

Influence of Inorganic Nano-powders on the Structure and Conductive Properties of the Network Polymer Electrolytes for Lithium Batteries

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The paper describes investigation on the network polymer electrolytes based on polyethylene glycol diacrylates and polyester diacrylates PEDA with introduction the nanopowders TiO_2 , Li_2TiO_3 and SiO_2 , with different size and shape. Much attention is paid to effects of nanoparticles additives on the ionic conductivity of network polymer electrolytes. The work is aimed to explanation of the mechanism of additives action on Li^+ - ion transport and structural changes of the polymer chains and the solvent molecules. For these purposes the NMR method with rotation under a magic corner on nuclei ^1H and NMR method with a pulsed magnetic field gradient at the nuclei ^7Li were used.

Keywords: Polymer Electrolyte, Nanopowders, Lithium Batteries, NMR Spectroscopy, Ionic Liquid.

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1. INTRODUCTION

At present, more attention has been attracted to investigations of nanocomposite polymer electrolytes (NPE) obtaining for lithium batteries. From the viewpoint of synthesis characteristics and of the resulting properties they are divided into two large classes:

- 1) solid nanocomposite polymer electrolytes;
- 2) gel-electrolytes based on nanocomposite polymer membranes (NCPM).

Solid NPE prepared by casting method from solution or by hot pressing a mixture polymer (mainly, polyethylene oxide), lithium salt, nanopowder of Al_2O_3 , TiO_2 , SiO_2 , CeO_2 , etc.

Gel-electrolytes based on NCPM prepare in two stages. At first researchers have a porous nanocomposite membrane mainly based on poly(vinylidene fluoride-co-hexafluoropropylene) and nanoparticles of the inorganic oxides which have been listed above. Then it is soaked in a liquid aprotic electrolyte.

Despite large differences in the preparation and operation of the electrolytes, a large contribution of nanoparticles to improvement conductive properties of the electrolyte, and also the increase in mechanical strength of these thin-film materials doesn't raise doubts and is confirmed with numerous literary data [1, 2]. In addition there are works on receiving NPE with introduction of ionic liquids [3, 4].

This research area continues to develop and, apparently, nanocomposite polymeric electrolytes will soon force out usual polymeric in lithium-polymer batteries and other electrochemical devices.

2. EXPERIMENTAL

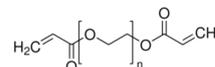
2.1 Synthesis of nanocomposite polymer electrolyte

The network polymer electrolytes received by reaction of radical polymerization, it is impossible to include to listed two classes NPE. Crosslinking of the three-dimensional polymer network takes place in the

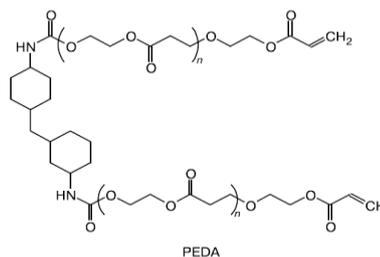
environment of liquid organic electrolyte (or without it), in the presence of inorganic nanoparticles by radical mechanism. The radical initiator is benzoyl peroxide. By methods of an isothermal calorimetry and DSC it is shown that introduction of TiO_2 nanoparticles doesn't influence on completeness of curing of polyester diacrylates, although, as known from [5] the acrylate polymerization reaction rate increases in the presence of nanoparticles.

In IPCP RAS developed network polymer electrolytes based on polyethylene glycol diacrylate (Dac-PEG) [6], and the original polyester diacrylate (PEDA) [7]:

- 1) DAc-PEG ($M_w=575$), Aldrich:



- 2) PEDA ($M_w=2780$), development of IPCP RAS [8]



Network polymer electrolytes based on these polymer systems with introduction the nanopowders TiO_2 , Li_2TiO_3 and Aerosil SiO_2 , with different size and shape (Fig. 1), including the introduction of ionic liquids have been developed.

