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Influence of Nanodisperse Li_3N on the Electrochemical Properties of a Polymeric Electrolyte

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Abstract—Influence of additives fine-dispersed powder Li_3N on electrochemical properties polymer gel- electrolyte and its interface with metal Lithium is investigated. Lithium nitride was received by reaction of dry nitrogen with metal Lithium within 5 hours at 100°C, and then it was crushed on a spherical grinding mill in an inert atmosphere. The size of particles has made 100 nanometers. Dependence of an electrochemical impedance of polymer electrolyte on the added amount of fine-dispersed powder of Li_3N—0.5 w/w% and 1.0 w/w% was measured. It is found, that introduction 0.5 w/w% Li_3N improves volume conductivity of polymer electrolyte in 2.4 times, but further increase amount of Li_3N (1.0 w/w%) does not change this characteristic. On interface with metal Lithium, on the contrary, Li_3N—additive increases charge transfer resistance in 1.5 times that speaks about difficulty of electrochemical reaction $Li^+ + e \longleftrightarrow Li$ at presence Li_3N.

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A polymeric electrolyte is an important component of various electrochemical devices, such as electrochromic displays and electroluminescent devices, primarily, most promising lithium batteries. The substitution of a solid electrolyte for a solid polymeric one in lithium batteries expands their use from microelectronics to electrical engines.

Preparation of polymeric electrolytes having high electrochemical parameters is an important scientific task. To fulfill this task, in addition to varying polymeric matrices, the electrolyte composition is modified; that is, additives of various characters (organic or inorganic) and in various phase states (liquids or solids) are used for this purpose.

The conductivity of useful polymeric electrolytes should exceed 10^{-5} S/cm at room temperature. A concept proposed and developed in [1–6] is to add Al_2O_3, $LiAlO_2$, SiO_2, TiO_2 and other powders to improve the physicochemical properties of polymeric electrolytes. Krawiec et al. [6] modified a polyethylene oxide–based polymeric electrolyte by fine Al_2O_3 powders with particle sizes of 1 and 10^{-3} μm. Comparison of the influence of ceramic powders having various particle sizes (less than 10 μm and 10^{-2} μm nanoparticles) showed that the increase in conductivity induced by nanoparticles is more than one order of magnitude greater than the increase induced by 10 μm particles.

Our goal in this work is to study the influence of Li_3N on the physicochemical properties of a polyester diacrylate–based polymeric gel-electrolyte PGE [7].

Li_3N is a crystalline solid, which is unstable in air (lithium nitride rapidly reacts with water molecules to yield ammonia). Li_3N is one of the best known and most promising materials with high ionic conductivity, which amounts to 10^{-4} S/cm at 25°C [8].

In our prior work [9], we showed that the presence of lithium nitride on the surface of a lithium anode decreases the charge-transfer resistance at the lithium/polymeric electrolyte interface. Therefore, it is of interest to study this compound as an additive to a polymeric electrolyte and its influence on the electrochemical properties of the polymeric gel-electrolyte itself and its interface with lithium metal.

In this work, we prepared lithium nitride by reacting dry nitrogen with metallic lithium for 5 h at 100°C. X-ray powder diffraction analysis was carried out on an ARL X'TRA Thermo Electron instrument using $CuK_{\alpha 1}/K_{\alpha 2}$ radiation and a Peltier semiconductor detector in θ–θ geometry. The analysis of the received X-ray diagram has shown that the sample contains 93.7% Li_3N. Li_3N was ground on a Pulverizette ball mill Model 6 (Fritsch) under argon. The particle size was 100 nm.

Then, we prepared thin polymeric gel-electrolyte films based on 20 wt % polyester diacrylate [7] and a 1 M $LiClO_4$ solution in a propylene carbonate/γ-butyrolactone mixture (1 : 1 wt/wt) with 0.5 wt % or 1.0 wt % of a fine Li_3N powder added. Unlike the initial transparent films, the Li_3N-doped film was dark with inorganic filler inclusions.

