The influence of absorption current on the results of measuring the ionic conductivity of the LiPON solid electrolyte

© A.S. Rudy [1], A.V. Novozhilova [2]

[1] Demidov State University, Yaroslavl, Russia
[2] Russian Peoples' Friendship University, Moscow, Russia
E-mail: rudy@uniyar.ac.ru

An alternative interpretation of the impedance spectra of the LiPON solid electrolyte is proposed. It is suggested that the experimental value of conductivity is due to the absorption and displacement current, while the drift current is mainly shielded by the electrical double layer. The impedance of an alternative LiPON equivalent circuit containing a non-ideal absorption element is calculated. It is shown that the Bode diagrams of the alternative equivalent circuit well approximate the experimental curves, and the conductivity values are consistent with theoretical data and calculations based on the concentration and mobility of lithium ions.

Keywords: LiPON, impedance spectroscopy, electrical double layer, absorption element, displacement current.

Solid-state thin-film lithium-ion batteries are relatively new and promising chemical energy sources. The solid electrolyte used in such batteries is lithium phosphorus oxynitride (LiPON), which was developed in the mid-1990s by the group led by J. Bates from the Oak Ridge National Laboratory (ORNL). The most important characteristics of LiPON were detailed by Bates et al. in [1–7]. Specifically, conductivity $\sigma = 2.3 \cdot 10^{-6}$ S $\cdot$ cm^{-1} was reported in the very first publication [1]. These results were verified in later studies of Bates et al. and experimental [8–15] and theoretical [16] research performed by other groups. In all cases, conductivity was understood as drift conductivity, which characterizes the ability of the electrolyte to transport lithium ions. It is demonstrated below that, for a number of reasons, the obtained conductivity values should be ascribed to the displacement current.

Figure 1, a shows the structural model of LiPON, which was used in [5] to approximate Bode diagrams and was reproduced in general in other studies. Active resistances of the electrolyte and the reaction layer are denoted in this figure as R_{el} and R_r. Elements Z_{el}, Z_r, and Z_i model the impedance of the electrolyte, the reaction layer, and Pt—LiPON—Pt interfaces, respectively. Symbol Z was used in [5] to denote constant phase elements (CPEs): $Z = A(j\omega)^{-\alpha}$, where A is a constant, ω is the cyclic frequency, and α is the nonideality factor. Elements R_r and Z_r, which characterize the reaction layer, are relevant only at a bias voltages upward of 5 V and, consequently, are excluded from further analysis.

This diagram and other simplified structural models or equivalent circuits [1–15] have two major drawbacks. First, they contradict the laws of electrodynamics of continuous media, since they take into account neither the absorption current nor the displacement current. Since LiPON has a high ionic relaxation polarizability [17,18], the contribution of the absorption current to conductivity should be at least comparable to the drift current. Second, the mentioned models do not feature an electrical double layer (EDL). It may be assumed that the LiPON−metal interface (in [5], this is CPE Z_i with capacitance $C_i = 0.77\,\mu$F) acts as such a layer, but the nature of this capacitance is beyond the scope of the cited works.

The shortcomings of [5,8–15] may be rectified if we assume that the current through the electrolyte is the absorption and displacement current and ImZ_i is the EDL capacitance. The presence of an EDL implies that the alternating electric field in the internal electrolyte layer is weakened by $\varepsilon(\omega)$ and the potential difference is $U_0 e^{j\omega t}/\varepsilon(\omega)$. Accordingly, the experimental (apparent) value of ohmic resistance $R = U_0/I_0$ and its internal resistance R_{int} are related as $R = \varepsilon(0)R_{int}$. Here, $\varepsilon(\omega)$ is replaced by $\varepsilon(0)$, since the active resistance does not depend on frequency.