2.2 The measurements techniques

The a.c. impedance was measured in the frequency range of 20 to 500,000 Hz at amplitude of the measurement signal 10 mV, using Impedancometry Z-2000 from

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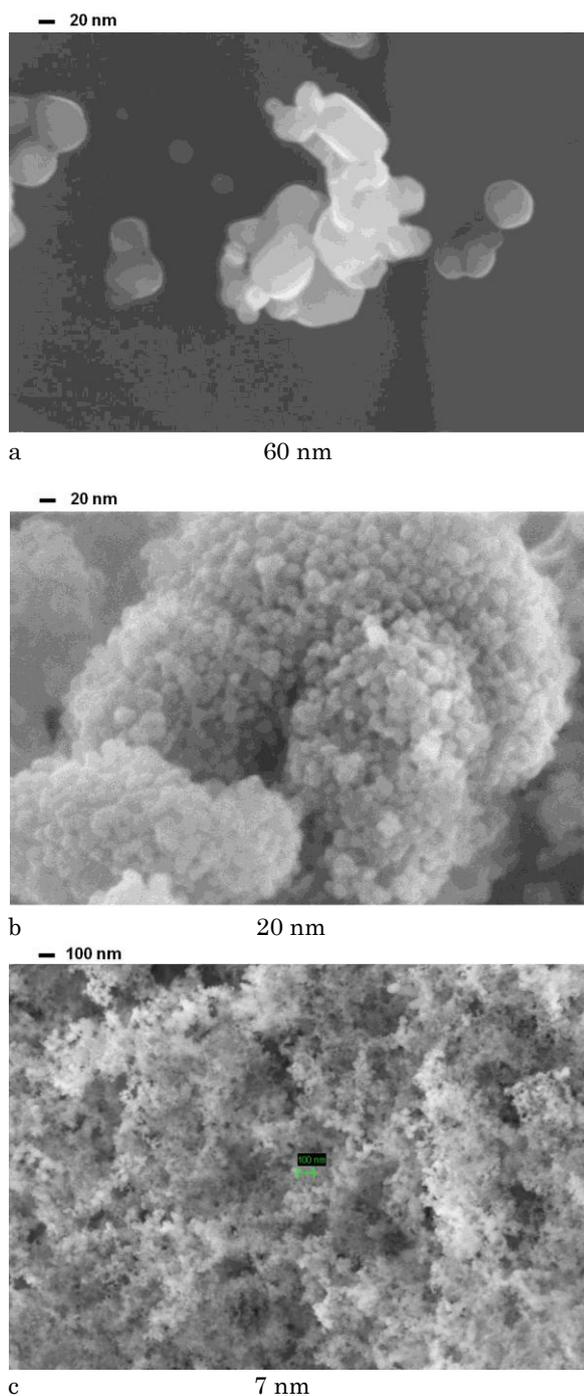


Fig. 1 – Micrographs of TiO_2 (a), Li_2TiO_3 (b) and SiO_2 (c) with the indication of the particles average size

Elins (Russia) in symmetric cells made of stainless steel with an area of 0.2 cm^2 .

NMR spectra of ^7Li nuclei were made on high-resolution spectrometer Bruker Avance III at a frequency of 194.4 MHz. NMR spectra with rotation under a magic corner on nuclei ^1H were made on same device.

Self-diffusion coefficients (D) of Li^+ ions were measured by NMR pulse magnetic field gradient at the nucleus ^7Li at a frequency 155.5 MHz.

3. RESULTS AND DISCUSSION

Let's consider various aspects of influence of the nanopowders on properties of network polymer electrolytes of different composition.

3.1 Influence of TiO_2 nano-additives on ionic conductivity of network solid polymeric electrolytes

Additives TiO_2 (60 nm) greatly increases the ionic conductivity of the solid polymer electrolyte composition PEDA: DAc-PEG with molar ratio of 1:12 and LiClO_4 salt. Figure 2 shows the dependence of the solid polymer electrolyte conductivity on temperature at different content of TiO_2 (0, 1, 5, 10 wt.%).

