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ORIGINAL PAPER

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Characterization of the conduction properties of a solid electrolyte by short-circuiting a potentiometric galvanic cell

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Abstract By short-circuiting a solid electrolyte galvanic cell, the ionic conductivity of the electrolyte employed in the cell can be determined. There is no other potential involved in this technique with regard to the characterization of the conduction properties of the electrolyte. In particular, the method does not offer any information about the electronic conductivity.

Keywords Solid electrolyte galvanic cell · Ionic conductivity · Electronic conductivity · Short-circuiting method

Introduction

In classical electrochemistry, short-circuiting a galvanic cell, e.g. a battery, over an external resistance for a short time is a routine procedure for checking the status of that cell. The voltage decay observed under this condition provides an information about the capacity of the battery and its total resistance. Basically, the same applies to a solid state electrochemical cell. All the more it is astonishing that in the literature on solid state electrochemistry there is still confusion about what really happens in such a cell if it is gradually short-circuited. This might have to do with the fact that a solid electrolyte, unlike an aqueous one, always shows an electronic contribution in addition to the ionic conductivity which makes the situation comparatively more complex.

An indication for the complexity is that there are different views in the literature as to the use of a short-circuiting procedure for determining the conduction properties of a solid electrolyte. In [1–3] this technique is described as being suitable for delivering the ionic conductivity provided that the extent of the short-circuit is as small as possible. On the other hand, in [4] it is propagated that the same information can be obtained only if the cell is totally short-circuited. Finally, in [5] the technique of short-circuiting is considered to be capable of providing information about the electronic conductivity of the electrolyte.

Proceeding from the theoretical relationships that reflect the situation of the electrolyte under the condition of short-circuiting, the different views as to the content of information of the technique are critically discussed in the following.

Voltage of and current through a cell under load

The situation of a cell short-circuited over an external load resistance R_L (cf. Fig. 1) is characterized by the fact that, in addition to the current I_e due to the electronic conductivity of the electrolyte, a finite current I_{ext} is flowing through the external circuit. Therefore, the total ion current I_i is (cf. [6]):

$$I_i = -(I_e + I_{ext}) \tag{1}$$

with I_{ext} being defined as:

$$I_{ext} = -\frac{U}{R_L} \tag{2}$$

As a result, the voltage U generated between the surfaces of the electrolyte, the total ionic polarization current and the internal electronic current are functions of the load conditions [6]:

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$$U = -\frac{RT}{\kappa.\mathrm{F}}.\left[\mathrm{In}\left(\frac{a''_{\mathrm{X}_\xi}}{a'_{\mathrm{X}_\xi}}\right)^{1/z_i\xi} + \mathrm{In}\frac{\left(1+(1/\kappa)\left(a'_{\mathrm{X}_\xi}/a_\ominus\right)^{1/z_i\xi}\right)\left(1+(1/\kappa)\left(a_\oplus/a''_{\mathrm{X}_\xi}\right)^{1/z_i\xi}\right)}{\left(1+(1/\kappa)\left(a''_{\mathrm{X}_\xi}/a_\ominus\right)^{1/z_i\xi}\right)\left(1+(1/\kappa)\left(a_\oplus/a'_{\mathrm{X}_\xi}\right)^{1/z_i\xi}\right)}\right] \tag{3}$$

$$I_\mathrm{i} = \frac{\sigma_\mathrm{i}A_\mathrm{SE}}{d_\mathrm{SE}}.\frac{RT}{\mathrm{F}}.\left[\left(\frac{1}{\kappa}-1\right).\mathrm{In}\left(\frac{a''_{\mathrm{X}_\xi}}{a'_{\mathrm{X}_\xi}}\right)^{1/z_i\xi} + \frac{1}{\kappa}.\mathrm{In}\frac{\left(1+(1/\kappa)\left(a'_{\mathrm{X}_\xi}/a_\ominus\right)^{1/z_i\xi}\right)\left(1+(1/\kappa)\left(a_\oplus/a''_{\mathrm{X}_\xi}\right)^{1/z_i\xi}\right)}{\left(1+(1/\kappa)\left(a''_{\mathrm{X}_\xi}/a_\ominus\right)^{1/z_i\xi}\right)\left(1+(1/\kappa)\left(a_\oplus/a'_{\mathrm{X}_\xi}\right)^{1/z_i\xi}\right)}\right] \tag{4}$$

