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POLYVINYLIDENE FLUORIDE BASED COMPOSITE ELECTROLYTES FOR LITHIUM-ION BATTERIES

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Abstract

Solid polymer electrolytes, which are currently replacing traditional liquid electrolytes, are currently considered as an important strategy in the development of lithium ion batteries that are safe and with high energy density. But poor ionic conductivity and weak mechanical characteristics have significantly limited the development of solid polymer electrolytes. To improve these characteristics six composite polymer electrolytes (CPEs) with a composition of PVDF-PEG-LiClO₄-X and different fillers (where X = LiF, Ce_2O_3, Na_2SO_4, Li_3PO_4, MgO, LiH_2PO_4) were synthesized in this work. The optimal composition of the CPE and filler of PVDF-PEG-LiClO₄-Li_3PO_4 has been determined (σ = 2,36·10⁻⁵ Ohm⁻¹·cm⁻¹.). The result of the filler concentration effect on the ionic conductivity of films was studied where optimal filler concentration of 5 % Li_3PO_4 had the highest ionic conductivity of 1.43·10⁻⁴ Ohm⁻¹·cm⁻¹. The surface morphology, electrochemical and thermal stability of the obtained CPEs have been studied by various techniques. Investigation of physicochemical aspects of the effect of fillers on the solid polymer electrolytes properties will make it possible to derive the regularities and universal methods for obtaining effective separators that ensure stable operation of the battery.

Keywords: lithium-ion polymer batteries; ionic conductivity; composite polymer electrolyte; filler; films.

КОМПОЗИТНІ ЕЛЕКТРОЛІТИ НА ОСНОВІ ПОЛІВІНІЛІДЕНФТОРИДУ ДЛЯ ЛІТІЙ-ІОННИХ АКУМУЛЯТОРІВ

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Анотація

У роботі синтезовано шість композиційних полімерних електролітів (КПЕ) зі складом PVDF-PEG-LiClO₄-X та різними наповнювачами (де X = LiF, Ce_2O_3, Na_2SO_4, Li_3PO_4, MgO, LiH_2PO_4). Визначено оптимальний склад КПЕ та наповнювача PVDF-PEG-LiClO₄-Li_3PO_4. Досліджено вплив концентрації наповнювача на іонну провідність плівок, де оптимальна концентрація наповнювача 5 % Li_3PO_4 має найвищу іонну провідність 1.43·10⁻⁴ Ом⁻¹·см⁻¹. Морфологію поверхні, електрохімічну та термічну стабільність отриманих ЦПЕ досліджено різними методами.

Ключові слова: літій-іонні полімерні акумулятори; іонна провідність; композиційний полімерний електроліт; наповнювач; плівки.

Introduction

In connection with the growing role of autonomous energy in various fields of technology, it is necessary to create power supplies with higher performance, primarily with a large electrochemical capacity, energy density, and stability in charge/discharge cycles. Lithium-ion batteries (LIB) have higher energy density than many other systems. However, when cycling a lithium-ion battery, lithium metal is plated in the form of a dendrite on the surface of the carbon matrix anode. As a result, there is a threat of intense exothermic chemical interaction of lithium with electrolyte, or short circuiting.

The safety of the battery is improved by replacing the liquid organic electrolyte with polymer ones. The idea of implementing lithium-polymer electrolytes is based on the ability of polymers to prevent dendrite growth by evenly distributing its deposition. Thus, composite polymer electrolytes are a promising type of electrolytes for LIBs. The advantages of the CPE are the improved ionic conductivity, mechanical properties, greater chemical stability at the electrolyte/electrode interface and possibility to obtain composites in the form of thin, durable and elastic films [1–4]. Polymer electrolytes, where lithium salts in a polymer matrix, are currently gaining attention [5–8].

The disadvantages of some polymer electrolytes are higher anion conductivity, which often exceeds that of lithium-ions. Therefore, a new generation of polymer electrolytes with unipolar lithium conductivity was developed, in which the lithium salt's anions are grafted into the polymer chain [9]. This makes it possible to avoid the formation of a passivation film on lithium and improve the electrochemical characteristics of LIB.

The choice of polymer matrix is a fundamental factor in the formation of CPE. The polymers used in the production of polymer electrolytes exhibit only insignificant conductivity (10^{-12}–10^{-10} Ohm$^{-1}\cdot$cm^{-1}), and generally they are insulators [10]. Polymers for the CPE should contain heteroatoms with a high electron density, which are capable of coordinating Li$^+$, facilitating the dissociation of the salt. In the literature, polymers such as polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and polyvinylidene fluoride (PVDF) are most frequently used [11–15]. PEO was the most popular one until recently. This is due to its high coordinating ability for the lithium ions and stability with respect to the lithium electrode [11]. However, the required ionic conductivity (10^{-3}–10^{-4} Ohm$^{-1}\cdot$cm^{-1}) manifests itself only at elevated temperatures of 80–100 °C, and at room temperature of 10^{-7}–10^{-8} Ohm$^{-1}\cdot$cm^{-1}. PAN-based composites have shown improved ionic conductivity of 10^{-3} Ohm$^{-1}\cdot$cm^{-1} at ambient temperature, a large transfer number of 0.6 and electrochemical stability up to < 4.5 V, but, unfortunately, such system causes passivation of the lithium anode. The disadvantage of CPE with PMMA is insufficient mechanical strength. At the moment, the most promising CPE matrix is PVDF. The relatively high dielectric constant of ε = 8.4, ensures the ionization of lithium salts and contributes to an increase in the concentration of charge carriers. In addition, the polymer is more compatible with the anode, due to the strong electron acceptor groups [12; 13]. Also, PVDF-based CPEs have good mechanical strength, thermal stability, film-forming ability, and high electrolyte absorption rates [14; 15].

