*ISSN 1070-4272, Russian Journal of Applied Chemistry, 2014, Vol. 87, No. 12, pp. 1868−1871. © Pleiades Publishing, Ltd., 2014.*
*Original Russian Text © G.P. Dukhanin, A.N. Gaidadin, I.A. Novakov, 2014, published in Zhurnal Prikladnoi Khimii, 2014, Vol. 87, No. 12, pp. 1790−1794.*

# A Solid Polymeric Electrolyte Based on the Poly(propylene carbonate)–Lithium Perchlorate System

**G. P. Dukhanin, A. N. Gaidadin, and I. A. Novakov**

*Volgograd State Technical University, pr. Lenina 28. Volgograd, 400131 Russia*
*e-mail: lit@vstu.ru*

Received January 13, 2015

**Abstract**—Composites based on the poly(propylene carbonate)–lithium perchlorate system were prepared. Interaction in the poly(propylene carbonate)–lithium perchlorate system in a wide composition interval was studied by IR spectroscopy, differential thermal analysis, and X-ray diffraction. The specific electrical conductivity of the obtained composites was measured. In the series of studied aliphatic polycarbonates, the specific conductivity of the composites increases with an increase in the degree of branching of the polymer.

**DOI:** 10.1134/S107042721412012X

The development of new high-performance solid lithium-conducting electrolytes is a promising direction of polymeric materials science [1–4]. Replacement of a liquid nonaqueous electrolyte by a polymeric electrolyte will allow the development of fully solid-state electrochemical cell (ECC). The most widely used materials of the polymeric matrix are polyesters, polyamides, polysulfones, etc. [3, 5]. The use of many polymers in solid electrolytes is restricted by insufficient conductivity of lithium-containing composites at room temperature and elevated temperatures, and also instability of their electrochemical characteristics. Therefore, study of polymers containing electron-donor groups that are capable to interact with the lithium salt, promoting its dissociation and ensuring lithium ion transport, is a topical problem.

Aliphatic polycarbonates, e.g., poly(ethylene carbonate) (PEC) and poly(propylene carbonate) (PPC), containing complex polar groups –O–CO–O– in the backbone, are promising polymers, which are potentially capable of interaction with the lithium salt due to features of their chemical structure.

Previously [6] we studied the interaction in the PEC–lithium perchlorate system and determined the specific electrical conductivity of composites based on this system. The results of the research show that solid polymeric electrolytes (SPEs) based on poly(ethylene carbonate) exhibit conducting properties similar to those of a well-studied electrolyte, unmodified poly(ethylene oxide).

Proceeding the research in this field, we examined in this work polymeric electrolyte systems based on poly(propylene carbonate) matrices with lithium perchlorate.

## EXPERIMENTAL

IR spectroscopic, differential thermal, X-ray diffraction, and electrochemical impedance methods were applied for research. Poly(propylene carbonate) produced by AOOT Kaustik (Volgograd) was used as polymeric matrix. This polymer granules were white, soluble in acetonitrile, methylene chloride, and acetone. The molecular mass of PPC was 18580; ether units were not detected.

Methods of preparation of the polymer, the lithium salt, and the solution and preparation of films by castingwere described previously [6]. The films obtained were transparent and elastic; their thickness was 40–60 μm.

For our studies, we prepared samples of composites with the following molar ratios of poly(propylene

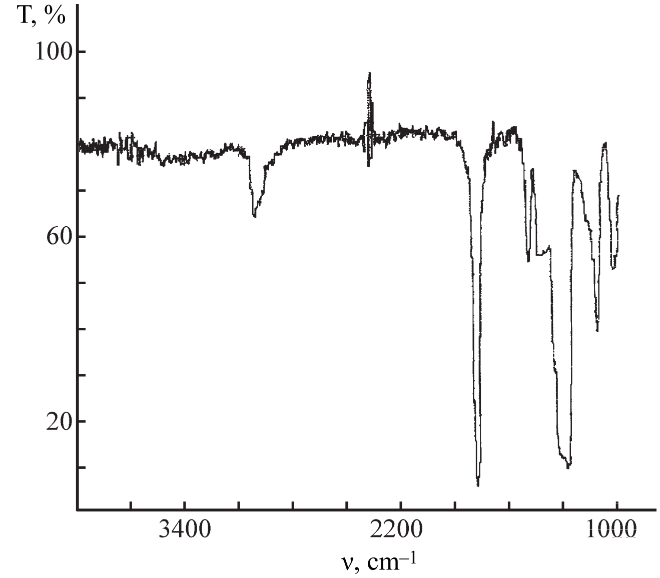

**Fig. 1.** IR spectrum of poly(propylene carbonate) containing no lithium salt. (T) Transmission and (ν) wavenumber; the same for Fig. 2.