$$I_\mathrm{e} = \frac{\sigma_\mathrm{i}A_\mathrm{SE}}{d_\mathrm{SE}}.\frac{RT}{\mathrm{F}}.\mathrm{In}\,\frac{\left(1+(1/\kappa)\left(a'_{\mathrm{X}_\xi}/a_\ominus\right)^{1/z_i\xi}\right)\left(1+(1/\kappa)\left(a_\oplus/a''_{\mathrm{X}_\xi}\right)^{1/z_i\xi}\right)}{\left(1+(1/\kappa)\left(a''_{\mathrm{X}_\xi}/a_\ominus\right)^{1/z_i\xi}\right)\left(1+(1/\kappa)\left(a_\oplus/a'_{\mathrm{X}_\xi}\right)^{1/z_i\xi}\right)} \tag{5}$$

with:

$$\kappa = 1 + \frac{d_\mathrm{SE}}{A_\mathrm{SE}.R_\mathrm{L}.\sigma_\mathrm{i}} \tag{6}$$

where R, T, F, σ_i, z_i, A_SE, d_SE, and R_L are the gas constant, the absolute temperature, the Faraday constant, the ionic conductivity of the electrolyte, the charge number of the mobile ion of the electrolyte, the area of the electrolyte the ions are flowing through, the thickness of the electrolyte and the load resistance, respectively. a'_{X_ξ} and a''_{X_ξ} stand for the thermodynamic activities of the potential determining species X_ξ at both of the electrolyte surfaces. X_ξ is the neutral particle that corresponds to the mobile ion of the electrolyte with ξ being the association number of that species in its standard state. $a_\oplus$ and $a_\ominus$ are the electronic conduction parameters of the electrolyte for the p- and n-type electronic conduction, respectively. The latter parameters define those X_ξ-activities at which the p- and n-electronic conductivity, respectively, is equal to σ_i.

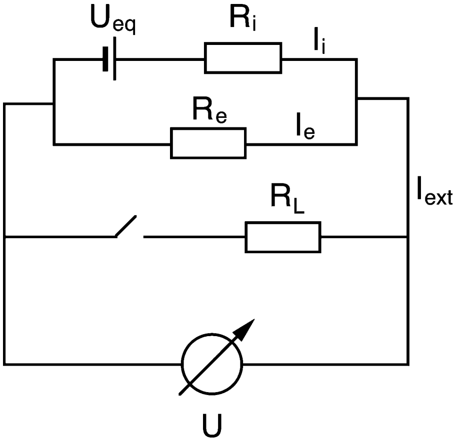

Fig. 1 The dc electrical equivalent circuit for a solid electrolyte galvanic cell under short-circuit conditions with negligible electrode resistance. (U_{eq} Nernst equilibrium cell voltage, U cell voltage, R_i resistance of the ion conduction of the electrolyte, R_e resistance of the electron conduction 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)

Strictly, the relationships of Eqs. 3, 4 and 5 are valid only if the condition:

$$\frac{4}{\kappa^2}.\left(\frac{a_\oplus}{a_\ominus}\right)^{1/z_i\xi} << 1 \tag{7}$$

is fulfilled.

Under load, independent of whether this is due to the internal and/or external short-circuit of the electrolyte, there is always a potential drop at the electrodes in addition to that within the electrolyte. The electrode polarization η is a function of the polarization current I_i and can be described as the product of that current and the polarization resistance R_η that in its turn is, in general, a function of I_i (cf. [7]). As a consequence, the activities a'_{X_ξ} and a''_{X_ξ} established at the outermost interfaces of the electrolyte differ from those activities that are adjusted within the respective electrode compartments, i.e. in a certain distance from the electrolyte surfaces. The latter activities are denoted by $a'_{\mathrm{X}_{\xi O}}$ and $a''_{\mathrm{X}_{\xi O}}$. Therefore, it holds that:

$$\eta(I_\mathrm{i}) = I_\mathrm{i}.R_\eta(I_\mathrm{i}) = \frac{RT}{\mathrm{F}}.\left[\mathrm{In}\left(\frac{a''_{\mathrm{X}_\xi}}{a''_{\mathrm{X}_{\xi O}}}\right)^{1/z_i\xi} - \mathrm{In}\left(\frac{a'_{\mathrm{X}_\xi}}{a'_{\mathrm{X}_{\xi O}}}\right)^{1/z_i\xi}\right] \tag{8}$$