All these assumptions are reflected in the alternative equivalent circuit shown in Fig. 1, b. Absorption element A in Fig. 1, b models the absorption and displacement currents. Its impedance is given by
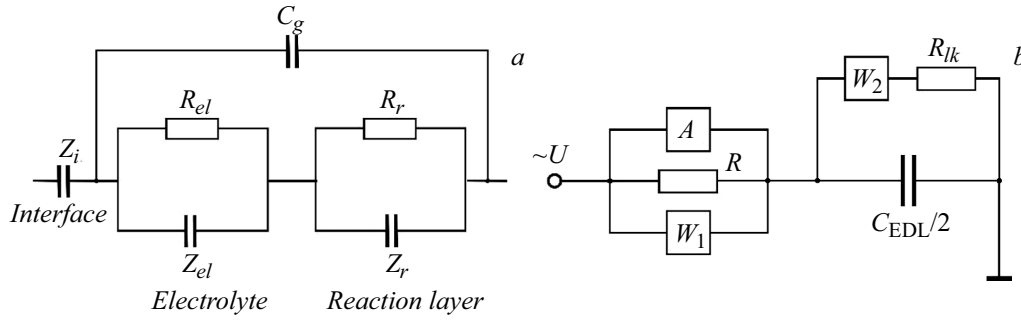
$$Z_A = \frac{\delta}{j\omega S \varepsilon_0 \varepsilon(\omega)}, \qquad (1)$$

where δ is the EDL thickness, ω is the cyclic frequency, and j is the imaginary unit.

The Cole−Cole model [18]

$$\varepsilon(\omega) = \frac{\varepsilon(0) - \varepsilon_\infty}{1 + (j\omega\tau)^\beta} + \varepsilon_\infty, \qquad (2)$$

which is more versatile in nature than the Debye one (it provides an opportunity to approximate oscillations of both relaxation and resonance types), is used to approximate the

Figure 1. *a* — Equivalent circuit of the Pt—LiPON—Pt test structure. R_{el} and R_r — active resistances of the electrolyte and the reaction layer, Z_{el} and Z_r — constant phase elements, Z_i — Pt—LiPON—Pt interface impedance, and C_g — „geometric capacitance" of the test structure [5]. *b* — Alternative equivalent circuit. *A* — is an absorption element, $R = \varepsilon(0)R_{int}$ is the „apparent" ohmic resistance of the electrolyte, and W_1 is a Warburg element. Elements W_2 and R_{lk} model the leakage current circuit.
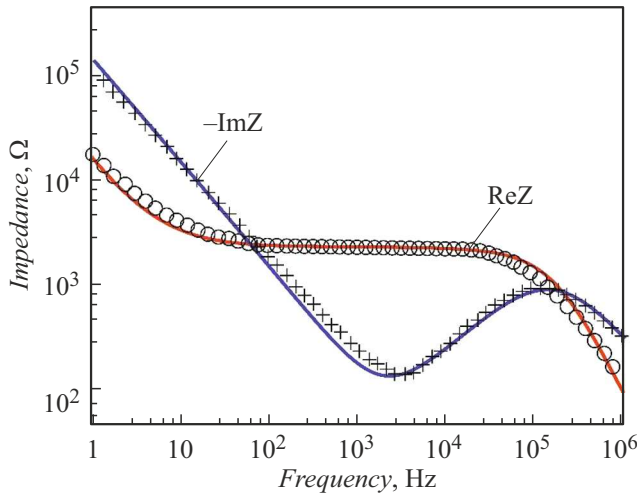
Figure 2. Bode diagrams (lines) for the equivalent circuit shown in Fig. 1, *b* and the following parameter values: $\tau = 0.017$ s, $\beta = 1.015$, $C_{EDL} = 9.7 \cdot 10^{-5}$ F, $R = 5 \cdot 10^8 \Omega$, $\rho = 3.5 \cdot 10^{-4}$, $A_{W1} = 1.5 \cdot 10^6 \, \Omega \cdot s^{-1/2}$; $A_A = 1.31 \cdot 10^5 \, \Omega \cdot s^{-1}$. The diagrams from [5] are denoted by crosses and circles. Parameters R_{lk} and A_{W2} are undefined, since they are affected only by the low-frequency parts of diagrams, which are lacking in [5].

