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Solid electrolyte galvanic cell under load*

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Abstract

Relationships are derived which describe the voltage of and the ionic and electronic currents through a solid electrolyte galvanic cell under load as an explicit function of the independent variables. These relationships result from an appropriate extension of the classical Wagner approach for the open circuit case to the conditions of a cell in charge or discharge mode. The formulae represent generalized versions of the Wagner–Schmalzried equations. They readily allow determination of the chemical potential distribution throughout the electrolyte under load conditions.

1. Introduction

Recently, formulae describing the flux of oxygen ions through a single and multilayer mixed conducting oxide under the influence of an external load and chemical potential gradient were derived, which lead to rather complicated relationships [1]. Actually, much simpler formulae considering the single-layer case have already been used in the literature [2, 3] which can easily be transferred to more general conditions. These formulae which represent generalized Wagner–Schmalzried equations have practical relevance for a number of solid electrolyte applications, for example, in a fuel cell, a battery, the alkali metal thermal-to-electric converter. Likewise, they are the theoretical background for the method of partial short-circuit to determine the ion conductivity of a mixed ionic-electronic conductor. The approach resulting in these relationships is presented in the following account.

2. General relationships

The current density i of the charge carrier 'k' reads:

$$i_{\mathrm{k}} = -\frac{\sigma_{\mathrm{k}}}{z_{\mathrm{k}}F}\ \mathrm{grad}\ \eta_{\mathrm{k}} \tag{1}$$

where F is the faradaic number and σ_{k}, z_{k}, η_{k} are the conductivity, the charge number, and the electrochemical potential, respectively, of the charge carrier k.

Suppose the ionic crystal MA under consideration may be either a predominantly metal ion (k = m) (i.e., cationic) or anionic (k = a) conductor. Within this crystal an equilibrium can be assumed to exist between the ions, the electrons and the respective neutral particles [4]:

$$\mathrm{M}^{z_{\mathrm{m}}+} + z_{\mathrm{m}}\mathrm{e}' \rightleftharpoons \mathrm{M} \tag{2a}$$

$$\mathrm{A}^{|z_{\mathrm{a}}|-} \rightleftharpoons \mathrm{A} + |z_{\mathrm{a}}|\mathrm{e}' \tag{2b}$$

Therefore the electrochemical potentials of these species are interrelated. Independent of whether MA is conductive for anions or cations, in the following an arbitrary ion (i.e., k = i), with the charge number z_{i} is considered to be the mobile species. The neutral particle corresponding to 'i' is taken to be X_{ξ} where ξ is the number of atoms associated in the standard state of X. Then the generalized relationship for the electrochemical potentials reads as follows:

$$\mathrm{grad}\,\eta_{\mathrm{i}} + z_{\mathrm{i}}\,\mathrm{grad}\,\eta_{\mathrm{e}} = \frac{1}{\xi}\mathrm{grad}\,\mu_{\mathrm{X}_{\xi}} \tag{3}$$

with $\mu_{\mathrm{X}_{\xi}}$ denoting the chemical potential of X_{ξ} and $\mathrm{grad}\,\mu_{\mathrm{X}_{\xi}} = R\ \mathrm{grad}(T\ln a_{\mathrm{X}_{\xi}})$ (where $a_{\mathrm{X}_{\xi}}$ is the thermodynamic activity of X_{ξ}, R the gas constant and T the temperature).

The electrochemical potential difference of the electrons between the surfaces (′) and (″) of the electrolyte corresponds to the voltage U between these two points provided the metallic contacts are made of the same material (cf. [5]):

$$\eta'_{\mathrm{e}} - \eta''_{\mathrm{e}} = FU \tag{4}$$

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* This paper is dedicated to Carl Wagner (1901–1977) to mark the centenary of his birth.

If grad η_i in Equation 3 is zero and the interfaces of the electrolyte are in equilibrium with their surroundings, the integration of Equation 3 together with the definition according to Equation 4 leads to a voltage that is identical with the Nernst equilibrium cell voltage U_{eq}:

$$U_{eq} = -\frac{RT}{F} \ln\left(\frac{a''_{X_\xi}}{a'_{X_\xi}}\right)^{1/z_i\xi} \tag{5}$$

Every solid electrolyte is characterized by a comparatively high level of the activity a_i of the mobile ion 'i', which is usually achieved by a strong intrinsic disorder or by doping. As a consequence, the activity of 'i' does practically not change, if the activity of the corresponding neutral species varies in the surroundings of the electrolyte. Hence, a_i remains constant within a broad region of the chemical potential of X_ξ:

$$a_i \approx \text{const.}\ (a_{X_\xi}) \tag{6}$$

This condition is in accordance with the experimental observation that, within the chemical potential region under consideration, the ionic conductivity is a constant. This applies to all practically relevant electrolyte materials.