CPE fillers can be conditionally divided into highly conductive ceramics, zeolites, ionites and neutral fillers [16]. Ceramic fillers are classified into active and passive. Active materials provide the conduction process, e.g. Li$_3$N, LiAl$_2$O$_3$, while passive materials, such as Al$_2$O$_3$, SiO$_2$, MgO, are not directly involved in providing the lithium transport process [15]. However, Panero et al. [17] noticed that the addition of 30 mas. % of the active additive of γ-LiAlO$_2$ causes only a slight improvement in ionic conductivity, while in a number of studies [18–21] with the help of passive additives such as Al$_2$O$_3$, SiO$_2$ achieved its significant increase. In this paper, TiO$_2$ particles were selected to improve ionic conductivity due to their shape and surface nature, which effectively disrupt the packing order of the polymer matrix. This contributes to a significant decrease in the crystallinity of the polymer and an improved ion transport. There are many electron-donating centers on the surface of titanium oxide crystals that provide sorption and migration of lithium cations [22–24].

Thus, this work on the development of lithium-conducting polymer electrolytes with the following properties is currently relevant: high electrical conductivity in a wide temperature range, chemical and electrochemical stability, good physical and mechanical qualities.

In this context, the findings of producing composite polymer electrolytes and studying their physicochemical properties are presented in this article.

Experimental

The following materials and reagents were used for the research: polyvinylidene fluoride (PVDF) of the chemically pure grade (powder), M = 534000; polyethylene glycol (PEG), M = 8000; N,N-dimethylformamide of the chemically pure grade; polyethylene glycol of the "chemically pure grade" brand, M = 8 000; $LiClO_4$, degree of purity 99.98 %; LiF, Ce_2O_3; Na_2SO_4; Li_3PO_4; MgO; LiH_2PO_4 of the "chemically pure grade" brand.

An ES-4610 oven with a built-in fan was used for heat treatment of the obtained films and removal of solvents and moisture. To remove residual moisture, a vacuum drying cabinet was used, equipped with a deep vacuum oil pump and a temperature control microprocessor. In order to uniformly distribute the filler particles in the volume of the polymer solution and prepare the latter, a VELP SCIENTIFICA heated magnetic stirrer was used in this work.

Electrochemical measurements were carried out at room temperature on an AUTOLAB-30 potentiostat-galvanostat device with a computer control station. The morphology of the obtained polymer membranes, the number of phases in the material and their distribution were studied using a scanning electron microscopy, "Quanta 200i 3D" with an amplification of 5–30 kV, and magnification of 20 000 x. The SEM images were taken at the National Nanotechnology Laboratory of al-Farabi Kazakh National University.

The thermal characteristics and thermal stability of the obtained CPEs were determined based on the analysis of thermogravimetric curves made on the NETZSCH STA 449F3 Jupiter synchronous thermal analysis device provided by the Laboratory of Inorganic Materials Science of the DGP CFHMA.

The calculation method was used to calculate the values of ionic conductivity, which were mathematically approximated. [25]. The calculation was carried out based on Ohm's law:
$$R = \Delta E / I,$$
where R – resistance of external circuit elements, ohms;

ΔE – circuit voltage, V;

I – current, A.

Ionic conductivity was calculated by the formula:
$$\sigma = l / (R \cdot S),$$
where σ – ionic conductivity, $Ohm^{-1} \cdot cm^{-1}$;

l – membrane thickness, cm;

S - working area equal to 1.77 cm^2.

Results and discussion

In this study, six thin films of composite polymer electrolytes containing various inorganic fillers were produced and investigated. Table 1 shows qualitative and quantitative data on the synthesized solid composite polymer electrolytes.

Table 1

Data for synthesis polymer electrolytes based on PVDF

№	Matrix-polymer	Polymer	Lithium salt	Filler	Filler concentration, %
1				LiF	
2				Ce_2O_3	
3	PVDF	PEG	$LiClO_4$ (20 %)	Na_2SO_4	10
4				Li_3PO_4	
5				MgO	
6				LiH_2PO_4	

To determine the ionic conductivity of the synthesized CPEs, the results were processed using pulsed galvanostatic curves (Figure 1) taken at the AUTOLAB PGSTAT-30 installation. After removing the pulsed galvanostatic curves, the ohmic voltage drop was determined by the vertical potential jump at the beginning of the pulse and after its completion. As can be seen from Fig. 1, the peaks of the ohmic and Faraday components are flat, so we can assume that the membrane is stable, and the results are reliable.

The calculated values of the ionic conductivity of polymer membranes are shown in Table 2. The approximation of the results was carried out graphically according to the dependence of the ohmic jump on the current density (Fig. 2). The resistance of the polymer membrane was calculated, which was 93.26 ohms, which in terms of the electrical conductivity of the film is $1.52 \cdot 10^{-5}$ $Ohm^{-1} \cdot cm^{-1}$.
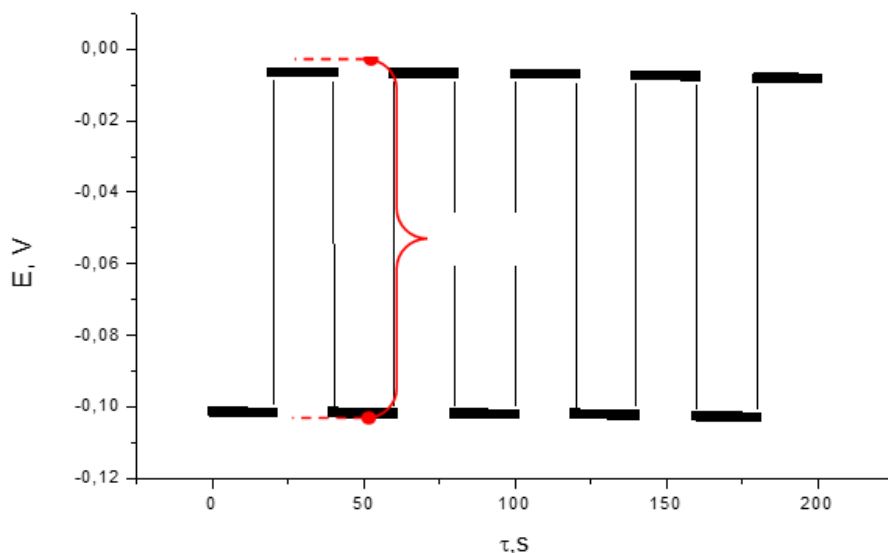
Fig. 1. Pulsed galvanostatic curve of a polymer membrane taken in an aqueous electrolyte