permittivity. Here, τ is the oscillation damping constant and β is the nonideality factor related to the corresponding parameter from [18] as $\beta = 1 - \alpha$. Inserting (2) into (1), one finds the real and imaginary parts of impedance of the sorption element

$$\text{Re}Z_A = \frac{A_A}{\omega} \frac{(1-\rho)(\omega\tau)^\beta \sin\left(\beta\frac{\pi}{2}\right)}{1 + 2\rho(\omega\tau)^\beta \cos\left(\beta\frac{\pi}{2}\right) + \rho^2(\omega\tau)^{2\beta}},$$

$$\text{Im}Z_A = -\frac{A_A}{\omega} \frac{1 + \rho(\omega\tau)^{2\beta} + (1+\rho)(\omega\tau)^\beta \cos\left(\beta\frac{\pi}{2}\right)}{1 + 2\rho(\omega\tau)^\beta \cos\left(\beta\frac{\pi}{2}\right) + \rho^2(\omega\tau)^{2\beta}},$$

$$(3)$$

where $\rho = \varepsilon_\infty/\varepsilon(0)$, $A_A = \delta/S\varepsilon_0\varepsilon(0)$. The Bode diagrams for the equivalent circuit shown in Fig. 1, *b* are presented in Fig. 2 together with the diagrams from [5].

The equivalent circuit in Fig. 1, *b* allows one to generate not only the diagrams in Fig. 2, but also any Bode or Nyquist diagram from [8–15]. The fitting parameters will have different values in this case. Specifically, capacitance C_{EDL} increases from $0.77 \, \mu$F [5] to $97 \, \mu$F, which agrees well with the results of direct measurements [19]. If L is the distance between the centers of mass of the potential-determining charge and the charge of counterions, the EDL capacitance may be calculated as $C_{EDL} = \varepsilon_0 \varepsilon_{els} S/L$, where ε_{els} — permittivity governed by elastic ionic polarization. Calculations yield the value of $L = 0.69\lambda_D$, where $\lambda_D = 1.2 \cdot 10^{-11}\sqrt{\varepsilon_{els}}$ [m] is the Debye screening length with the corresponding EDL capacitance taking the form of $C_{EDL} = 4.3 \cdot 10^{-6}\sqrt{\varepsilon_{els}}$ [F]. This value matches the fitting parameter at $\varepsilon_{eds} = 1.5 \cdot 10^3$, which is quite close to the value of $\varepsilon_{els} = 4.4 \cdot 10^3$ obtained in [17].

In order to evaluate the conductivity of LiPON, we determine $\varepsilon(0) = 1.37 \cdot 10^6$ from relation $C_{EDL}/2 = \varepsilon_0\varepsilon(0)S/d$, where $S = 4 \cdot 10^{-6}$ m and $d = 10^{-6}$ m, and internal resistance $R_{int} = 3.65 \cdot 10^2 \, \Omega$ and conductivity $\sigma_{int} = 6.5 \cdot 10^{-6} \, S \cdot cm^{-1}$ from relation $R_{int} = R/\varepsilon(0)$. This conductivity value may only be compared with theoretical results or the results of calculations based on the data on concentration and mobility of lithium ions. The conductivity calculated for diffusion coefficient $D = 1.5 \cdot 10^{-11} \, cm^2 \cdot s^{-1}$ [20] and concentration $c = 7.5 \cdot 10^{22} \, cm^{-3}$, which was given in [16] for ratio Li/P = 3.0, is $\sigma_{int} = 7.0 \cdot 10^{-6} \, S \cdot cm^{-1}$, which is fairly close to the above value.