In view of Eq. 8, with I_i approaching to zero, η vanishes implying that $a'_{\mathrm{X}_\xi} = a'_{\mathrm{X}_{\xi O}}$ and $a''_{\mathrm{X}_\xi} = a''_{\mathrm{X}_{\xi O}}$. Under these conditions, i.e. $a_{\oplus}^{1/Z_i\xi} \to 0$ and $a_{\ominus}^{1/Z_i\xi} \to 0$ as well as $\kappa = 1$, it follows from Eqs. 3 and 8 that the voltage of the cell becomes identical with the Nernst equilibrium voltage U_{eq}:

$$U_{eq} = -\frac{RT}{F}.\mathrm{In}\left(\frac{a''_{X_{\xi O}}}{a'_{X_{\xi O}}}\right)^{1/z_i\xi} \tag{9}$$

When substituting Eq. 4 into Eq. 3 and taking Eq. 8 into account, one obtains:

$$U = U_{eq} - I_i \cdot \frac{d_{SE}}{\sigma_i A_{SE}} - \eta \tag{10}$$

According to Eq. 10, the voltage of the galvanic cell at an arbitrary state of load is equal to the equilibrium voltage reduced by both the voltage drop across the ionic resistance of the electrolyte and the polarization voltage within the electrodes.

Ionic conductivity

Proceeding from Eq. 10, the voltage difference $\Delta U = U(\kappa) - U(\kappa = 1)$ between two different states of load, e.g. $\kappa > 1$ (R_L finite) and $\kappa = 1$ ($R_L \to \infty$), is:

$$\Delta U = -\frac{d_{SE}}{\sigma_i A_{SE}}.(I_i(\kappa) - I_i(\kappa = 1)) - \Delta\eta \tag{11}$$

with $\Delta\ \eta$ standing for the change of the electrode polarization under the same conditions, i.e. $\Delta\eta = \eta(\kappa) - \eta(\kappa = 1)$.

In the most general case, if the electron conduction properties of the electrolyte are unknown, the current difference $I_i(\kappa) - I_i(\kappa = 1)$ is unknown as well. As follows from Eq. 1, this current difference can approximately be set equal to the measurable current I_{ext}, provided that the change of the electron current caused by the short-circuit, i.e. $I_e(\kappa) - I_e(\kappa = 1)$, is negligible. 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, provided that one wants to concentrate on distinct mixed conductors, it has to be guaranteed that κ only slightly differs from 1, i.e. $\kappa \geqslant 1$.This implies that the resistance R_L is chosen to be 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 to be short-circuited only partially. Under these conditions the following approximation can be derived from Eq. 3:

$$U(\kappa) \approx \frac{1}{\kappa}.U(\kappa = 1) \tag{12}$$

Using this approximation, $U(\kappa = 1)$ can be substituted in the quantity ΔU of Eq. 11. Taking Eqs. 2 and 6 into account, with negligible $\Delta\ \eta$ Eq. 11 reveals that:

$$I_i(\kappa) - I_i(\kappa = 1) \approx -I_{ext} \tag{13}$$

Substitution into Eq. 11 yields:

$$\Delta U = \frac{d_{SE}}{\sigma_i A_{SE}}.I_{ext} - \Delta\eta \tag{14}$$

Equation 14 relates the measurable quantities ΔU, I_{ext}, d_{SE}, and A_{SE} to σ_i, thus allowing to determine the ionic conductivity of an arbitrary mixed conducting solid electrolyte provided that the change of the electrode polarization $\Delta\ \eta$ is negligible or can be separated from the total voltage drop ΔU. Since, under these circumstances, the polarization current I_i will always be finite, even if $\kappa = 1$, the requirement $\Delta\ \eta \to 0$ is only met if $R_{\eta \to 0}$. That would mean ideal electrodes. The reality is usually different which is why, by applying Eq. 14 and by neglecting $\Delta\ \eta$, the resulting values for σ_i are necessarily found to be smaller compared to the true values. In addition, the temperature dependence of the ionic conductivity may be concerned as well, namely if the temperature dependence of $\Delta\ \eta$ is significantly different from that of σ_i. In general, the smaller $\Delta\ \eta$, i.e. the smaller I_i and R_η, the lower the deviation from the true value.

