Modeling of polarization relaxation of solid electrolyte LiPON in the low temperatures range

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Abstract. The paper presents the results of studying the polarization relaxation mechanism in solid electrolyte LiPON by the method of discharge through an external load. Test cells made in the form of encapsulated multilayer structures SiO₂/Pt/LiPON/Pt/Ti/SiO₂/Si were tested on a stand for discharge characteristics measuring. To explain the discharge curves, an equivalent LiPON circuit and a mathematical model of polarization relaxation during discharge are proposed. By fitting the parameters of a mathematical model, the Maxwellian relaxation times of lithium ions and that of the LiPON ionic polarization relaxation are determined.

1. Introduction

In modern portable electronic devices such as smartphones, smart cards, RFID tags, wrist gadgets, transdermal patches, implants, etc. solid-state thin-film lithium-ion batteries (SSLIBs) are used. The solid electrolyte in most electrochemical systems is lithium phosphorus oxynitride (LiPON). Obtained more than 20 years ago at the Oak Ridge National Laboratory [1, 2], this material is still in demand due to its relatively high ionic conductivity (2×10⁻⁶ S/cm at 25°C), a low electron transfer number (ν ≤ 10⁻⁵), and a rather wide potential window (0 - 5.5 V). However, with a decrease in temperature, the conductivity of LiPON, which is two to three orders of magnitude lower than the conductivity of liquid electrolytes, rapidly decreases. This is because the main charge carriers in LiPON are lithium ions, as can be seen from the transfer number. Their generation is of an activation nature [3], and the mechanism of charge transfer at room temperatures is diffusion-drift, therefore the conductivity of LiPON strongly depends on the temperature and electrolyte structure. With decreasing temperature, the density of localized states of lithium ions increases and the concentration of delocalized carriers decreases so much that transitions between localized states begin to play the main role in the charge transfer. The conductivity due to such transitions is referred to as hopping.

Thus, lowering the temperature changes the ratio of the concentrations of free (delocalized), localized and bound charge carriers. In turn, this changes the ratio of the components of the transfer current, which is clearly manifested in the dynamics of relaxation of the LiPON polarization. Since the characteristic relaxation times of ionic polarization and polarization due to diffusion-drift and hopping conductivities differ by orders of magnitude, this is clearly manifested in the discharge curves. A description of the method for obtaining discharge curves in the temperature range from ~50°C to...
25°C and the results of their interpretation and approximation within the framework of the proposed mathematical model are presented below.

2. Experimental
Test structures \( \text{SiO}_2 / \text{Pt} / \text{LiPON} / \text{Pt} / \text{Ti} / \text{SiO}_2 / \text{Si} \) (further \( \text{Pt} / \text{LiPON} / \text{Pt} \)) were deposited using magnetron sputtering technique, described in [4]. The thickness of the LiPON layer was 1 μm, and the area under the platinum contacts was \( 8 \times 8 \text{ mm}^2 \). The ionic conductivity of the test structure \( \text{Pt} / \text{LiPON} / \text{Pt} \) was investigated by the method of discharge through precision resistors of different ratings at different temperatures. The measurements were carried out on a stand, the schematic of which is shown in Figure 1 and were performed in two stages. At the first stage, the structure under study was charged through a resistor \( R_0 = 0.1 \text{MOm} \) from a voltage source stabilized over a wide range of loads with an output voltage of 1.18 V. During charging, the dependence \( U(t) \) (Figure 2) was recorded using an OWON PDS8202T oscilloscope, the maximum sampling value of which in real time is 2 GHz.

![Figure 1. Schematic of the stand for investigating the discharge characteristics of test structures Pt/LiPON/Pt.](image)

In the process of charging the test structure (Figure 2), the voltage across the platinum plates tends to the limiting value. This is below the voltage 1.07 V that is expected at the node of \( U_C(t) \rightarrow 1.02 \text{ V} \) voltage divider formed by the resistor \( R_0 \) and input resistor \( R_{\text{osc}} \) of the oscilloscope in the absence of leaks. This means that a Faraday process takes place on the electrodes, as a result of which the concentration of neutral lithium in the cathode region increases. This leads to diffusion of lithium into the anode region, where oxidation (ionization) of lithium occurs, after which, the ions again drift in an electric field towards the cathode and the process is repeated (Figure 3). In the equivalent circuit in Figure 1, the leakage current circuit is depicted as a loop formed by the resistor \( R_{\text{lk}} \) and the diffusion element \( D_f \). Simple calculations reveal that the leakage amperage is \( 0.58 \times 10^{-6} \text{ A} \), while the equivalent leakage resistance makes 1.76 MΩ.
Figure 2. Time dependence of voltage on the Pt/LiPON/Pt structure in the charging mode in the temperature range from $-50^\circ$C to $25^\circ$C.