The total electronic conductivity, σ_e, is the sum of the contributions due to electrons (subscript n) and holes (subscript p):

$$\sigma_e = \sigma_n + \sigma_p \tag{7}$$

The application of the mass action law to the electrochemical equilibria (Equation 2(a) and (b)) and the consideration of Equation 6 lead to the chemical potential dependence of the partial electronic conductivities σ_n and σ_p [6, 7]:

$$\sigma_p = \sigma_i \left(\frac{a_\oplus}{a_{X_\xi}}\right)^{1/z_i\xi} \tag{8a}$$

and

$$\sigma_n = \sigma_i \left(\frac{a_{X_\xi}}{a_\ominus}\right)^{1/z_i\xi} \tag{8b}$$

In the above relationships, the constants $a_\oplus$ and $a_\ominus$ are the electron conduction parameters which were introduced in analogy to Schmalzried [8]. They relate the partial electronic conductivities to the ionic conductivity σ_i of the electrolyte and to the activity of the neutral species X_ξ. $a_\oplus$ and $a_\ominus$ represent those X_ξ-activities at which the electronic conductivities σ_p and σ_n, respectively, are equal to the ionic conductivity σ_i. Thus, the electron conduction parameters characterize the limits of the ionic domain of the electrolyte (cf. [9]).

3. Balance of the charge carrier current densities under charge and discharge

According to Wagner [4], in an unloaded cell the ionic current density i_i flowing through the electrolyte is induced by the partial internal short-circuiting current density i_e due to electronic conduction. In contrast, the situation under load is characterized by the fact that the total polarization current density that corresponds to i_i results from the sum of i_e and an additional current density i_{ext} that flows through the external circuit (Figure 1). Thus, the classical balance equation of the charge carrier current densities must be extended as follows:

$$i_i = -(i_e + i_{ext}) \tag{9}$$

The current density i_{ext} is, like i_e, of electronic nature and acts in the same way as an electronic current would act within the electrolyte. However, i_{ext} is not at all an electrolyte-related quantity. In order to describe i_{ext} in a way corresponding to Equation 1, the fictitious conductivity σ_{ext} must be introduced. σ_{ext} can be understood as being determined by the ratio between the external current density and the electric field strength that would cause this current density to flow through the electrolyte. As concerns the current density, it is equal to the ratio between the external current I_{ext} and the electrolyte area A_{SE}. The field strength, in its turn, can be represented by the ratio between the cell voltage U and the electrolyte thickness d_{SE}. Thus, σ_{ext} can be written as

$$|\sigma_{ext}| = \frac{|I_{ext}|/A_{SE}}{|U|/d_{SE}} \tag{10}$$

In Equation 10, both the current and voltage may be either positive or negative. They are related to each other by the extent of the external load. While the sign of the cell voltage U is determined by Equation 4, there is, at first glance, no strict definition regarding the direction and the appropriate sign of I_{ext}. However, the definition of I_{ext} has to fulfil the requirement that, in view of Equation 9, the sign is compatible with the signs of the electrolyte-related currents I_i and I_e. For that reason I_{ext} is defined as follows:

$$I_{ext} = \frac{U_{ext} - U}{R_L} \tag{11}$$

U_{ext} denotes the voltage which, in a charge or pumping mode of the cell, may be externally applied. R_L is the load resistance (cf. Figure 1).

According to Equation 11, even if U is nonvarying, I_{ext} can change sign by changing U_{ext}. Thus, the fictitious conductivity σ_{ext} may be either positive or negative. Its sign is consistent with the signs of all the other quantities involved, only if, in place of Equation 10, σ_{ext} is defined as

$$\sigma_{ext} = \frac{-I_{ext}/A_{SE}}{U/d_{SE}} = \frac{d_{SE}\left(1 - \frac{U_{ext}}{U}\right)}{A_{SE}R_L} \tag{12}$$

Using Equation 12, i_{ext} can be formulated as though the external current were an apparent electron current density of the electrolyte with the same driving force as the internal electron current density i_e:

$$i_{\text{ext}} = \frac{d_{\text{SE}}\left(1 - \frac{U_{\text{ext}}}{U}\right)}{A_{\text{SE}} R_{\text{L}} F} \operatorname{grad} \eta_{\text{e}} \tag{13}$$