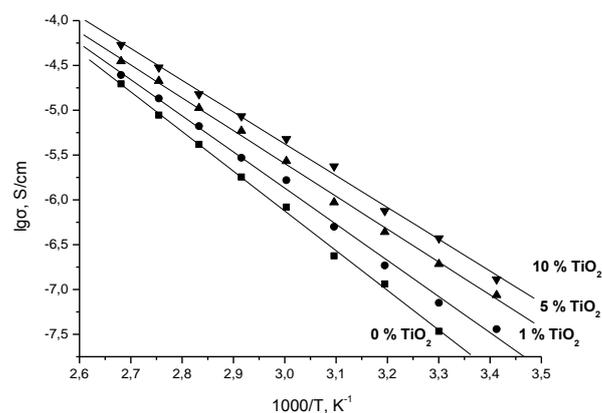


Fig. 2 – The conductivity of the solid NPE on temperature at different content of TiO_2 (0, 1, 5, 10 wt.%) in Arrhenius coordinates

Fig. 2 shows that ionic conductivity of sample with 10 wt.% TiO_2 is increased by the order at 30°C and only about 0.5 order at 100°C . This is due to the increase of polymer chains mobility with increasing temperature. And its contribution to the ionic conductivity hides the contribution of the surface layer of nanoparticles one.

3.2 Influences of TiO_2 and Li_2TiO_3 nano-additives on the ionic conductivity, Li^+ ions self-diffusion coefficients and structure of polymer electrolytes components

Nanoparticles don't make a contribution to increase of ionic conductivity in solid-phase gel-electrolytes where solvent (ethylene carbonate) isn't emitted in a separate phase, and is present mainly at solvate complexes shells of $\text{Li}^+(\text{EC})_4$ [9].

Let's compare influence of two various additives (TiO_2 and Li_2TiO_3 , fig.1) on the gel-electrolytes conductivity. The based composition electrolyte is PEDA- ethylene carbonate (1:1 by weight) + 7.5 wt. % LiClO_4 . We have chosen this electrolyte system as the most studied from the point of view of the fine structure and lithium ion transport [10-11].

Fig. 1 shows that TiO_2 and Li_2TiO_3 nanopowders have different shape and size of particles. This difference affected their influence on the structure of components of polymer electrolyte.

In preparation of initial solutions of nanocomposite

electrolyte ultrasonic processing for the best distribution of nanoparticles on all volume of electrolyte is always used.

By NMR with rotation under a magic corner on nuclei ^1H it is established (fig. 3) that in the presence of the TiO_2 nanopowder there is breaking the $-\text{CH}_2-$ link in the polymer structure and formation of terminal $-\text{CH}_3$ bond.

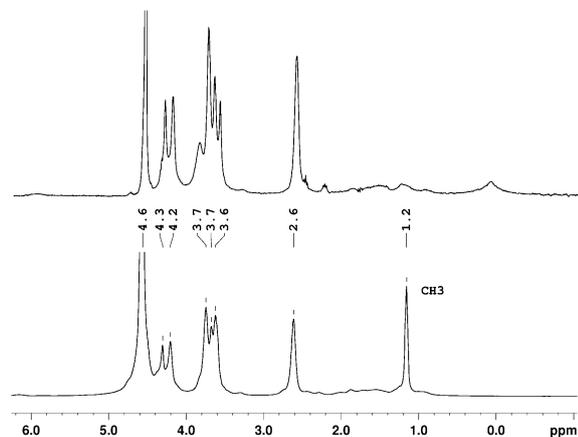
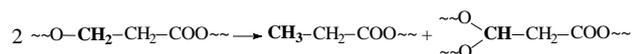


Fig. 3 – ^1H NMR spectra of polymer electrolytes based on PEDA, LiClO_4 with introduction of ethylene carbonate with at 10kHz without additives (the upper spectrum), added with 10 wt.% TiO_2 (lower spectrum)

Fig. 3 shows that signal in the field of 3.94 ppm of (group $-\text{CH}_2-$) ^1H NMR spectrum with addition of TiO_2 nanoparticles disappears and a signal in the field of 1.2 ppm appears. With the account composition of polymer electrolyte contribute to the signal in this spectral region can give only protons $-\text{CH}_3$ group bonded to the $-\text{CH}_2-$ group.

By quantum - chemical calculations it is shown that the gap of C-H bond near oxygen atom of ether group in PEDA structure is most probable:



In work [12] we supposed that the gap of C-H occurs at atom of the carbon, connected with a carbonyl of ester group, but based on calculation of NMR spectra and energy of the metathesis σ -bonds preference of this mechanism follows.