At the second stage of measurements, using transistor switches $S_1-S_3$, the plates of the Pt/LiPON/Pt structure were switched to a precision resistor $R_{ld}$, and the voltage drop $U_C(t)$ across the load was recorded. The time of synchronous operation of the switches was no more than 50 ns. The measurements were carried out at different load ratings in the temperature range $-50^\circ$C to $25^\circ$C. The discharge curves are shown in Figure 4.

Figure 3. Diagram of the leakage current arising during the charging of the Pt/LiPON/Pt structure.

Figure 4. Time dependences of the voltage at the contacts of the structure Pt/LiPON/Pt during discharge through a load resistor of 10 k$\Omega$ at different temperatures.
3. Discharge mathematical model
During the discharge, the processes of relaxation of free (external), localized and bound charges concentration take place in the electrolyte. Earlier, when deriving a model of the discharge [4], the current of bound charges was not taken into consideration, since at room temperatures, its value is negligible compared to the current of free charges. At a temperature of about -20°C, these currents become comparable, and at a temperature of -50°C, the free charge current decreases to the noise level. Therefore, in the model below, the displacement current is considered instead of the transfer current, as in the work [4].

The displacement current can be expressed in terms of the charge of the electric double layer as

$$I_D = \frac{d}{dt} \left( Q + Q' \right),$$

where $I_D$ is the displacement current, $Q$ is the free charge of the double electric layer (EDL), $Q'$ is the bound charge of the EDL. The rate of the bound charge alteration in equation (1) in the relaxation time approximation can be represented in the form $\frac{dQ'}{dt} = -Q' / \tau_p$, where $\tau_p$ is the polarization relaxation time. In turn, the rate of the EDL free charge alteration is contributed by the sum of internal drift and diffusion currents $I_{in}$, the leakage current $I_{lk} = -Q / \tau_F$, the rate of volume recombination $-Q / \tau_V$, and the rate of generation of lithium ions $G$

$$\frac{dQ}{dt} = I_{in} - \frac{Q}{\tau} + G,$$

where $\tau = \tau_V \tau_F / (\tau_V + \tau_F)$. Taking into account equation (2), equation (1) transforms into the expression

$$I_D = I_{in} + G - \frac{Q}{\tau} - \frac{Q'}{\tau_p},$$

from which the current of free electrolyte ions can be expressed as

$$I_{in} = I_D - G + \frac{Q}{\tau} + \frac{Q'}{\tau_p}.$$

Kirchhoff's second rule, as applied to the circuit shown in Fig. 1, gives a second independent relationship between currents and charges

$$I_D R_{ld} + I_{in} R_{tr} + 2 \frac{Q + Q'}{C_{dl}} = 0,$$

allowing elimination of unknown current $I_{in}$

$$I_D \left( 1 + \frac{R_{ld}}{R_{tr}} \right) + \frac{Q}{\tau} + \frac{Q'}{\tau_p} - G + 2 \frac{Q + Q'}{R_{tr} C_{dl}} = 0.$$

Replacing the displacement current in equation (6) by equation (1) after separation of variables gives two differential equations for free and bound charges

$$\frac{dQ}{dt} \left( 1 + \rho \right) + \frac{Q}{\tau_1} - G = 0,$$

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\[
\frac{dQ'}{dt} (1 + \rho) + \frac{Q'}{\tau_2} = 0, \tag{8}
\]

where \(\tau_1 = \tau_{RC} \tau / (\tau_{RC} + \tau)\), \(\tau_2 = \tau_{RC} \tau_p / (\tau_{RC} + \tau_p)\), \(\tau_{RC} = R_{RC} C_{dl} / 2\), \(\rho = R_{ld} / R_{tr}\). Obviously, the solutions to the equations (7), (8) must satisfy the following initial conditions

\[
Q(0) + Q'(0) = Q_0, \tag{9}
\]

\[-I_D(0) R_{ld} = U_0. \tag{10}\]