By substitution of Equations 1 and 13 into Equation 9, as well as taking Equation 3 into account, η_{i} can be eliminated so that the electrochemical potential of the electrons is obtained as a function of the chemical potential of X_ξ:

$$\operatorname{grad} \eta_{\text{e}} = \frac{1}{z_{\text{i}}\xi} \left(\frac{1}{\frac{\sigma_{\text{e}}}{\sigma_{\text{i}}} + \kappa} \right) \operatorname{grad} \mu_{X_\xi} \tag{14a}$$

With:

$$\kappa = 1 + \frac{d_{\text{SE}}\left(1 - \frac{U_{\text{ext}}}{U}\right)}{A_{\text{SE}}\, R_{\text{L}} \sigma_{\text{i}}} \tag{14b}$$

Equation 14(b) proves that κ is constant with respect to μ_{X_ξ}, only if $U_{\text{ext}} = 0$, and then it is an explicit function of the independent variables of the operational conditions of the cell. Otherwise, if $U_{\text{ext}} \neq 0$, κ is related to the dependent quantity U and, since U is an unknown function of μ_{X_ξ}, the relationship between κ and μ_{X_ξ} is likewise unknown.

4. Current and voltage

In view of Equations 1, 3 and 14, the ionic current density can be expressed in terms of the gradient of the chemical potential of the respective neutral species:

$$i_{\text{i}} = -\frac{\sigma_{\text{i}}}{z_{\text{i}}\xi F} \left(1 - \frac{1}{\frac{\sigma_{\text{e}}}{\sigma_{\text{i}}} + \kappa} \right) \operatorname{grad} \mu_{X_\xi} \tag{15}$$

Confining the consideration to only the one-dimensional case of the chemical potential gradient, the integration of Relationship 15 over the space coordinate x between the positions $(x = 0;\ \mu_{X_\xi}(x = 0) = \mu'_{X_\xi})$ and $(x = d_{\text{SE}};\ \mu_{X_\xi}(x = d_{\text{SE}}) = \mu''_{X_\xi})$ yields the ion current I_{i} that flows through the electrolyte. To solve the integral, Equation 7 and the chemical potential dependence of the partial electron conductivities (i.e., Equations 8(a) and (b)), have to be taken into account. According to the foregoing statement about the chemical potential dependence of κ, the κ against μ_{X_ξ} relationship is known only if the special case $U_{\text{ext}} = 0$ is considered. Only then or if κ is approximately taken to be a constant with respect to μ_{X_ξ}, the integration can be carried out as described subsequently.

The analytical form of the solution of the integral depends on the relative magnitude of the electron conduction parameters $a_\oplus$ and $a_\ominus$. On condition that:

$$\frac{4}{\kappa^2} \left(\frac{a_\oplus}{a_\ominus} \right)^{1/z_{\text{i}}\xi} \ll 1 \tag{16}$$

which is usually fulfilled, especially for materials serving as solid electrolytes, the integration gives:

$$I_{\text{i}} = \frac{\sigma_{\text{i}} A_{\text{SE}}}{d_{\text{SE}}} \frac{RT}{F} \left[\left(\frac{1}{\kappa} - 1 \right) \ln \left(\frac{a''_{X_\xi}}{a'_{X_\xi}} \right)^{1/z_{\text{i}}\xi} + \frac{1}{\kappa} \ln \frac{\left(1 + \frac{1}{\kappa} \left(\frac{a'_{X_\xi}}{a_\ominus} \right)^{1/z_{\text{i}}\xi} \right) \left(1 + \frac{1}{\kappa} \left(\frac{a_\oplus}{a''_{X_\xi}} \right)^{1/z_{\text{i}}\xi} \right)}{\left(1 + \frac{1}{\kappa} \left(\frac{a''_{X_\xi}}{a_\ominus} \right)^{1/z_{\text{i}}\xi} \right) \left(1 + \frac{1}{\kappa} \left(\frac{a_\oplus}{a'_{X_\xi}} \right)^{1/z_{\text{i}}\xi} \right)} \right] \tag{17}$$

To obtain expression 17, one has to make use of the inequality (Expression 16) on different approximation levels. Besides, it also has to be assumed that the conductive area A_{SE} of the solid electrolyte is a constant with respect to the x axis. This normally applies to most real cases.