Table 2

Data for calculating the ionic conductivity of the CPE

| №	Filler	l,cm	I, A	E_1, B	E_2, B	ΔE, B	R, Ом	σ, Ohm$^{-1}\cdot$cm^{-1} (10^5)
1	LiF	0.0025	−0.001	−0.1017	−0.0065	−0.0952	95.25	1.483
			−0.005	−0.4836	−0.0126	−0.4710	94.21	1.499
			−0.01	−0.9451	−0.0103	−0.9347	93.48	1.511
2	Ce_2O_3	0.0038	−0.001	−0.1118	−0.0104	−0.1015	101.52	2.115
			−0.005	−0.5084	−0.0059	−0.5025	100.49	2.136
			−0.01	−1.0047	−0.0012	−1.0035	100.35	2.139
3	Na_2SO_4	0.0023	−0.001	−0.0963	0.0012	−0.0975	97.54	1.332
			−0.005	−0.4864	0.0005	−0.4869	97.40	1.334
			−0.01	−0.9696	0.0003	−0.9698	96.98	1.340
4	Li_3PO_4	0.0042	−0.001	−0.1024	−0.0013	−0.1011	101.07	2.348
			−0.005	−0.5065	−0.0007	−0.5058	101.16	2.346
			−0.01	−1.0078	−0.0012	−1.0066	100.66	2.357
5	MgO	0.0036	−0.001	−0.1197	0.0012	−0.1209	120.92	1.682
			−0.005	−0.6032	−0.0002	−0.6030	120.60	1.686
			−0.01	−1.2038	−0.0011	−1.2026	120.26	1.691
6	LiH_2PO_4	0.0034	−0.001	−0.0980	0.00005	−0.0979	97.99	1.960
			−0.005	−0.4917	0.00047	−0.4922	98.43	1.951
			−0.01	−0.9824	0.00043	−0.9828	98.28	1.954
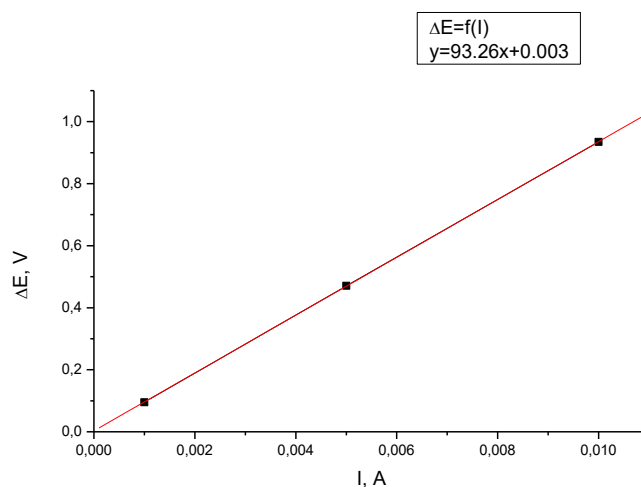
Fig. 2. Dependence of the ohmic component of the potential jump at galvanostatic polarization on the current density

As can be seen from the data in Table 2, the CPE of the following composition PVDF-PEG-LiClO₄-Li₃PO₄ has the greatest ionic conductivity, therefore, a filler - Li₃PO₄ was used for further studies. Further, the effect of the concentration of Li₃PO₄ on the ionic conductivity of polymer electrolytes was established. The studies were carried out with the following filler concentrations of 1 %, 3 %, 5 %, 7 %. The results are presented in table 3.

The dependence of the ionic conductivity of CPE – PVDF-PEG-LiClO₄-Li₃PO₄ on the filler concentration is shown in Fig. 3.

Table 3.

Experimental data for calculating the ionic conductivity of CPE - PVDF-PEG -LiClO₄-Li₃PO₄

№	Filler	l, cm	I, A	E_1, V	E_2, V	ΔE, V	R, Ohm	σ, Ohm^{-1}·cm^{-1} (10^5)
1	Li₃PO₄, 1 %	0.0036	−0.001	−0.0678	0.0095	−0.0774	77.39	2.628
			−0.005	−0.3752	0.0091	−0.3843	76.87	2.646
			−0.01	−0.9617	0.0018	−0.9598	95.98	2.119
2	Li₃PO₄, 3 %	0.0028	−0.001	−0.0883	0.0063	−0.0946	94.64	1.672
			−0.005	−0.4697	0.0023	−0.4721	94.42	1.675
			−0.01	−0.9364	0.0007	−0.9357	93.57	1.691
3	Li₃PO₄, 5 %	0.008	−0.001	−0.0115	0.0201	−0.0316	31.66	14.276
			−0.005	−0.1359	0.0217	−0.1577	31.54	14.330
			−0.01	−0.2939	0.0210	−0.3149	31.49	14.353
4	Li₃PO₄, 7 %	0.0032	−0.01	−0.2552	0.0276	−0.2828	28.28	6.393
			−0.03	−0.8229	0.0236	−0.8465	28.22	6.406
			−0.05	−1.3599	0.0218	−1.3817	27.63	6.543
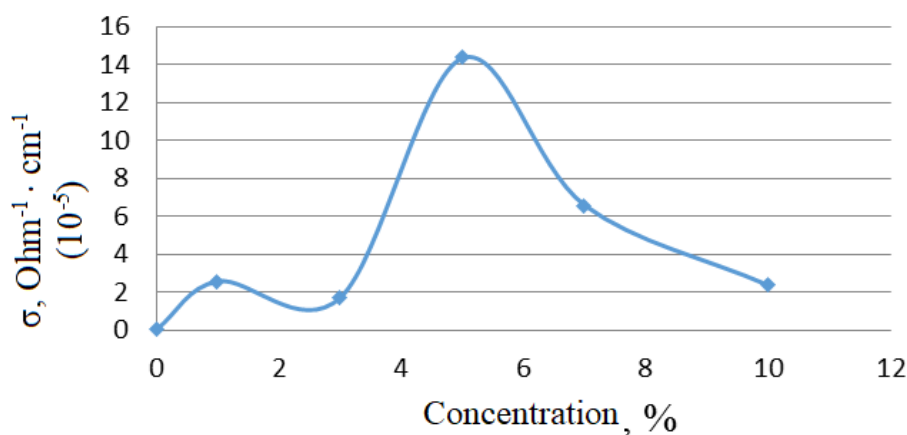
Fig. 3. Dependence of ionic conductivity of CPE – PVDF-PEG-LiClO₄-Li₃PO₄ from Li₃PO₄ concentration

