POLYMER MATERIALS FOR PROMISING SOLID-STATE IONIC CONDUCTORS

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Introduction

Conductivity of polymer electrolytes (PE) is believed to depend on ion carrier mobility in polymer matrix intermolecular space. This is provided by the amorphous and cross-linked polymer structure. High mobility of polymer matrix segments plays its part, which is determined both by the peculiarity of its chemical structure and availability of plasticizing additive in polymer material composition. At present, a large number of gel-like and plasticized PE which are the compositions of polymer matrix, plasticizer (aprotic solvents) and lithium salt are developed. Such systems have the conductivity ~10-3-10-4 Sm/cm at room temperature and are widely used in the composition of lithium power sources.

Increasing PE conductivity can be easily reached by increasing plasticizer content in their composition. However, this approach is ineffective due to:

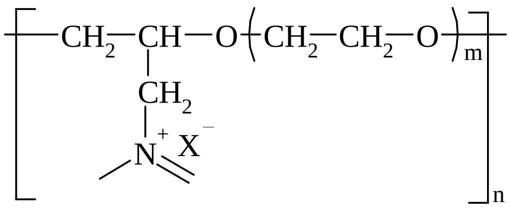
1) The limited ability of the most of polymer matrixes to hold surplus liquid plasticizer (electrolyte);
2) Decreasing physical–mechanical characteristics of polymer material with increasing liquid component content;
3) The problems connected with decreased high-temperature serviceability and the fire risk of plasticized systems.

These investigations are devoted to development of the synthesis methods and investigations of solid (solvent-free) polymer materials with a high ionic conductivity.

Experimental

We are developed the synthesis methods of polymer quaternary ammonium salts of common chemical structure:

and on their basis the solid (solvent-free, plasticizer-free) polymer materials with the conductivity ~10-3-10-5 Sm/cm within the temperature range from minus 20°C up to +100°C have been produced (see Table 1). Such materials are the compositions of polyvinylidene fluoride (PVdF), polymer quaternary ammonium salts (PQAS) and lithium salts.



In Fig.1 the typical impedance characteristics of synthesized solid PE and in the table design data of their conductivity are shown.

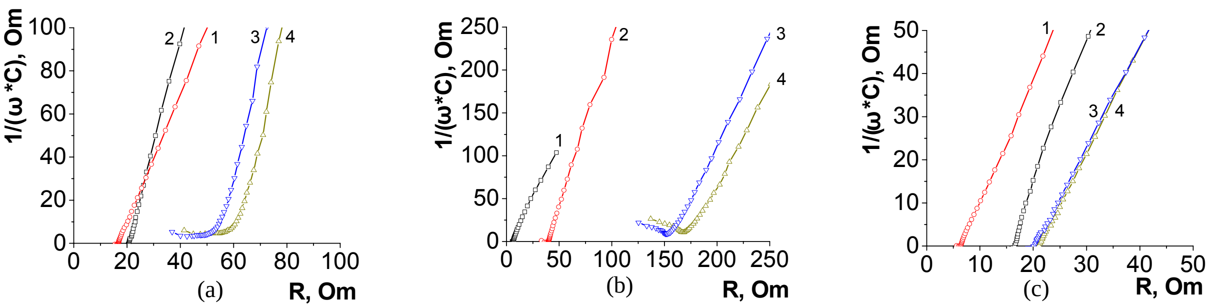


Fig.1 *Impedance characteristics of Ni-Ni systems with solvent-free solid PE: a) PVdF:PQAS:$LiClO_4$; b) PVdF:PQAS:$LiCF_3SO_3$; c) PVdF:PQAS:LiN $(CF_2SO_3)_2$ at temperatures: 1 – plus 40°C; 2 – plus 20°C; 3 – minus 17°C; 4 – minus 20°C. Mass ratio of PVdF:PQAS:lithium salt is 5:4:1.*