In the same way as the ionic current is obtained, the electronic current can be derived from Equation 1 (with k = e) in which grad η_{e} is substituted by Equation 14. Then the electronic current density reads:

$$i_{\text{e}} = \frac{1}{z_{\text{i}}\, \xi F} \frac{\sigma_{\text{e}}}{\left(\frac{\sigma_{\text{e}}}{\sigma_{\text{i}}} + \kappa \right)} \operatorname{grad} \mu_{X_\xi} \tag{18}$$

The procedure of integrating Equation 18 is basically the same as that used in integrating Equation 15. Provided that the conductive area the electron current is flowing through is identical with A_{SE}, the resulting equation for the electronic current, I_{e}, becomes:

$$I_{\text{e}} = -\frac{\sigma_{\text{i}} A_{\text{SE}}}{d_{\text{SE}}} \left(\frac{RT}{F} \right) \ln \frac{\left(1 + \frac{1}{\kappa} \left(\frac{a'_{X_\xi}}{a_\ominus} \right)^{1/z_{\text{i}}\xi} \right) \left(1 + \frac{1}{\kappa} \left(\frac{a_\oplus}{a''_{X_\xi}} \right)^{1/z_{\text{i}}\xi} \right)}{\left(1 + \frac{1}{\kappa} \left(\frac{a''_{X_\xi}}{a_\ominus} \right)^{1/z_{\text{i}}\xi} \right) \left(1 + \frac{1}{\kappa} \left(\frac{a_\oplus}{a'_{X_\xi}} \right)^{1/z_{\text{i}}\xi} \right)} \tag{19}$$

In view of Equation 4 the integration of Equation 14 leads directly to the cell voltage U. The integral can again be solved by analogy to the previous approach. Similarly, the resulting formula for U is correct only if condition 16 is fulfilled:

$$U = -\frac{RT}{\kappa F}\left[\ln\left(\frac{a''_{X_\xi}}{a'_{X_\xi}}\right)^{1/z_i\xi} + \ln\frac{\left(1+\frac{1}{\kappa}\left(\frac{a'_{X_\xi}}{a_\ominus}\right)^{1/z_i\xi}\right)\left(1+\frac{1}{\kappa}\left(\frac{a_\oplus}{a''_{X_\xi}}\right)^{1/z_i\xi}\right)}{\left(1+\frac{1}{\kappa}\left(\frac{a''_{X_\xi}}{a_\ominus}\right)^{1/z_i\xi}\right)\left(1+\frac{1}{\kappa}\left(\frac{a_\oplus}{a'_{X_\xi}}\right)^{1/z_i\xi}\right)}\right] \qquad (20)$$

Equations 17, 19 and 20 represent the most general relationships for the ionic and electronic current as well as the voltage of an arbitrary solid electrolyte galvanic cell in a charge or discharge mode. Thus, these relationships are extensions of the classical Wagner–Schmalzried equations which themselves are included in Equations 17, 19 and 20 as the special case $\kappa = 1$.

The condition $\kappa = 1$ is realized when $R_L \to \infty$. This corresponds to an open circuit potentiometric measurement (cf. Table 1). $\kappa = 1$ is likewise fulfilled, if $U_{ext} = U$ and R_L is arbitrary. Such conditions are met in a compensating circuit after Poggendorf formerly used for currentless measurement of a voltage. With arbitrary U_{ext} and a finite value of R_L, which corresponds to the charge or discharge mode of operation, the circumstances of other practically relevant applications of a solid electrolyte galvanic cell, such as pumps, coulometric and amperometric sensors or electrochromic devices, can be simulated (cf. Table 1). Finally, with finite R_L and $U_{ext} = 0$, the conditions of a cell under load in, for instance, a battery, a fuel cell, or the alkali metal thermal-to-electric converter are met. The same applies to the conditions in a partially short-circuited cell used to determine the ionic conductivity of the employed electrolyte (see below). As mentioned in the preceding paragraph, the latter conditions are particular ones insofar as, from a mathematical point of view, with $U_{ext} = 0$ the dependent variables I_i, I_e and U exclusively become explicit functions of those quantities that are independent variables in view of the operation of the galvanic cell, that is, load resistance, temperature, the chemical potentials at the electrodes and the electrical properties of the electrolyte.