As can be seen from Fig. 3, at a filler concentration of Li₃PO₄ of 5 %, the maximum value of the ionic conductivity of the CPE is observed.

Next, the morphology of the surface, the electrochemical and temperature stability of the obtained CPEs are investigated. The analysis of the surface morphology of polymer membranes allows us to evaluate the effect of various fillers on the change in the microstructure of samples, which in turn facilitates the assessment in predicting the properties of electrolytes in electrochemical systems. The role of the fine-crystalline phase of the filler is to provide conductivity along the lithium cation due to the introduction of heterogeneous grains into the polymer volume and the passage of charge along the grain surface. Accordingly, an important factor is the possibility of uniform distribution of the filler in the membrane structure. In Figure 4, it can be seen that the polymer in the membrane tends to form two types of structures: dense and globular. Also, during the analysis, it is possible to make an assumption about the different affinity of filler particles to a mixture of polymers. Thus, on a micrograph of a sample with the addition of lithium fluoride, it is possible to note a dense structure with channels of voids filled with crystals of a heterogeneous phase and the obvious immiscibility of lithium fluoride with a polymer mixture of polyvinylidene fluoride and polyethylene glycol, while on other samples with other fillers, the effect of separation of the heterogeneous phase from the polymer is less

noticeable. In a sample with the addition of cerium oxide, a dense structure is observed with the absence of any pores and channels. This effect may be related to the particle size of the heterogeneous phase, because unlike other fillers with micro-sizes, cerium oxide is represented in the nanometer range, which, however, does not exclude the local aggregation of some particles, which is observed in Fig. 4.
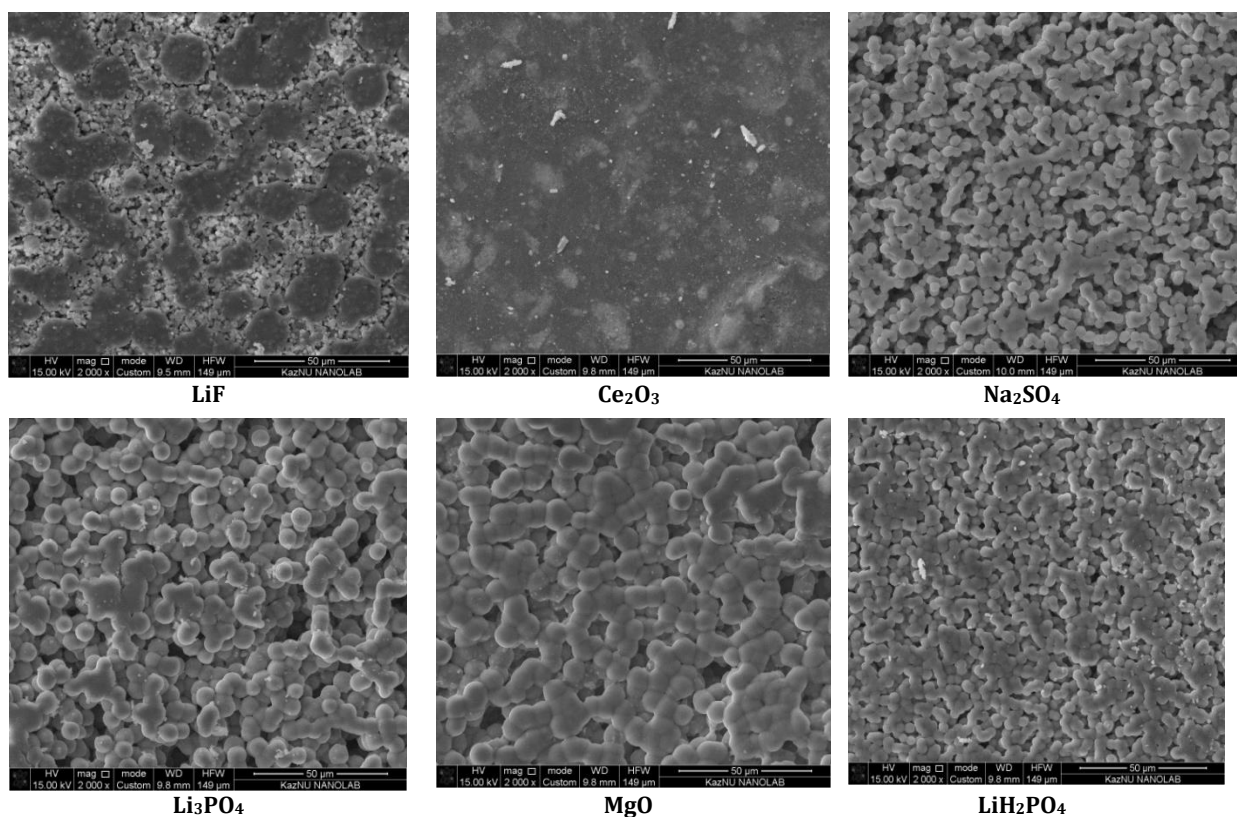

Fig. 4. Micrographs of the surface of synthesized CPEs (x2 000 magnification)