The advantage of the described approach to determining the ionic conductivity is that it is independent of any knowledge about the extent of the electronic conduction of the material under study and also independent of the extent of possible stray currents in the experimental apparatus. Such currents may occur by a lack in the electrical insulation which results in an uncontrollable increase of the external load of the cell in question. Unknown thermoionic currents may act in the same way. An example of application of the approach is described in [1–3].

It follows from Eqs. 3, 5 and 6 that under the extreme condition of a total short-circuit, i.e. $R_L \to 0$, the situation with respect to U and I_e appears to be more straightforward than described above for the case of a partial short-circuit. It is true insofar as $U = 0$ is exactly fulfilled and, as a consequence of the zero driving force, it holds that $I_e = 0$ as well as $I_{ext} = -I_i$. For that reason there are several instances in the literature in which the well defined "zero driving force" situation rather than the partial short-circuit has been taken as the basis for determining the ionic conductivity [4]. The resulting relationship reads as follows:

$$\sigma_i = \frac{I_{ext}(R_L = 0)}{U_{eq}} \cdot \frac{d_{SE}}{A_{SE}} \tag{15}$$

This relationship was derived in a way different from the present approach. It is the consequence of a treatment of limiting cases in the operation of a galvanic cell without introducing the load resistance as an independent variable.

Equation 15 is identical with Eq. 10 if U and η are set zero. However, the larger the polarization current is, the smaller the justification of the electrode polarization being neglected. In terms of Eq. 8, it holds that:

$$I_1.R_\eta(I_1) < I_2.R_\eta(I_2) \quad \text{if } I_2 > I_1 \tag{16}$$

Since the polarization current reaches the maximum value upon total short-circuit, the error involved in Eq. 15 due to a non-negligible η is significantly larger than under more moderate polarization conditions. Consequently, the method of short-circuiting a cell for providing reasonable data on the ionic conductivity of the electrolyte does make sense only if the cell is short-circuited as little extensive as possible. In view of Eq. 8, it holds:

$$I_i.R_\eta(I_i) \to 0 \quad \text{if } I_i \to 0 \tag{17}$$

Electronic conductivity

Recently, the method of short-circuiting has also been considered as suitable for providing information about the electronic conductivity of the electrolyte [5] which originally goes back to a paper published by Gorelov [8]. The background of this idea results from Eq. 10 with Eqs. 1, 2 and 8 being taken into account:

$$\frac{U_{\mathrm{eq}}}{U} - 1 = \left(\frac{d_{\mathrm{SE}}}{\sigma_{\mathrm{i}} A_{\mathrm{SE}}} + R_\eta\right) . \left(\frac{1}{R_{\mathrm{e}}} + \frac{1}{R_{\mathrm{L}}}\right) \tag{18}$$

along with the definition:

$$-\frac{I_{\mathrm{e}}}{U} = \frac{1}{R_{\mathrm{e}}} \tag{19}$$

According to [8], relationship (18) promises to determine $1/R_{\mathrm{e}}$ and thus the electronic conductivity of the electrolyte from measuring the voltage of a galvanic cell upon short-circuiting the cell successively over varying load resistances R_{L} and plotting the quantity $U_{\mathrm{eq}}/U-1$ against the inverse load resistance. This is graphically demonstrated by Fig. 2 in which the quantity to be determined, i.e. $1/R_{\mathrm{e}}$, corresponds to the length of the abscissa section between zero and the intersection point of the extrapolated line of the $U_{\mathrm{eq}}/U-1$ vs. $1/R_{\mathrm{L}}$ plot with the x-axis.

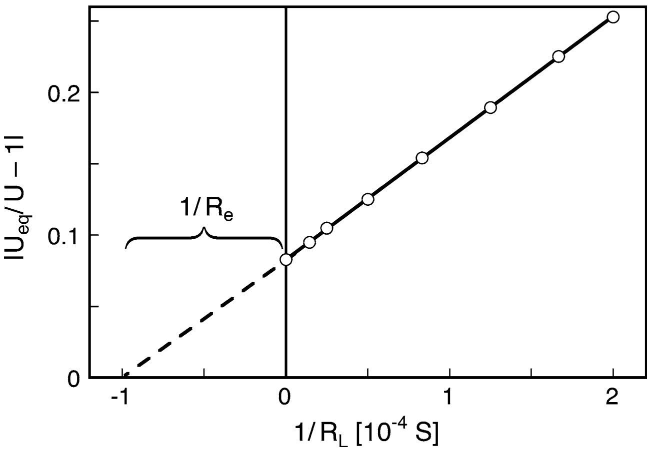

Fig. 2 Plot of the quantity $U_{\mathrm{eq}}/U-1$ vs. $1/R_{\mathrm{L}}$ according to Eq. 18 (example taken from [8])

To answer the question as to whether this approach indeed enables to extend the potential of the method of short-circuiting beyond the determination of the ionic conductivity, one has to consider the way of generating the $U_{\mathrm{eq}}/U-1$ vs. $1/R_{\mathrm{L}}$ plots and the procedure of data evaluation towards the determination of $1/R_{\mathrm{e}}$.