Table 1. Compilation of the operation modes of a solid electrolyte galvanic cell and the corresponding κ-values

Conditions	κ-Value	Application
$R_L \to \infty$	$\kappa = 1$	OC mode; potentiometry, e.g. sensors
$U_{ext} = U$; R_L arbitrary	$\kappa = 1$	Potentiometry with compensating voltage
$U_{ext} = 0$; R_L finite	$\kappa > 1$	Discharge mode; e.g. batteries, fuel cells, alkali metal thermoelectric converter
$U_{ext} \neq U$; R_L finite	$\kappa \geqslant 1$ or $\kappa \leqslant 1$	Charge/discharge mode; coulometry, amperometry, electrochemical pump, electro-chromic devices

Strictly, Equations 17, 19 and 20 exclusively reflect the situation which occurs between the outer surfaces of the solid electrolyte. Only if these surfaces are in equilibrium with the adjacent phases, implying that there is no polarization effect at the interfaces, do the relationships cover the situation of the whole cell. However, particularly in the case of finite R_L there will usually be a difference in the chemical potential between the electrolyte–electrode interface and the bulk of the adjacent electrode phase. Nevertheless, the relationships remain useful, if they are supplemented by additional relationships that quantify the contribution of electrode polarization (cf. [3, 10]).

When substituting Equations 5 and 20 into Equation 17, one obtains:

$$I_i = \frac{\sigma_i A_{SE}}{d_{SE}}(U_{eq} - U) \qquad (21)$$

which agrees with Kirchhoff's theorem of the divided circuit of Figure 1. Analogously one gets for I_e:

$$I_e = \frac{\sigma_i A_{SE}}{d_{SE}}(\kappa U - U_{eq}) \qquad (22)$$

Combining Equation 21 with Equation 22 and taking Equations 11 and 14(b) into account yields:

$$I_e + I_{ext} = -I_i \qquad (23)$$

This relationship demonstrates that the integrated equations are in accordance with the differential ones (cf. Equation 9).

According to Equation 19, the magnitude of the internal electronic short-circuiting current I_e decreases, if the galvanic cell is partially short-circuited over an external resistance (R_L finite; $U_{ext} = 0$; implying $\kappa > 1$). The reason for that is obvious. Due to the external short-circuit of the cell, the electrical potential difference across the electrolyte, and hence the driving force for the electron conduction, is diminished. In Equation 19 this reduction of the driving force is expressed by the factor

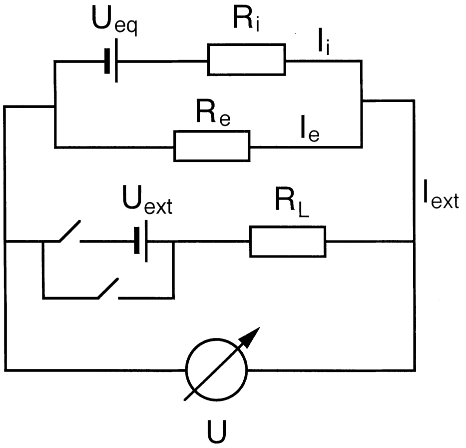

Fig. 1. Electrical equivalent circuit for a solid electrolyte galvanic cell under charge and discharge conditions. (U_{eq}: Nernst equilibrium cell voltage; U: cell voltage; U_{ext}: externally applied voltage; R_i: resistance of the ion conduction of the electrolyte; R_e: resistance of the electron conduction of the electrolyte; R_L: load resistance; I_i: total ionic polarization current through the cell; I_e: internal short-circuiting current due to electron conduction of the electrolyte; I_{ext}: external short-circuiting current).

$1/\kappa$ in front of the electron conduction parameters. With $\kappa > 1$ the factor corrects the extent of the internal electronic short-circuit towards smaller magnitudes. Thus the condition $\kappa > 1$ acts as if the width of the ionic domain of the electrolyte were extended into both the n- and p-conduction region with the electrolyte exhibiting apparently smaller n- and p-conductivities.

4.1. *Determination of the ionic conductivity by the method of partial short-circuit*

Proceeding from Equation 21, the voltage difference $\Delta U = U(\kappa) - U(\kappa = 1)$ between two different states of load of the galvanic cell, that is, $\kappa > 1$ (R_L finite; $U_{ext} = 0$) and $\kappa = 1$ ($R_L \to \infty$; $U_{ext} = 0$), is related to the change in the polarization current flowing through the cell and also to the magnitude of the ionic conductivity of the electrolyte:

$$\Delta U = -\frac{d_{SE}}{\sigma_i A_{SE}}(I_i(\kappa) - I_i(\kappa = 1)) \tag{24}$$