However, it should be noted that the bulk of the particles are distributed inside the polymer mass in nanometer dimensions, which makes it possible to obtain such a dense structure. Due to the extremely small size of the heterogeneous phase, the membrane conductivity is expected to show relatively high results. The remaining four samples have a globular structure, the size of the globules of which increases in the series : $LiH_2PO_4 < Na_2SO_4 < Li_3PO_4 < MgO$. If consider the effect of the size of globules on the ability to conduct lithium cations through the membrane, it can be hypothesized that with an increase in the size of globules, the volumes of voids in the membrane also increase, which subsequently affects the retention of the liquid agent in the volume of the membrane and creates the effect of a "gel". As is known, "gels" have the property of conducting ions better, however, it should be noted that it is necessary to determine some optimal size of globules [26]. Indeed, with an increase in the size of globules, the space of channels also increases, however, when a certain size is reached, the ability to retain a liquid agent in these channels decreases. According to this hypothesis, the ionic conductivity should increase in the series: LiH_2PO_4, Na_2SO_4, Li_3PO_4 and, after passing through the maximum, decrease sharply for MgO. There is an assumption that the size of the globules depends on the size of the filler particles, because this structure involves enveloping the surface of the particle with a polymer, however, this process occurs before some saturation of the polymer with particles. When the maximum concentration of the distributed particles in the polymer is exceeded, the process of planting excess on the surface of the globules occurs, which leads to clogging of the pore channels and, accordingly, to a decrease in conductivity.
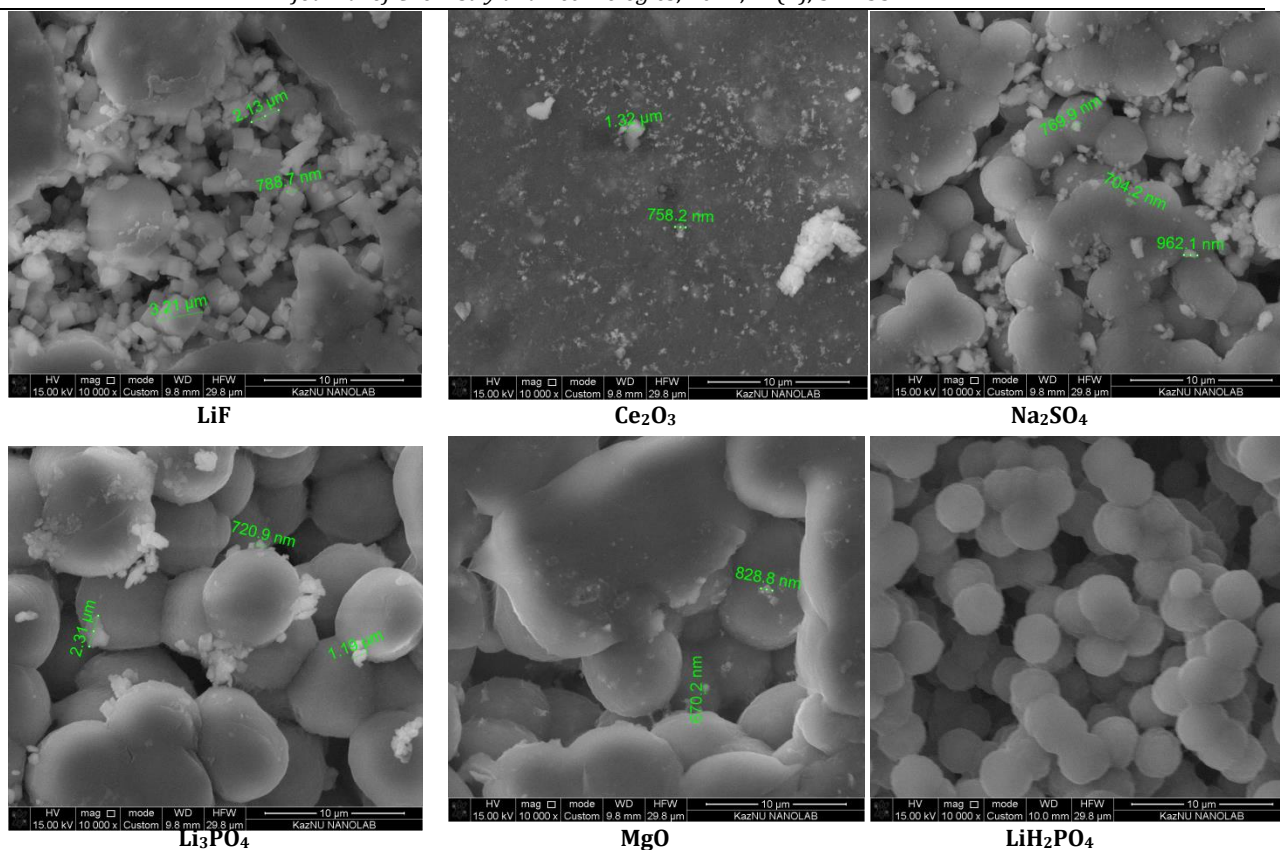
LiF

Ce₂O₃

Na₂SO₄

Li₃PO₄

MgO

LiH₂PO₄

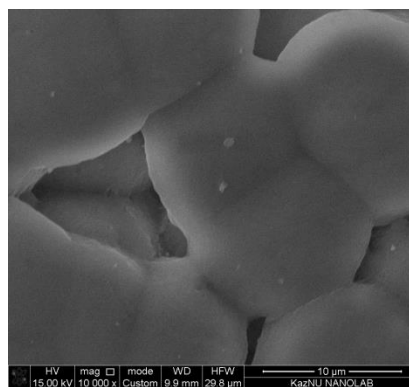**Fig. 5. Samples of micrographs of the surface of synthesized CPEs (x10,000 magnification)**

According to Fig. 5, a similar effect is observed in a membrane with a filler - sodium sulfate. Based on the analysis, a globular structure with an average pore size of 5 microns without the effect of planting salt crystals on the surface will be preferable.

