ABSTRACT BOOK

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Synthesis and investigation of components of composite solid electrolyte based on inorganic nano-particles of NASICON and $LiClO_4$-doped polyethylene oxyurea

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The stand-alone small-size lithium-ionic chemical current sources with metallic lithium anode and a ceramic electrolyte are required for practical application in modern electronics. At present, the compounds with perovskite structure $Li_{3x}La_{2/3-x}TiO_3$ are the most promising electrolytes as oxides with highest conductivity ($\alpha_{20°C} \sim 3\cdot10^{-3}$ S/cm). However, the metallic lithium interacts with lanthanum lithium titanate in contact area to form Ti^{3+}, resulting in unwanted electron conductivity of the ceramic electrolyte. Phosphate-containing compounds NASICON ($Li_{1+x}Al_xTi_{2-x}(PO_4)_3$) and LiPON ($Li_{3+y}PO_{4-x}N_{(y+2x)/3}$) are chemically stable in contact with a metallic lithium anode. However, NASICON-based ceramics are very fragile. The deposition methods of the LiPON compound (RF magnetron sputtering, laser spraying) are complex. The ionic conductivity of LiPON is low ($\alpha_{20°C} \sim 10^{-6}$ S/cm), but in the form of thin film (<1 μm) can be used as electrolyte. Therefore, the development of solid electrolyte of lithium-ion chemical current sources as a film composite is promising.

The purpose of the work is to check the possibility of preparation a composite solid electrolyte as a film based on inorganic nanoparticles and an organic polymer with an ion-conductive component that will be characterized by high ionic conductivity and chemical stability in contact with a metallic lithium anode. At the first stage of work, the synthesis and investigation of individual components of a composite solid electrolyte is important.

As inorganic component, the nanoparticles of compound with NASICON structure ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) were used. Particles were synthesized by solid phase reactions technique at 850 °C for 4 hours. As the initial reagents, lithium carbonate, aluminum nitrate, titanium oxide and phosphoric acid were used. Fine particles down to the nanometre range were produced by a grinding in a planetary mill. The conductivity of synthesized inorganic compounds was evaluated using ceramic sintered based on them. The complex impedance measurements in a wide frequency (1 Hz-32 MHz) and temperature (20-150 °C) ranges were performed. The X-ray diffraction analysis revealed that the inorganic particles of the NASCON compound were single-phase. An electron spectroscopy shown a particle size of <1 μm. The total conductivity and conductivity of grain inner of the NASICON ceramic at room temperature was $1.6 \cdot 10^{-6}$ and $3.6 \cdot 10^{-5}$ S/cm respectively. The temperature dependence of the total conductivity of the ceramic material NASICON was found to have an activation character with an activation energy of 0.41 eV.

The synthesis method of $LiClO_4$-doped polyethylene oxyurea as a model lithium-conductive polymer system has been developed. This system was expected to be effective as ion-conductive polymer component of film composite electrolytes. As initial reagents, oligoethylene oxide with a molecular weight of 1000 and 4,4'-diphenylmethane di-isocyanate were used. Polymer was synthesized at 80 °C in dimethyl formamide under a nitrogen atmosphere followed by the introduction of $LiClO_4$ and removal of the solvent under low pressure. The oligo-oxyethylene flexible segments of prepared polymer contribute to lithium-ionic conductivity due to the cation solvation and high self-segmental mobility. The rigid urethane segments form and maintain the domain structure of the system that is one of the basic conditions for ensuring a high level of ionic conductivity. At the ratio $(CH_2CH_2O)/Li^+ = 8$, the maximum conductivity of prepared systems was observed. For impedance spectroscopy, discs of Li-conductive polymer with a diameter of 11 mm and thickness of 80 μm were used. The total conductivity of lithium conductive polymer at room temperature was found to be $3.8 \cdot 10^{-7}$ S/cm. The temperature dependence of the total conductivity of the Li-conductive polymer was found to have an activation character with an activation energy of 0.3 eV.

Thus the experimental results indicate that NASCON inorganic nanoparticles ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) and $LiClO_4$-doped polyethylene oxyurea has significant prospects for the development of a composite solid electrolyte with high ionic conductivity and chemical stability in contact with a metallic lithium anode. Lithium-ion current sources containing a composite solid electrolyte based on inorganic nanoparticles and a polymer will be characterized by a low cost of the initial reagents, a simple preparation technology, and give the possibility to effectively solve the issues of miniaturization of modern electronic equipment.

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