Suppose the electron conduction properties of the electrolyte are unknown, then the current difference $I_i(\kappa) - I_i(\kappa = 1)$ is also unknown. It can be set approximately equal to the measurable current I_{ext}, if the change in electronic current caused by the short-circuit (i.e., $I_e(\kappa) - I_e(\kappa = 1)$) is negligible (cf. Equation 23). This is better fulfilled as κ approaches 1 and/or as the electronic conductivity of the electrolyte becomes negligible. Since the latter condition is inapplicable for mixed conductors, it has at least to be guaranteed that κ differs only slightly from 1 (i.e., $\kappa \gtrapprox 1$). This implies that the resistance R_L is chosen to be very high in relation to the internal resistance of the cell, and hence, the load and the voltage decay are small. In other words, the cell has only to be partially short-circuited. Then the following approximation can be derived from Equation 20 (see also a different approach to the same problem in [2, 3]):

$$U(\kappa) \approx \frac{1}{\kappa} U(\kappa = 1) \tag{25}$$

Invoking this approximation to substitute $U(\kappa = 1)$ in the quantity ΔU and taking Equations 11 and 14(b) into account, Equation 21 reveals that:

$$I_i(\kappa) - I_i(\kappa = 1) \approx -I_{ext} \tag{26}$$

Substitution into Equation 24 yields:

$$\Delta U = \frac{d_{SE}}{\sigma_i A_{SE}} I_{ext} \tag{27}$$

Equation 27 relates the measurable quantities ΔU, I_{ext}, d_{SE} and A_{SE} to σ_i, thus offering an opportunity to determine the ionic conductivity of an arbitrary mixed conducting solid electrolyte without knowing the extent of the electronic conduction of the material under study and also without knowing the extent of possible stray currents in the experimental apparatus (cf. [11]). Those currents would act in the same way as the internal electronic short-circuit.

The foregoing relationships ignore any effects of electrode polarization. To minimize their impact on the result of the conductivity measurement is, from a practical point of view, not always easy (cf. [10]). At any rate, it holds that the conductivity data determined by means of the short-circuiting method are less affected by electrode polarization the less intensive the short-circuiting of the cell is.

5. Chemical potential distribution throughout the electrolyte

In the unloaded case the ionic and electronic currents are identical. Hence, it does not matter which of the currents is taken for balancing the steady-state flux. This is different under load conditions insofar as the ionic current increases steadily with increasing external load while the electronic current simultaneously decreases and finally vanishes altogether. Therefore, the ionic rather than the electronic current is preferable as a basis for the profile calculation.

According to Choudhury and Patterson [12], the balance between the ionic current flowing through the whole electrolyte from $x = 0$ to $x = d_{SE}$ (i.e., $I_i(d_{SE})$) and the ionic current flowing in the same direction but only through a part of the electrolyte up to the position x (i.e., $I_i(x)$) may be written as

$$I_i(d_{SE}) = I_i(x) \tag{28}$$

In view of Equation 17 this leads to

$$\frac{x}{d_{\mathrm{SE}}}=\frac{\left(\frac{1}{\kappa}-1\right)\ln\left(\frac{a_{\mathrm{X}_\xi}}{a'_{\mathrm{X}_\xi}}\right)^{1/z_{\mathrm{i}}\xi}+\frac{1}{\kappa}\ln\frac{\left(1+\frac{1}{\kappa}\left(\frac{a'_{\mathrm{X}_\xi}}{a_\ominus}\right)^{1/z_{\mathrm{i}}\xi}\right)\left(1+\frac{1}{\kappa}\left(\frac{a_\oplus}{a_{\mathrm{X}_\xi}}\right)^{1/z_{\mathrm{i}}\xi}\right)}{\left(1+\frac{1}{\kappa}\left(\frac{a_{\mathrm{X}_\xi}}{a_\ominus}\right)^{1/z_{\mathrm{i}}\xi}\right)\left(1+\frac{1}{\kappa}\left(\frac{a_\oplus}{a'_{\mathrm{X}_\xi}}\right)^{1/z_{\mathrm{i}}\xi}\right)}}{\left(\frac{1}{\kappa}-1\right)\ln\left(\frac{a''_{\mathrm{X}_\xi}}{a'_{\mathrm{X}_\xi}}\right)^{1/z_{\mathrm{i}}\xi}+\frac{1}{\kappa}\ln\frac{\left(1+\frac{1}{\kappa}\left(\frac{a'_{\mathrm{X}_\xi}}{a_\ominus}\right)^{1/z_{\mathrm{i}}\xi}\right)\left(1+\frac{1}{\kappa}\left(\frac{a_\oplus}{a''_{\mathrm{X}_\xi}}\right)^{1/z_{\mathrm{i}}\xi}\right)}{\left(1+\frac{1}{\kappa}\left(\frac{a''_{\mathrm{X}_\xi}}{a_\ominus}\right)^{1/z_{\mathrm{i}}\xi}\right)\left(1+\frac{1}{\kappa}\left(\frac{a_\oplus}{a'_{\mathrm{X}_\xi}}\right)^{1/z_{\mathrm{i}}\xi}\right)}} \tag{29}$$

with a_{X_ξ} denoting the activity of X_ξ at an arbitrary position x inside the electrolyte.