The solutions of the equations (7), (8) have the form

\[
Q = \tau_1 G + C_1 \exp\left(-\frac{t}{(1 + \rho)\tau_1}\right), \tag{11}
\]

\[
Q' = C_2 \exp\left(-\frac{t}{(1 + \rho)\tau_2}\right), \tag{12}
\]

where \(C_1\) and \(C_2\) are integration constants, which are determined from the initial conditions (9), (10). Then the solutions take their final form

\[
I = -\left(\frac{\tau_1 G - Q_0}{1 + \rho} + \frac{U_0 \tau_2}{R_{ld}}\right) \frac{1}{\tau_1 - \tau_2} \exp\left(-\frac{t}{(1 + \rho)\tau_1}\right) \tag{13}
\]

\[
I' = \left(\frac{Q_0 - \tau_1 G}{1 + \rho} - \frac{U_0 \tau_2}{R_{ld}}\right) \frac{1}{\tau_2 - \tau_1} \exp\left(-\frac{t}{(1 + \rho)\tau_2}\right). \tag{14}
\]

The total displacement current will be the sum of the currents (13), (14), thus the time dependence of the voltage drop across the external load will be described as follows

\[
U(t) = I(t) R_{ld} + I'(t) R_{ld} = -\left(\frac{\tau_1 G - Q_0}{1 + \rho} + \frac{U_0 \tau_2}{R_{ld}}\right) \frac{R_{ld}}{\tau_2 - \tau_1} \exp\left(-\frac{t}{(1 + \rho)\tau_1}\right)
+ \left(\frac{\tau_1 G - Q_0}{1 + \rho} + \frac{U_0 \tau_1}{R_{ld}}\right) \frac{R_{ld}}{\tau_2 - \tau_1} \exp\left(-\frac{t}{(1 + \rho)\tau_2}\right). \tag{15}
\]

Figure 5 shows the experimental and theoretical time dependences of the voltage drop across the resistor \(R_{ld} = 10 \, \text{k}\Omega\) during the Pt/LiPON/Pt test structure discharge.

**Figure 5.** Experimental (solid lines) and theoretical (dashed lines) dependences of the voltage drop across the resistor \(R_{ld} = 10 \, \text{k}\Omega\) during Pt/LiPON/Pt discharge.
The calculations were performed for the following model parameters: \[ \tau = 0.053 \text{ s} \]; \[ G = 0.128 \text{ C} \cdot \text{s}^{-1} \]; \[ C = 9 \cdot 10^{-4} \text{ F} \]; \[ Q_0 = 6 \cdot 10^{-3} \text{ C} \]; \[ R_{tr} = 400 \text{ \Omega} \]; \[ R_{ld} = 10 \text{ k\Omega} \]. Curve 1: \[ t = -22^\circ\text{C}, \quad \tau_p = 4 \cdot 10^{-5} \text{ s} \]. Curve 2: \[ t = -34^\circ\text{C}, \quad \tau_p = 4 \cdot 10^{-7} \text{ s} \].

4. Conclusion

The proposed model for the relaxation of the solid electrolyte LiPON polarization at low temperatures explains the main feature of the experimental curves, such as an abrupt drop in the discharge current over a relatively short period of time and a subsequent monotonic decrease in the current. Within the framework of the proposed model, this behavior of the discharge current is explained by the contribution of the polarization current, which at low temperatures is comparable to the free charges current. Judging by the experimental curves, there is one more polarization mechanism with a relaxation time \[ \tau_{hc} > \tau_p \], which is due to localized ions. This is indicated by a smooth decline in the initial section of the discharge curve at a temperature of -22°C. This mechanism contribution to polarization is intermediate between free and bound charges. Obviously, with decreasing temperature, the contribution of the hopping conductivity to polarization decreases, as indicated by a \[ \tau_p \] decrease by two orders of magnitude. It is essential that with temperature decreasing the other model parameters do not undergo any changes.

It should be emphasized that the proposed polarization relaxation model is intended to explain the features of the experimental curves. In this case, the goal of precise approximation of these dependences is not pursued, thus the model itself is as simplified as possible. For instance, all the parameters of the model are assumed to be lumped, only two mechanisms of polarization relaxation are considered, and nonlinear effects, which are inevitable in such a strongly nonequilibrium system, are not taken into consideration. Though, all these refinements can be introduced into the model as the experimental material accumulates.

5. References

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