Figure 6 shows micrographs of the surface morphology of membranes with the addition of different amounts of lithium phosphate. As can be seen from Fig. 6, at low concentrations of filler, the heterogeneous phase is evenly distributed in the polymer volume, which is observed in samples with concentrations of 1 % and 3 %. When 5 % of the filler concentration is reached, extreme saturation occurs and the crystals begin to plant on the surface, a further increase in the concentration of lithium phosphate enhances this effect of planting, which is undesirable.

Li₃PO₄, 1 %
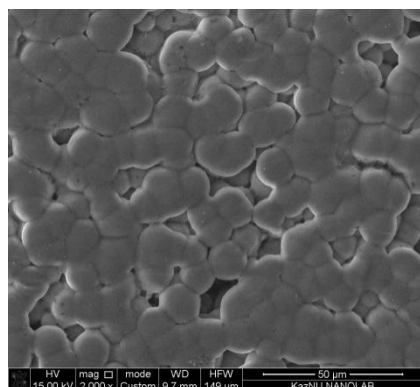
Li₃PO₄, 3 %

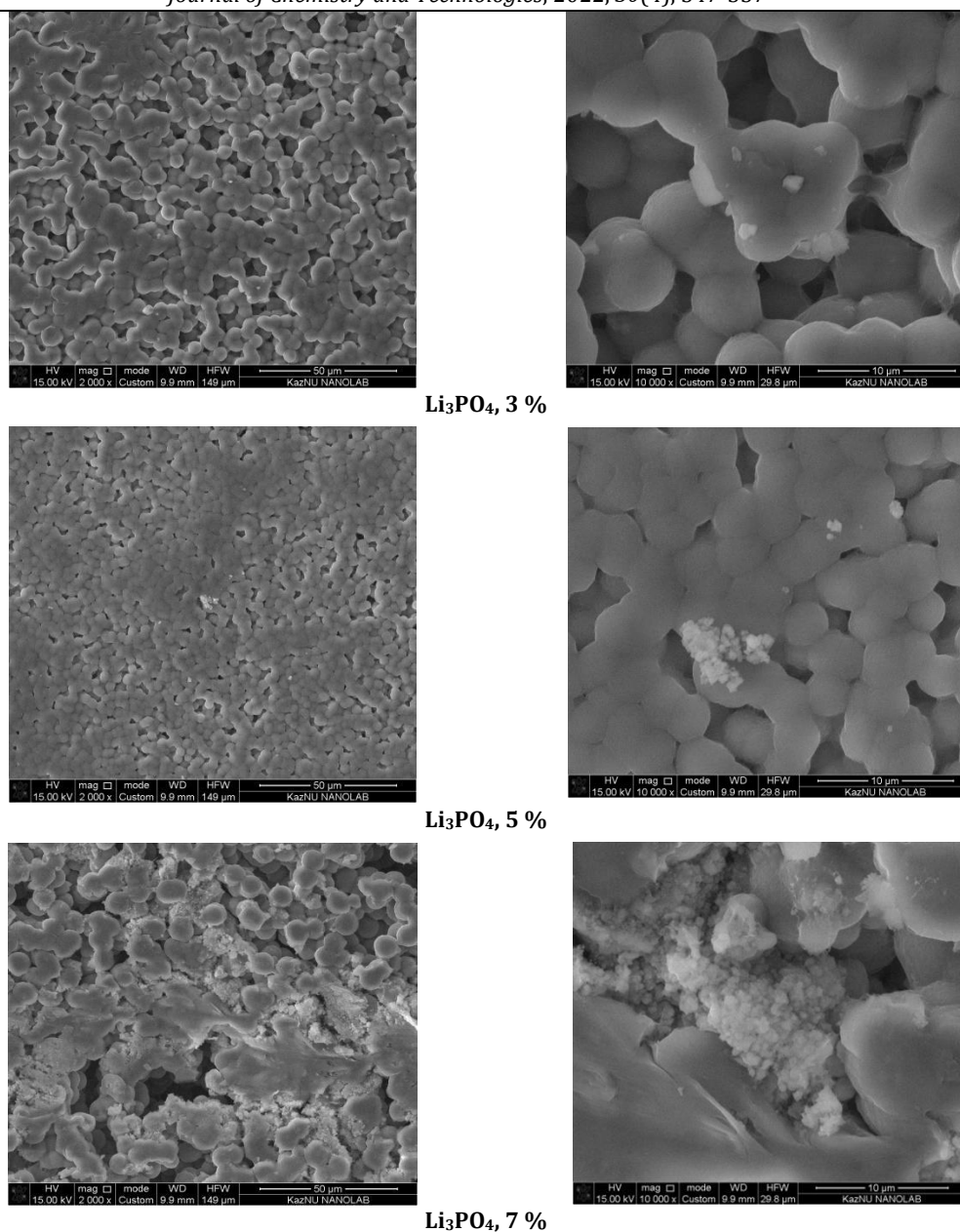**Li₃PO₄, 5 %**

Li₃PO₄, 7 %

Fig. 6. Samples of micrographs of the surface of synthesized CPEs at different concentrations of Li₃PO₄ (x2 000 magnification)

Thus, according to experimental data, the optimal filler concentration is 5% lithium phosphate, since it is characterized by the maximum allowable number of particles of the inert phase without the effect of clogging porous channels.