NMR method with rotation under a magic corner on ^1H nuclei shown that nanoparticles Li_2TiO_3 with ultrasonic treatment is much stronger influence on the structure of electrolyte components. In addition to the above-mentioned polymer degradation is occurs the breakdown of ethylene carbonate molecules. Apparently, smaller Li_2TiO_3 particles to which agglomerate (fig. 1b) breaks up much more strongly activate organic compounds bonds. At ultrasonic processing of solution of electrolyte without nanopowders these structural changes weren't observed.

Research of influence of TiO_2 nanoparticle additives on coefficients of lithium ions self-diffusion is conducted in polymer electrolyte PEDA-EC- LiClO_4 of the same structure. By NMR method with a pulsed magnetic field gradient at the nuclei ^7Li shown that there are

two types of lithium ions in the nanocomposite polymer electrolyte [13]. The first type is characterized by the Li^+ self-diffusion coefficient $1.2 \cdot 10^{-11} \text{ m}^2/\text{s}$. The relative proportion of these ions is 0.9. The second type of ion Li^+ has a self-diffusion coefficient $1.7 \cdot 10^{-12} \text{ m}^2/\text{s}$ and their relative proportion, respectively, equal to 0.1. We can assume that the area of the polymer electrolyte with a high mobility of lithium ions is near the nanoparticles surface. Lithium ions in volume of the polymer electrolyte are little mobile. This conclusion agrees with theoretical results presented in paper [14].

3.3 Effect of SiO_2 aerogel nano-additive on the ionic conductivity of network gel - polymer electrolytes

In network gel-electrolytes with the high content of a liquid phase the influence of nanopowder on conductivity strongly depends on degree of a crosslinking of a polymeric matrix.

We studied influence of an additive of 10 wt.% SiO_2 nanopowder (AEROSIL 380, average particle size 7 nm) on conductivity of electrolytes based on of DAC-PEG + 1M of LiBF_4 in gamma-butyrolactone with various degree of polymeric matrix crosslinking (Fig. 4).

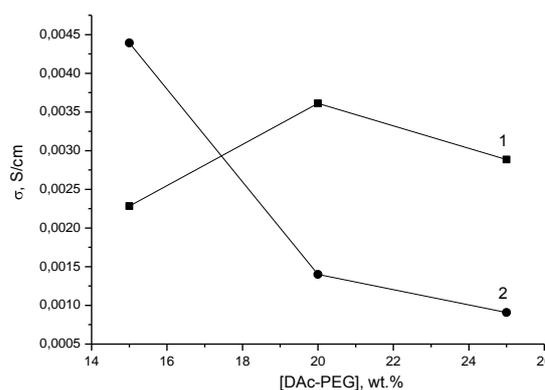


Fig. 4 – The dependence of conductivity of the polymer electrolyte without (1) and with 10 wt.% of SiO_2 (2) on the degree of polymer matrix crosslinking

Fig. 4 shows that conductivity of nanocomposite electrolyte increases 2 times in slightly network matrix (15 wt.% DAC-PEG) and decreases 2.5-3.0 times in dense network matrix.

The model representation of an effective ionic conducting pathway through the space charge layer of the neighboring SiO_2 grains at the boundaries was proposed by the authors of work [15] (fig.5).

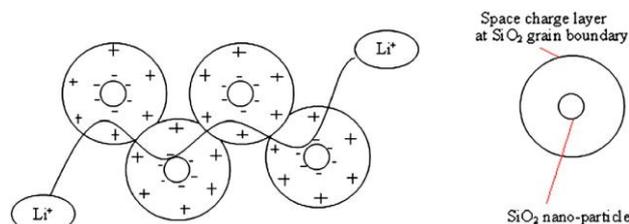


Fig. 5 – Model representation of an effective ionic conducting pathway through the space charge layer of the neighboring SiO_2 grains at the boundaries

The highest ionic conductivity is closely related to the formation of nano-sized filler grain boundaries. The nano-particles become more and more packed and initiate the formation of grain boundary with increasing SiO₂ concentration, which results an additional ionic hopping mechanism. The distance of inter-particles is decreased as increases SiO₂ mass fraction. So, these space charge layers tend to overlap with each other. At optimal SiO₂ filler content, the particles are getting closer to contact with their neighbors and this assist to form a continuous interpenetration of silica grains in the inter-particles region. When the particles becomes very much they are aggregated and ion transport is slowed down.