Equation 29 is an implicit relationship for the functional dependence $a_{\mathrm{X}_\xi}=f(x)$ and hence for the chemical potential profile across the electrolyte under load conditions. In contrast to the unloaded case (cf. [13]), this relationship cannot be resolved analytically with respect to a_{X_ξ} provided κ is arbitrary. Nevertheless, Equation 29 proves to be a useful tool to throw light on the behaviour of a solid electrolyte under external load. It is particularly easy to handle if $U_{\mathrm{ext}}=0$.

Figures 2 and 3 show two examples of an oxygen chemical potential profile inside an yttria stabilized zirconia (YSZ) pellet when this pellet is, as part of a loaded galvanic cell, exposed to air on the left side and to a hydrogen/water gas mixture on the right side. The ordinate denotes the oxygen partial pressure of a hypothetical atmosphere with which the electrolyte layer at position x would be equilibrated if the solid was cut through at this position. In view of Equations 3 and 6, this oxygen pressure profile corresponds to the distribution of the electrical potential and the concentration of the electronic charge carriers inside the solid. The calculation of the profiles is based on data of the ionic and partial electronic conductivities which represents an average of literature data [14, 15]. Since one cannot rule out some inaccuracy in this data, especially in the electronic conduction parameters, the profiles of Figure 3 additionally illustrate the effect of a tentatively assumed deviation of the n-conduction parameter by five orders of magnitude towards a higher value.

It can be seen from Figures 2 and 3 that, due to the load of the cell, a remarkable change in the shape of the chemical potential profile occurs. This means that a change in the load conditions results steadily in a change in the distribution of the electron concentration throughout the electrolyte. The stronger the load, the more linear the profile. It follows from Equation 19 that, with an increasing extent of short-circuiting, that is, with κ increasingly exceeding the value 1, the electrolyte becomes more like a pure ionic conductor. In other words, the impact of the electronic properties of the solid electrolyte on the electrical behaviour of the whole cell vanishes in favour of the impact of the external circuit. Then the electrolyte behaves to an increasing extent like an ohmic resistor with the electrical potential

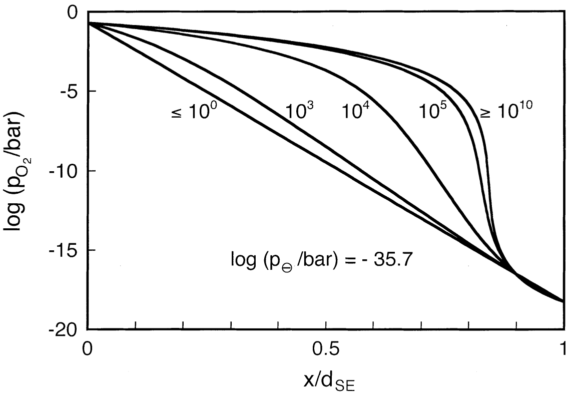

Fig. 2. Location-dependent distribution of the oxygen chemical potential inside the electrolyte of the galvanic cell: air ($p_{\mathrm{O}_2}=20.9$ kPa)|YSZ|$\mathrm{H_2}$, $\mathrm{H_2O}$ ($p_{\mathrm{H}_2}/p_{\mathrm{H_2O}}=0.1$) under different loads. (Load resistances in Ω are given as curve parameters; temperature: 900 °C; electrolyte pellet thickness: 1 mm; electrolyte area: 10 cm^2; ionic, n- and p-conductivity data are taken from [14, 15]).

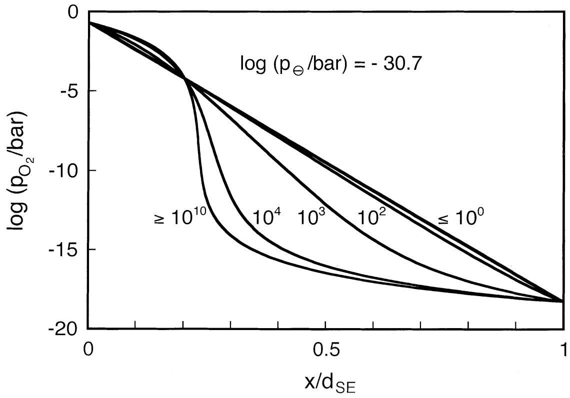

Fig. 3. Oxygen chemical potential profile through an YSZ pellet under the same conditions as given in the caption of Figure 2, except the n-conduction parameter $p_\ominus$ is assumed to be five orders of magnitude larger than that used for the calculation of Figure 2.

decreasing linearly over the length of the resistance, which corresponds to a linear decay of the chemical potential.