Thus-prepared gel-electrolyte films were characterized by electrochemical impedance over the frequency range from 12 to 10^5 Hz at a measured signal amplitude of 10 mV with the use of an Elins Impedance meter Z-350 in symmetrical cells equipped with two lithium electrodes. All manipulations with lithium nitride and litium metal were performed in an argon-filled drybox. Impedance spectra time curves were processed according to the adsorption relaxation model of the double

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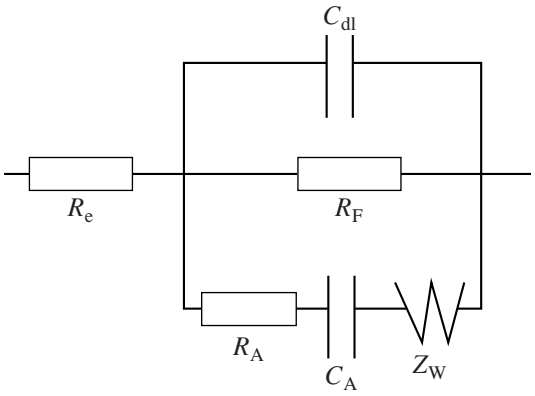

Fig. 1. Equivalent circuit of an electrochemical cell with reversible electrodes, where R_e is the volume resistance of the electrolyte, R_F is charge-transfer resistance, C_{dl} is the double-layer capacity, R_A is adsorption resistance, C_A is adsorption capacity, and Z_W is diffusion impedance.

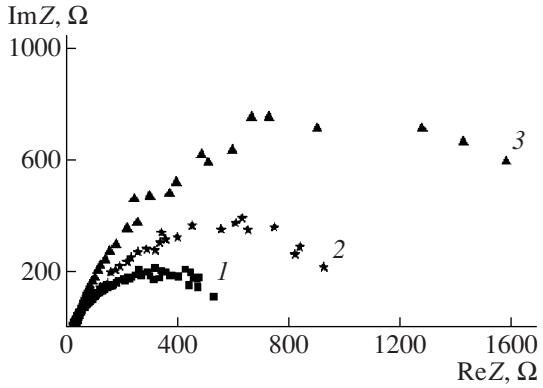

Fig. 2. Impedance spectra for a polymeric gel-electrolyte in an Li/PGE/Li symmetrical cell at room temperature (*1*) without lithium nitride additives, (*2*) with 0.5 wt % lithium nitride added, and (*3*) with 1.0 wt % lithium nitride added.

electric layer (Fig. 1), as proposed by Grafov and Ukshe [10]. The resulting impedance spectra are displayed in Fig. 2. The ZView2 software was used to calculate equivalent circuit parameters. In the start of calculations, R_e should be set (R_e is the volume resistance of the electrolyte, which can be derived from the measured impedance spectrum). The impedance spectrum in Fig. 2 is a semicircle. The origin of the semicircle lies on the ordinate axis (at high frequencies of 350 kHz) and is R_e. Then, with R_e fixed, the program calculates the other parameters of the equivalent circuit. After the first calculation, R_F is fixed; this is the charge-transfer resistance, which is determined with the least error. To refine the other parameters, R_e and R_F are fixed. By consecutively fixing these parameters, we find refined values for the other components of the equivalent circuit. The table summarizes the results of impedance calculations using the ZView2 program.

The table makes it clear that addition of 0.5 wt % fine Li_3N improves the volume conductivity of the polymeric electrolyte by a factor of 2.4; a further increase in Li_3N (1.0 wt %) does not change this parameter. A possible explanation is that small Li_3N percentages (0.5 wt %) facilitate lithium ion transport due to generating new track for Li^+ movement. The further increase in Li_3N percentage to 1 wt % nullifies this effect; that is, with the appearance of many new track for Li_3N transport, the excessive amount of nanosized particles interferes with lithium ion movement. Charge-transfer resistance at the polymeric gel-electrolyte/lithium interface increases in both cases.

Conductivity and charge-transfer resistance for gel-electrolytes as functions of Li_3N percentage at 20°C

No.	Li_3N, %	Film thickness, cm	σ_{sp}, S/cm	R_F, Ω cm^2
1	0	0.021	8.75×10^{-4}	281
2	0.5	0.033	2.10×10^{-3}	434
3	1.0	0.020	8.8×10^{-4}	772

In summary, we may infer that, when introduced to the polymeric gel-electrolyte in the optimal percentage (0.5 wt %), nanosized Li_3N particles facilitate lithium ion transport inside the polymeric matrix by a factor of 2.4. At the interface with metallic lithium, on the contrary, an Li_3N additive increases charge-transfer resistance by a factor 1.5, indicating the electrochemical reaction $Li^+ + 2e \longleftrightarrow Li$ is hindered in the presence of Li_3N.

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