac{D_1D_2 + D_i k_r c_{ie} L}{2D_1D_2 + k_r L(D_1c_{1e} + D_2c_{2e})} \right\}, \quad (A4)$$

$$\Delta c_{1L} = -I/ek_1, \quad (A5)$$

$$\Delta c_{2L} = \frac{I}{ek_1 k_r c_{1e}} \left\{ \frac{D_1D_2(2k_r c_{2e} + k_1) + k_r c_{2e} L[k_r(D_1c_{1e} + D_2c_{2e}) + D_2k_1]}{2D_1D_2 + k_r L(D_1c_{1e} + D_2c_{2e})} \right\}, \quad (A6)$$

$$\Delta c_{1R} = \frac{I}{ek_2 k_r c_{2e}} \left\{ \frac{D_1D_2(2k_r c_{1e} + k_2) + k_r c_{1e} L[k_r(D_1c_{1e} + D_2c_{2e}) + D_1k_2]}{2D_1D_2 + k_r L(D_1c_{1e} + D_2c_{2e})} \right\}, \quad (A7)$$

and

$$\Delta c_{2R} = -I/ek_2. \quad (A8)$$

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