Table.1 *Conductivity of solvent-free solid PE (in brackets mass ratio of electrolyte components).*

Electrolyte	Conductivity, Sm/cm				
	-20°C	+20°C	+40°C	+80°C	+120°C
PVDF + PQAS + $LiClO_4$ (5:4:1)*	$0.36.10^{-4}$	$1,19.10^{-4}$	$9.40.10^{-4}$	-	-
PVDF + PQAS + $LiCF_3SO_3$ (5:4:1)	$0.134.10^{-4}$	$0.51.10^{-4}$	$3.24.10^{-4}$	-	-
PVDF + PQAS + $LiN(CF_3SO_2)_2$ (5:4:1)	$0.793.10^{-4}$	$2.49.10^{-4}$	$9.74.10^{-4}$	-	-
PVDF + PQAS + $LiN(CF_3SO_2)_2$ (5:4:2)	-	-	$2,24.10^{-4}$ (at +52°C)	$6,69.10^{-4}$	$1.5.10^{-3}$

Results and discussion

The carried out investigations have shown that the properties of such materials depend on the micro-phase division which is realized in the system PVdF:PQAS:lithium salt.

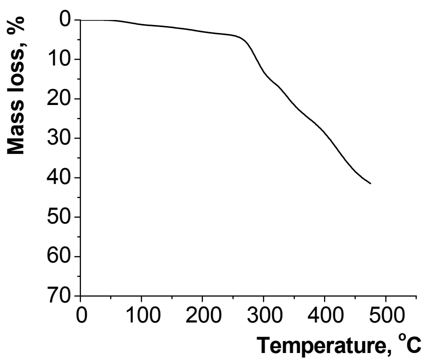


Fig. 2 *Data of thermogravimetric analysis of solvent-free solid PE: PVdF:PQAS:LiN(CF_3SO_2)$_2$ (5:4:2).*

Synthesized solid solvent-free PE are shown high thermal (Fig.2) and electrochemical (Fig.3) stability. That allows them to recommend for use in structure of high-temperature lithium power sources.

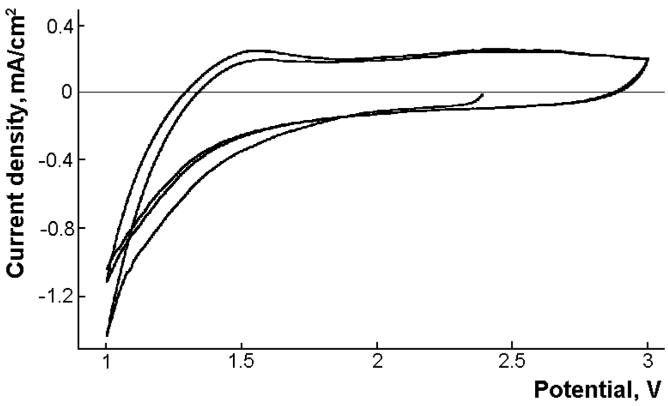


Fig. 3 *Cyclic voltammeter characteristics of solid PE: PVdF:PQAS:LiN(CF_3SO_2)$_2$ (5:4:1). Work electrode – carbon black, counter and reference electrodes – lithium. Scan rate of potential – 0.5 mV/sec.*

Conclusions

The results of the carried out investigations will be significant for creation of the theoretical basis of the synthesis of solid-state ionic conductors which can be applied for high-temperature electrolytes for Li-MnO_2 and Li-FeS_2 systems [1] and polymer electrolyte membranes (doped by inorganic acid or filed by metal oxide) for fuel cells [2].

References

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2. O.Chervakov, E.Shembel, K.Kylyvnyk, Yu.Kobelchuk, V.Ryabenko, P.Novak. Synthesis and Investigation of New Proton-Conducting Materials for Fuel Cells Membrane // 207th Meeting of The Electrochemical Society, Quebec City, Canada, May 15-20, 2005, Abstr.767.