3.4 Joint influence of TiO₂ nanoparticles and ionic liquid on ionic conductivity of network gel-electrolytes

TiO₂ nanoparticles don't affect the ionic conductivity of the polymer gel-electrolyte based on DAc-PEG, LiBF₄, ethylene carbonate and 1-butyl-3-methyl imidazol tetrafluorine borate. For initial composition of the gel-electrolyte conductivity is 1.60×10^{-3} S/cm, but in presence 10 wt.% TiO₂ nanoparticle - 1.62×10^{-3} S/cm at

20 °C. Although there is no increase in the conductivity, the mechanical properties of the thin film electrolyte are significantly better.

4. CONCLUSIONS

Thus, it can be concluded that the addition of inorganic nanopowder in network polymer electrolytes based on polyether and polyester diacrylates greatly affect on its structure and conductive properties. In the solid network polymer electrolytes nano-additive greatly increase the conductivity due to the formation a more mobile state of lithium ions near the surface of the nanoparticles TiO₂, as has been shown by NMR method with pulsed magnetic field gradient on the nuclei ⁷Li. In the gel network electrolyte is a strong dependence of conductivity on the type and content of the nanopowder, and the size of the nanoparticles. In every system needs a search for the optimal combination of network matrix and also nano-additive content.

ACKNOWLEDGMENTS

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REFERENCES

- O.V. Yarmolenko, *Nanocomposite polymer electrolytes. The nanostructured materials for storage and energy transformation* (Ivanovo: Ivanovo State University: 2009).
- S. Ahmad, *Ionics* **15**, 309 (2009).
- S. Ramesh, Ch.-W. Liew, *J. Non-Crystalline Solids* **358**, 931 (2012).
- S. Ramesh, Ch.-W. Liew, *Ceramics International*. **38**, 3411 (2012).
- H. Datta, N.K. Singha, A.K. Bhowmick, *Macromolecules* **41**, 50 (2008).
- O.V. Yarmolenko, K.G. Khatmullina, G.Z. Tulibaeva, L.M. Bogdanova, A.F. Shestakov *J. Solid State Electrochem.*, **16**, 3371 (2012).
- K.G. Khatmullina, O.V. Yarmolenko, L.M. Bogdanova, *Polymer Science, Ser. A* **52**, 1327 (2010).
- Patent RU 2356131* (15.10.2007).
- O.V. Yarmolenko, K.G. Khatmullina, G.Z. Tulibaeva, L.M. Bogdanova, A.F. Shestakov, *Rus.Chem.Bulletin* **61**, 539 (2012).
- A.A. Marinin, K.G. Khatmullina, V.I. Volkov, O.V. Yarmolenko, V.A. Zabrodin, *Rus. Chem. Bulletin* **60**, 1096 (2011).
- A.A. Marinin, K.G. Khatmullina, V.I. Volkov, O.V. Yarmolenko *Rus.J.Electrochemistry*, **47**, 717 (2011).
- O.V. Yarmolenko, K.G. Khatmullina, L.M. Bogdanova, N.I. Shuvalova, E.A. Javadian, A.A. Marinin, V.I. Volkov, *Rus. J. Electrochem.* **49**. in print (2013).
- O. Yarmolenko, A. Shestakov, V. Volkov, *Acta of the International Symposia on Metal Complexes – ISMEC Acta.* **3** Burgos, Spain (2013).
- O. Borodin, G.D. Smith, R. Bandyopadhyaya, P. Redfern, L.A. Curtiss, *Modelling Simul. Mater. Sci. Eng.* **12**, S73 (2004).
- M. Osinska, M. Walkowiak, A. Zalewska, T. Jesionowski, *J. Membrane Sci.* **326**, 582 (2009).