The following relationships are to help elaborating this matter. For an arbitrary load of the cell ($\kappa \geq 1$), the substitution of Eqs. 5, 8 and 9 into 3 provides:

$$I_{\mathrm{e}} . \frac{d_{\mathrm{SE}}}{\sigma_{\mathrm{i}} A_{\mathrm{SE}}} = \kappa U - U_{\mathrm{eq}} + \eta \tag{20}$$

With the definition of the medium ionic transference number t_{i}:

$$t_{\mathrm{i}} = \frac{1}{1 + (d_{\mathrm{SE}}/\sigma_{\mathrm{i}} A_{\mathrm{SE}} . R_{\mathrm{e}})} \tag{21}$$

and by taking into consideration Eqs. 6 and 19, one obtains from Eq. 20:

$$t_{\mathrm{i}} = \frac{U}{U_{\mathrm{eq}}} . \frac{1}{1 - \left(\eta/U_{\mathrm{eq}}\right) - \left(U/U_{\mathrm{eq}}\right).(\kappa - 1)} \tag{22}$$

Equation 22 relates the medium ionic transference number, and thus the extent of the electronic conductivity of the electrolyte, to the voltage of the cell comprising this electrolyte and the corresponding equilibrium cell voltage. It becomes obvious that in the open circuit case, i.e. $\kappa = 1$, and under the ideal condition of negligible electrode polarization, i.e. $\eta = 0$, the ionic transference number is equal to the ratio between U and U_{eq}. This is in accordance with the message of the Wagner equation. It must be kept in mind that the condition $\eta \to 0$ necessarily requires $R_{\eta \to 0}$ since I_{i} remains finite under the circumstances described above. Therefore in practice, if R_η is finite, the difference between the true t_{i} and the value taken for t_{i} by measuring U ($\kappa = 1$) and U_{eq} might become noticeable. In view of Eq. 22, this difference further increases by loading the cell, i.e. with rising κ up to values larger than 1. As a consequence, the total polarization current I_{i} increases (cf. Eq. 4) and so does η (cf. Eq. 16). The conclusion of these considerations is: The ionic transference number has to be determined by open circuit cell voltage measurements ($\kappa = 1$) with ideal electrodes, i.e. $R_{\eta \to 0}$, and this voltage has to be compared with the voltage U_{eq} of the same cell in which any electronic transference is definitely excluded. There are other approaches that yield the same information even without knowing the equilibrium cell voltage U_{eq} (cf. [9]), however, this is not supposed to be discussed here.

The aforementioned conclusion about avoiding any load of the cell in addition to the load that inevitably exists due to the internal electronic conduction of the electrolyte is in total contrast to the approach propagated in [5, 8]. Not only this discredits the claim of the authors of [5, 8] but first of all the fact that the procedure of generating the $U_{eq}/U{-}1$ versus $1/R_L$ plot needs, as a prerequisite, the knowledge of that quantity that after all is supposed to be obtained from the data evaluation, viz. the ratio between U and U_{eq} and thus the medium ionic transference number. Therefore, the approach described in [5, 8] is based on fallacy and, strictly, is not at all practicable. Any useful information about the extent of the electronic conductivity exclusively comes from an open-circuit measurement of the voltage but not from the procedure of short-circuiting. The measurement of U (κ) under load only enables the ionic conductivity of the electrolyte to be determined as described in the previous paragraph. Upon combining the information about the ionic conductivity with that about the ionic transference number provides R_e.

Summary

The method of short-circuiting a solid electrolyte galvanic cell provides the ionic conductivity of the electrolyte if the contribution of electrode polarization can be separated from the total polarization effect or is negligible. The latter condition is better fulfilled as the extent of load is as little as possible, i.e. upon partial short-circuiting. There is no other potential involved in this technique which aims at the characterization of the conduction properties of the electrolyte and goes beyond the information about the ionic conductivity.

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