An important factor for lithium-polymer batteries is the thermal stability of its components. This ensures the required degree of battery safety and performance. The thermogravimetry method (TGA-DTA) was used to study the thermophysical properties of polymeric membranes of optimal composition PVDF-PEG-LiClO₄-Li₃PO₄. Thermogravimetric curves of the obtained membranes are shown in Fig. 7a, 7b, 7c. As can be seen from the figures, the mass loss of the membranes with increasing filler concentration drops from 2.98 % to 1.89 %, which is a relatively small percentage of mass loss.
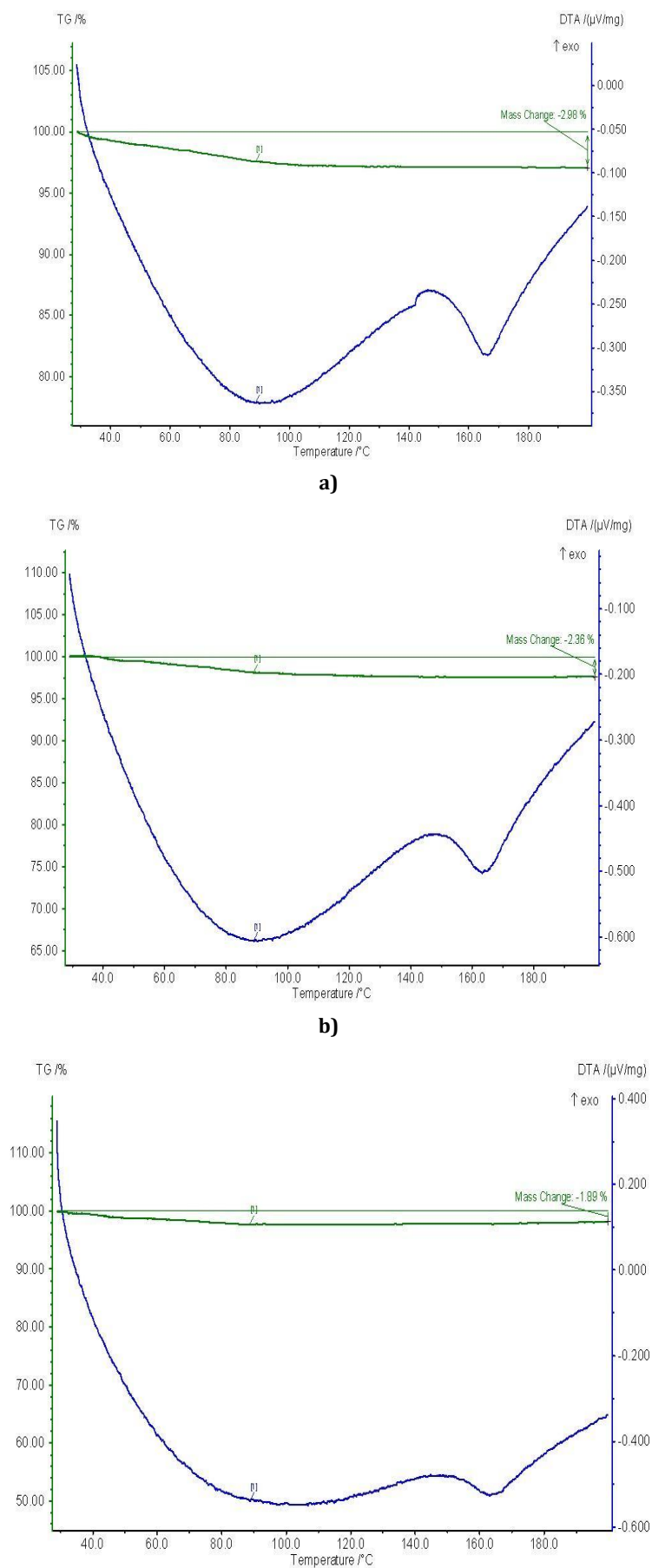
Fig. 7. Thermogravity curves of PVDF-PEG -LiClO$_4$-Li$_3$PO$_4$: 5 % Li$_3$PO$_4$ (a), 7% Li$_3$PO$_4$ (b), 10 % Li$_3$PO$_4$ (c)

Based on the analysis of the TGA and DTA curves, it can be assumed that this small mass loss is associated with the volatilization of the excess solvent or absorbed water. The decrease in mass intensifies when the temperature reaches 40 degrees and reaches a constant plateau, which does not correspond to the endothermic processes presented in the diagram, this fact excludes the possibility of mass loss due to the decomposition of the membrane.

The DTA data illustrate the ongoing endothermic changes in the sample. Using them, it is possible to put forward an assumption about possible transformations that have occurred, such as transition to a glassy state, crystallization, melting and sublimation.

Fig. 7a, 7b, 7b show that two endothermic processes occur during the gradual heating of samples within temperatures from 25 to 200 ^{0}C: the first is from 25 to 145 ^{0}C and the second is from 145 to 20 0^{0}C. The first process is probably associated with the transition to the glassy state of the polymer (PEG). The second process with a peak at 165 ^{0}C probably corresponds to the melting of the main polymer, the PVDF matrix. It was also found that with an increase in the filler concentration, these processes occur more fully according to an increase in the area of the corresponding peaks.

Thus, in the course of this work, six composite polymer electrolytes based on PVDF, PEG and LiClO$_4$ (20 %) with various fillers (10 %) were synthesized. The highest ionic conductivity corresponds to a membrane of the following composition: PVDF-PEG -LiClO$_4$ -Li$_3$PO$_4$: σ = 2.36 10^{-5} Ohm^{-1}·cm^{-1}.

Based on the analysis of the results on the effect of the filler concentration, it was concluded that the optimal concentration is 5% lithium phosphate, while the ionic conductivity of the membrane σ = 1.43·10^{-4} Ohm^{-1}·cm^{-1}. The surface morphology of the synthesized composite polymer electrolytes was studied using scanning electron microscopy. Thermogravimetric data indicate that the obtained membranes are thermally stable in the required temperature range (20–200 ^{0}C).

References

[1] Mukhametova, L. R., Akhmetova, I. G., Strielkovsky, V. (2019). Innovations in the field of energy storage. *Power Equipment, Technol*., 21, 4, 33–40. (In Russian).

[2] Gediri, A. (2021). Renewable energy sources — a new energy revolution, *Bulletin of the Peoples' Friendship University of Russia. Series: Economy*, *29*(1), 98–104. (In Russian).

[3] Mentbayeva, A., Sukhishvili, S., Naizakarayev, M., Batyrgali, N., Seitzhan, Z., Bakenov, Z. (2021). Ultrathin clay-containing layer-by-layer separator coating enhances performance of lithium-sulfur batteries. *Electrochimica Acta, 366*, 137454.