The derived relationships also prove useful in the more general case $U_{\text{ext}} \neq 0$. Then κ has to be approximated by a constant with respect to μ_{X_ξ} in order to render the respective equations integrable. Even though such an approximation may compromise the accuracy of the solution, it provides a way to achieve quantitative data. Successively this data can be improved by employing an iterative procedure. In the iteration process it is first necessary to choose a value of U from which to calculate a starting value of κ (cf. Equation 14(b)) the use of which allows determination of I_i and U using Equations 17 and 20. Taking the result for U, a new κ-value is determined. This procedure has to be repeated until κ, I_i, and U remain constant. Only then may Equation 29 be applied to determine the potential profile.

Figure 4 shows several examples of potential profiles calculated by employing the described iteration procedure. As solid electrolyte a ceria based material was chosen for the purpose of comparison with the oxygen chemical potential distribution described by Yuan and Pal [1]. It becomes evident from Figure 4 that the profiles for $U_{\text{ext}} = -0.5$ V and $U_{\text{ext}} = 0.5$ V arrange themselves in a reasonable order relative to the curve for $U_{\text{ext}} = 0$ V. This could be taken as an indication that the profiles for $U_{\text{ext}} \neq 0$ V resulting from the approach described above appear to be numerically correct.

Moreover, Figure 4 reveals that with increasing electrolyte thickness and increasing U_{ext} the profiles change in one direction. In both cases they gradually approach a straight line in the same way as they would if only the load resistance decreased (cf. this tendency in Figures 2 and 3). In view of Figure 1 this phenomenon appears to be plausible. The galvanic cell is expected to be more strongly short-circuited at lower load resistances or, if R_L = const., at higher internal resistances R_i of the electrolyte or higher oppositely applied external voltages. Keeping this in mind, the potential profile for the extremely high external voltage of 6 V, which represents a straight line in Figure 4, is much more probable than the curve calculated by Yuan and Pal [1]. They claimed a convex curvature for the same conditions.

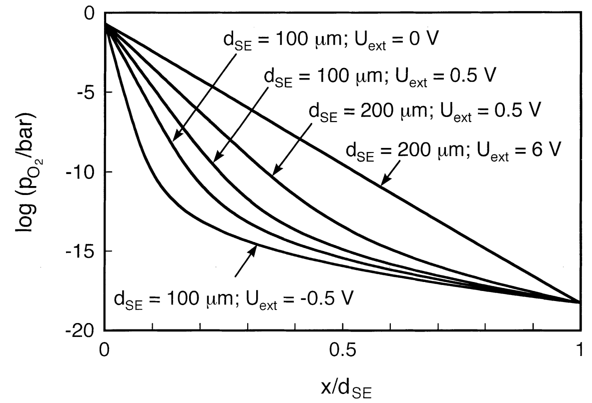

Fig. 4. Oxygen chemical potential profile through a doped ceria pellet under the same conditions as described by Yuan and Pal [1]. ($R_L = 1\ \Omega$; temperature: 900 °C; electrolyte area: 1 cm^2; ionic, n- and p-conductivity data similar to those used in [1]).

6. Summary

Wagner–Schmalzried type equations are derived for the voltage of and the ionic and electronic currents through a solid electrolyte galvanic cell under load. The approach is based on the usual assumptions going back to Wagner which implies that (i) apart from electronic charge carriers, only one kind of ions is mobile in the solid electrolyte; (ii) there is no cross-interaction in the transport of the charge carriers; (iii) the equilibrium between the charged species and the corresponding neutral particles is virtually established throughout the solid; (iv) the activity of the mobile ions remains constant over the whole cross-section of the solid, that is, within the whole region of the chemical potential of the neutral species surrounding the electrolyte; (v) the electrolyte materials under consideration have a wide ionic domain.

The equations enable the chemical potential distribution throughout the electrolyte to be readily determined under practically relevant conditions. Even though the foregoing approach is idealized as it concentrates on the electrolyte only and ignores all impacts of an electrode polarization, it may also represent a useful basis for inclusion of certain electrode effects.

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