**Electrochemical Properties of Composition Solid Electrolytes LiClO$_4$–MgO**

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**INTRODUCTION**

Composite solid electrolytes such as Li$_x$X–A, where X is anion and A is oxide, are known to exhibit high ionic conductivity [1–3]. Among them, the most thoroughly studied composites are Li$_x$–Al$_2$O$_3$ (X = Cl, Br, I) with the properties described in [1–4]. Earlier, new composition conductors LiClO$_4$–γ(α)-Al$_2$O$_3$ and LiClO$_4$–γ(α)-LiAlO$_2$ that exhibited high lithium conductivity, ~10$^{-2}$ S/cm at 200°C in vacuum were studied, and they were characterized by a high voltage of electrochemical decomposition (not lower than 4–4.5 V) [5, 6]. It was shown that the conductivity is determined not only by the specific surface area of the oxide but also by its crystal structure. Depending on the crystal structure type, the activation energy of conduction varies, which is explained by the different nature of adsorption sites on the oxide surface that exhibit activity in the reaction of lithium cations with the oxide surface by the Maier mechanism [7]. For simplicity sake, the mechanism of cation adsorption can be considered as a donor-acceptor interaction between a Lewis acid (lithium cation Li$^+$) and a basic site (ions O$^{2-}$ or OH$^-$) on the oxide surface. This is why an increase in the oxide basicity should lead to strengthening of surface interactions and, hence, to an increase in the ionic conductivity.

In this study, lithium perchlorate-based composition solid electrolytes containing heterogeneous additions of magnesium oxide were synthesized for the first time.

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**Abstract**—Composition solid electrolytes (1 – x)LiClO$_4$–xMgO are synthesized and their physicochemical properties are studied. According to the data of differential scanning calorimetry, for sufficiently high oxide concentrations, all lithium perchlorate is present in the composite in the amorphous state. Impedance spectroscopic studies demonstrate that the conductivity of composites passes through a maximum at x = 0.8–0.9, reaching ~10$^{-2}$ S/cm at 200°C. Based on voltammetric characteristics, it is shown that the voltage of electrochemical decomposition of composites in vacuum does not exceed 3.5–4.0 V, decreasing to 1.8–2.0 V in humid atmosphere. The conductivity of studied composites in vacuum may apparently be attributed to lithium ions, and these solid electrolytes can be used in solid-state electrochemical lithium cells.

**Key words:** composites, solid electrolytes, LiClO$_4$, ionic conductivity

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The latter oxide was chosen because it exhibits the higher basicity as compared with Al$_2$O$_3$ and LiAlO$_2$ [8]. The thermal analysis data are shown and also the transport and electrochemical properties of composites as a function of the specific surface of the added oxide.

**EXPERIMENTAL**

The synthesis of LiClO$_4$-based composition electrolytes involves the use nanocrystalline magnesium oxides MgO with the specific surface ($S_{sp}$ = 209 m$^2$/g). Lithium perchlorate was synthesized by neutralization of an aqueous solution of 1 M perchloric acid (HClO$_4$, special grade of purity) with 1 M lithium carbonate (Li$_2$CO$_3$, reagent grade) solution at 80°C. Lithium perchlorate trihydrate LiClO$_4$·3H$_2$O was deposited at the solution temperature of 10°C and analyzed by the powder diffraction method. The powder diffraction pattern corresponded to lithium perchlorate (JSTM 70–883).

The studied samples were synthesized by the ceramic method. Lithium perchlorate dehydrated at 300°C was thoroughly mixed with the oxide additive. Magnesium oxide was preliminarily heated at 400°C for 2 h for surface dehydration. The resulting mixtures were sintered at 300°C for 30 min and quickly cooled. Then, under a pressure of 400 MPa, pellets with aluminum electrodes were molded to be used in the conductivity measurements. Conductivity was recorded in a two-electrode cell in vacuum (5 × 10$^{-2}$ Torr) in the temperature range from 20 to 200°C, under alternating current conditions, using a precision recorder of electric parameters Hewlett Packard HP 4284A in the fre-
frequency range from 20 Hz to 1 MHz. The conductivity values were calculated from the frequency dependences of conductance measured by the impedance method. Voltammetric characteristics were recorded using a RA2 polarograph in the voltage range of 0–5 V with the scan rate of 10 mV/s, the current values were measured and transmitted to a computer by an APPA 107 multimeter.

RESULTS AND DISCUSSION

Figure 1 shows the results of differential thermal analysis (DTA) of lithium perchlorate and the \( (1 - \chi)\text{LiClO}_4 - \chi\text{MgO} \) for \( \chi = 0.2, 0.4, 0.6, \) and 0.8, respectively, synthesized on heating at a rate of 10 deg/min.

![Fig. 1. DTA curves for pure LiClO\(_4\) (1) and (2, 3, 4, and 5) its composites \((1 - \chi)\text{LiClO}_4 - \chi\text{MgO}\) for \(\chi = 0.2, 0.4, 0.6, \) and 0.8, respectively, synthesized on heating at a rate of 10 deg/min.](image)

A. The melting point changed, which was attributed to the size effect [9] and pointed to the substantial decrease in the size of \text{LiClO}_4 crystals in composites with the increase in \(\chi\), namely, at \(\chi > 0.2\), the ionic salt on the MgO surface is in the nanocrystalline state.

B. The enthalpy of melting of lithium perchlorate (\text{LiClO}_4) in composites decreased. This effect is probably due to the amorphization of the ionic salt in the interface region. Similar effects were observed earlier in the following composites: AgI–\text{Al}_2\text{O}_3 [10, 11], RbNO_3–\text{Al}_2\text{O}_3 [12], CsHSO_4–\text{SiO}_2 [13], and other [14].

C. An additional peak appeared at 140–150°C, which was associated with incongruent melting of admixtures of the hydrate phases \text{LiClO}_4·\text{nH}_2\text{O} formed as a result of partial hydration of anhydrous lithium perchlorate in air.

Figure 2 shows the dependences of the specific conductivity of composites on the temperature and the oxide concentration at \(T = 200^\circ\text{C}\). The conductivity of pure anhydrous \text{LiClO}_4 did not exceed \(10^{-5}\) S/cm at \(200^\circ\text{C}\) and sharply increased with its doping with oxide. The conductivity values were well reproducible in the “heating–cooling” cycles and stable at long-term exposure in vacuum under isothermal conditions. This fact provides grounds to assume that the conductivity of studied composites was associated with neither metastable defects, nor the contribution of surface conductivity, nor the effect of adsorbed water. The maximum conductivity is typical of composition electrolytes \((1 - \chi)\text{LiClO}_4 - \chi\text{MgO} \) with \(\chi = 0.8–0.9\) (Fig. 2b), which corresponds to the bulk oxide concentration of 40–50%. The analogous relationship is typical of composition solid electrolytes and is explained by the fact that the conduction is realized along \text{LiClO}_4/oxide interfaces. As

![Fig. 2. (a) Temperature dependences of conductivity of \((1 - \chi)\text{LiClO}_4 - \chi\text{MgO}\) composites for different magnesium oxide concentrations and (b) composite conductivity variations with the MgO concentration at \(200^\circ\text{C}\).](image)