[4] Li, B., Sun, Z., Zhao, Y., Bakenov, Z. (2019). A Novel Hierarchically Porous Polypyrrole Sphere Modified Separator for Lithium-Sulfur Batteries. *Polymers, 11*(8), 1344. https://doi.org/10.3390/polym11081344

[5] Li, Y., Wang, X., Liang, J., Wu, K., Xu, L., Wang, J. (2020). Design of a high performance zeolite/polyimide composite separator for lithium-ion batteries. *Polymers, 12*(4), 32244570. doi: 10.3390/polym12040764

[6] Kosova, N. V. (2004). Highly dispersed cathode materials for lithium-ion batteries obtained using mechanical activation. *Chemistry in the interests of sustainable development, 12*, 349–354.

[7] Li Ping, T., Mohd, H. B., Abdul, K. A. (2021). Development on Solid Polymer Electrolytes for Electrochemical Devices. *Molecules. 26*(21), 6499. doi: 10.3390/molecules26216499

[8] Wei, Z., Ren, Y., Wang, M. (2020). Improving the Conductivity of Solid Polymer Electrolyte by Grain Reforming. *Nanoscale Res Lett*., 15., 122, https://doi.org/10.1186/s11671-020-03355-4

[9] Andreev, O. L., Druzhinin, K. V., Roh, S. W. (2009). Composite lithium-conducting polymer electrolytes based on PVDF- GFP copolymer and solid electrolyte Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$. *Electrochemical power engineering*, 2, 76–81.

[10] Qingjiang, Yu., Kecheng, J., Cuiling, Yu., Xianjin, Ch., Chuanjian, Zh., Yi, Yao., Bin, Jiang, Huijin, Long. (2021). Recent progress of composite solid polymer electrolytes for all-solid-state lithium metal batteries. *Chinese Chemical Letters, 32*, 9, 2659–2678 https://doi.org/10.1016/j.cclet.2021.03.032

[11] Druzhinin, K. V., Andreev, O. L., Batalov, N. N. (2010). [Transport properties of composite materials based on a copolymer of vinylidene fluoride-hexafluoropropylene and lithium chloride crystallosolvate with dimethylformamide]. *"Fundamental problems of energy conversion in lithium electrochemical systems": Materials of the XI International Conference*, 245–249. (In Russian).

[12] Kumar, A, Deka, M. (2010). *Nanofibers: nanofiber reinforced composite polymer electrolyte membranes*. InTech.

[13] Baskakova, Yu. V., Yarmolenko, O. V., Efimov, O. N. (2012). Polymer gel electrolytes for lithium current sources. *Advances in chemistry, 81*, 367–380.

[14] Kenessova, A. K., Seilkhanova, G. A., Kurman-bayeva, T. S., Ussipbekova, E. Z., Kurbatov, A. P. (2020). Solid polymer electrolytes for energy storage systems. *Materials Today: Proceedings. – Elsevier Ltd*, 31, 588–591.

[15] Li, S., Zhang, W., Zheng, J., Lu, M., Song, H., Du, L. (2020). Inhibition of Polysulfide Shuttles in Li–S Batteries: Modified Separators and Solid-State Electrolytes, *Advanced Energy Materials*, https://doi.org/10.1002/aenm.202000779

[16] Panero, S., Scrosati, B., Greenbaum, S. G. (1992). Ionic conductivity and Li NMR study of poly(ethylene glycol) complexed with lithium salts. *Electrochimica Acta*, 37, 1533–1539.

[17] Liu, S., Imanishi, N., Zhang, T., Hirano, A., Takeda, Y., Yamamoto, O., Yang, J. (2010). Effect of nano-silica filler in polymer electrolyte on Li dendrite formation in Li/poly(ethylene oxide)–Li(CF$_3$SO$_2$)$_2$N/Li. *Journal of Power Sources*, *195*, 6847–6853.

[18] Laura, C., Merrill, Xi., Chelsea, Ch., Yiman, Zh., Hunter, O., Ford, K. L., Yubin, Zh., Guang, Y., Wang, Ya., Wang, Ya., Schaefer, Je. L. Dudney, N. J. (2020). Polymer–Ceramic Composite Electrolytes for Lithium Batteries: A Comparison between the Single-Ion-Conducting Polymer Matrix and Its Counterpart. *ACS Appl. Energy Mater,* 3, 8871–8881 https://doi.org/10.1021/acsaem.0c01358

[19] Sanaz, K., Keryn, L. (2013). Effect of SiO$_2$ on conductivity and structural properties of PEO–EMIHSO$_4$ polymer electrolyte and enabled solid electrochemical capacitors. *Electrochimica Acta*, 103, 174–178.

[20] Pandey, G. P., Hashmi, S. A., Agrawal, R. C. (2008). Hot-press synthesized polyethylene oxide based proton conducting nanocomposite polymer electrolyte dispersed with SiO$_2$ nanoparticles. *Solid State Ionics, 179*, 543–549.

[21] Yarmolenko, O. V., Khatmullina, K. G., Bogdanova L. M., Shuvalova, N. I., Javadyan, E. A., Marinin, A. A., Volkov, V. I. (2014). [Effect of the addition of TiO$_2$ nanoparticles on the conductivity of mesh polymer electrolytes for lithium current sources]. *Electrochemistry*, 50, 377–386. (In Russian).

[22] Sivets, M. V. (2016). [Chemical current sources. Actual problems of energy], 644–646. (In Russian).

[23] Yu, M., Hynan, P., Jouanne, A., Yokochi, A. (2019). Current Li-Ion Battery Technologies in Electric Vehicles and Opportunities for Advancements. *Energies, 12*, 1074; doi:10.3390/en12061074

[24] Arumugam Manthiram. An Outlook on Lithium Ion Battery Technology // ACS Cent. Sci. – 2017. – 3. – P. 1063-1069.

[25] Zarubin D.P. (2017). [*Physical Chemistry*]. M.: Vyshaja shkola. (In Russian).

[26] Shevchenko, V.G. (2010). [*Fundamentals of physics of polymer composite materials*]. M.: Vyshaja shkola. (In Russian).