Fitting parameter $\text{Re}Z_A$, which characterizes dielectric losses, does not exceed $\text{Re}Z_A = 2.6 \cdot 10^3 \, \Omega$, and the corresponding minimum conductivity value $\sigma_A = 9.6 \cdot 10^{-7} \, S \cdot cm^{-1}$ is quite close to the drift conductivity. The similarity of these values is attributable to the fact that the mechanisms of dielectric losses in the EDL and Joule losses in the bulk are the same. In essence, both absorption and drift currents are forced relaxation
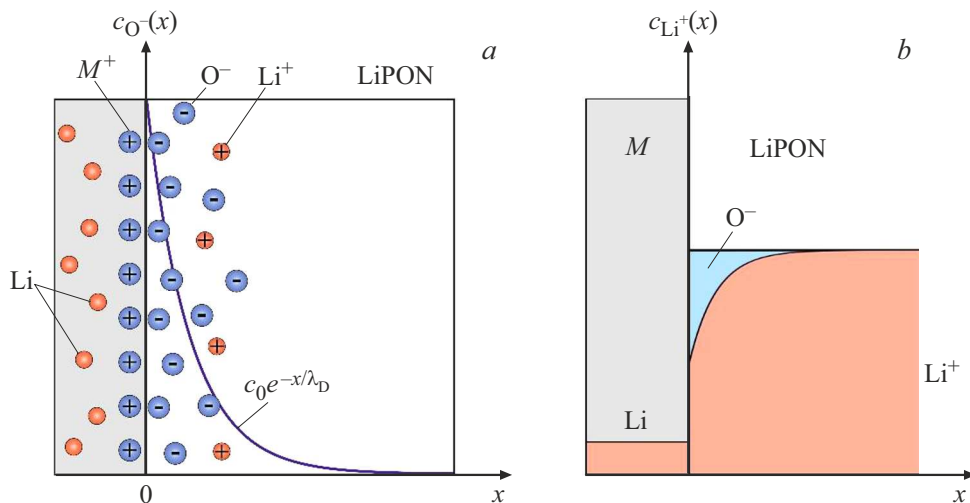
Figure 3. *a* — Qualitative model of the electrical double layer at the LiPON−metal interface. M^+ — potential-determining metal ions; O^- — cation vacancies (counterions). *b* — Lithium concentration distribution in the EDL region. The diffuse layer formed by cation vacancies is shown in blue. A color version of the figure is provided in the online version of the paper.

oscillations of lithium ions. The only difference is that they polarize the electrolyte strongly in the EDL and insignificantly in the bulk. Therefore, the replacement of one structural element of the equivalent circuit with another $(A \rightleftarrows R_{int})$ does not result in any significant discrepancy with theoretical predictions.

The concept of EDL was used above in the derivation of certain relations, but its nature was not discussed. The EDL hypothesis itself is based on the fact that lithium penetrates to the surface through any metal electrodes (platinum ones included). Products of interaction of lithium with the atmosphere then form on the surface in the shape of protuberances [21] or flower-like features [11]. The starting point for construction of the EDL model is the assumption that the transition of lithium ions into metal proceeds as a result of diffusion and is accompanied by their reduction with the formation of metal ions localized at the interface (Fig. 3). These ions and cation vacancies, which are bound by the Coulomb interaction, form an EDL. Metal ions act as potential-determining ions, and cation vacancies are counterions. Since the configuration of a layer of immobile cation vacancies is governed by the diffusion and drift of lithium ions, the concept of a „diffuse layer" is applicable here. In essence, the EDL is a space charge region; however, it is more convenient in this context to regard it as an electrical double layer.

Thus, the following facts support the hypotheses of absorption conductivity of the solid LiPON electrolyte in an alternating electric field and the electrical double layer. Bode diagrams plotted based on the alternative equivalent circuit with an absorption element and an apparent resistance reproduce in detail the experimental impedance spectra that were obtained earlier. The hypothesis resolves the obvious contradiction between the high polarizability of LiPON and the lack of absorption current in the equivalent circuit. The

electrical double layer hypothesis allows one to interrelate the apparent and intrinsic resistances of LiPON.

Conflict of interest

The authors declare that they have no conflict of interest.

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