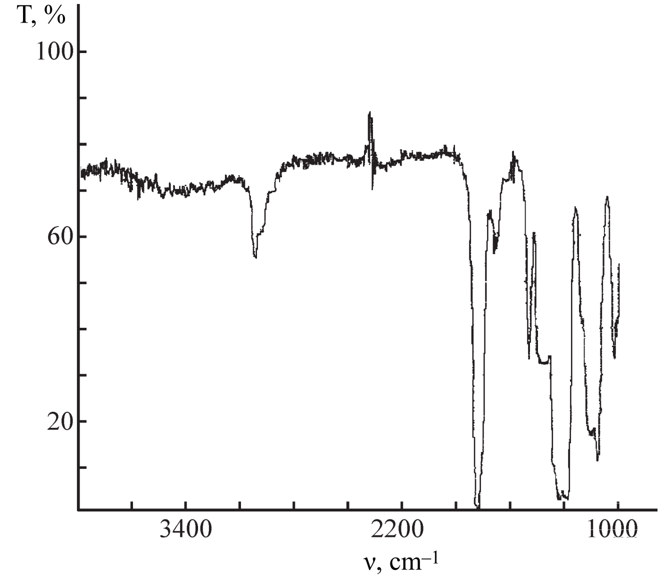

**Fig. 2.** IR spectrum of the $(PPC)_6$–$LiClO_4$ system.

carbonate) and lithium perchlorate ($[CO_3] : [Li^+]$): 50 : 1, 30 : 1, 20 : 1, 12 : 1, 10 : 1, 8 : 1, and 6 : 1.

Thermal properties of the polymer and composite films were studied with a MOM derivatograph (Hungary). The sample weight was 0.2 g, and the heating rate was 10 deg $min^{-1}$.

The IR measurements were performed with a Specord M-82 device. The spectra were taken from acetonitrile solutions.

X-ray diffraction analysis of samples was performed with a DRON-3 diffractometer using Fe-filtered $CuK_\alpha$ radiation. Samples were taken as 5-mm-thick plates.

The electrical conductivity of the samples was measured by the electrochemical impedance method in the frequency interval from 12 Hz to 100 kHz using an LCR-819 immittance meter (Goodwill Instek) in a sealed two-contact cell with blocking stainless steel electrodes. All the manipulations on the preparation of films and samples for analyses and measurements were performed under the conditions that exclude moisture in the films.

## RESULTS AND DISCUSSION

The maximum solubility of $LiClO_4$ in PPC at 298 K was determined by X-ray diffraction analysis and optical microscopy. At a lithium content in the polymer higher than the ratio $[CO_3] : [Li^+] = 6 : 1$, a free salt phase appears in the system, and it is no longer homogeneous. As a result, the physicomechanical properties of the polymeric film are drastically deteriorated, and there is no sense in studying them.

The parameters of the heat resistance of PPC in comparison with PEC were studied by differential thermal analysis. The decomposition temperature of the PPC is 481 K, whereas for PEC it is 463 K [6]. The activation energy of thermal degradation (kJ $mol^{-1}$), determined by the Freeman–Carroll method [7], was 49.5 for PEC and 96.4 for PPC. Similar relationship is observed for the composites with lithium perchlorate in the entire examined concentration range. Thus, poly(propylene carbonate) matrices exhibit the required stability for ECCs operating at ambient temperatures or close to them. Degradation of the polymer in an inert atmosphere is accompanied by the release of gaseous $CO_2$ and $H_2O$, and, in the presence of oxygen in the gas phase, the release of the monomer was also observed.

The IR spectrum of poly(propylene carbonate) is shown in Fig. 1. The effect of lithium perchlorate on the IR spectrum of the polymer is demonstrated in Fig. 2.

As seen from Figs. 1 and 2, both the polymer and its composite with lithium perchlorate are characterized by a peak at 1748 $cm^{-1}$, corresponding to vibrations of the –O–CO–O– group. Introducing lithium perchlorate into the polymer causes a noticeable shift in signal at 1648 $cm^{-1}$. This peak increases as the lithium salt concentration is increased, which indicates that lithium

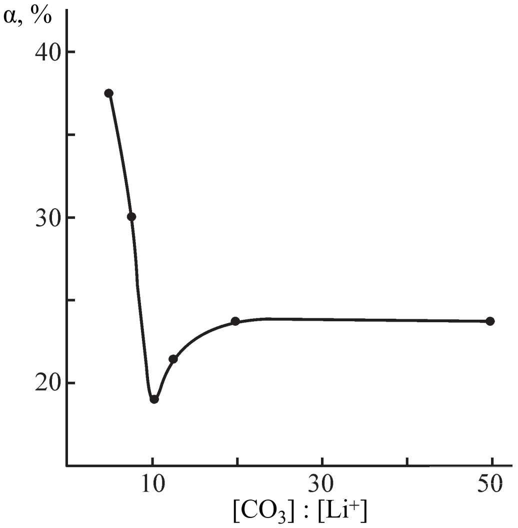

**Fig. 3.** Degree of crystallinity α of the composites as a function of the $[CO_3] : [Li^+]$ molar ratio.

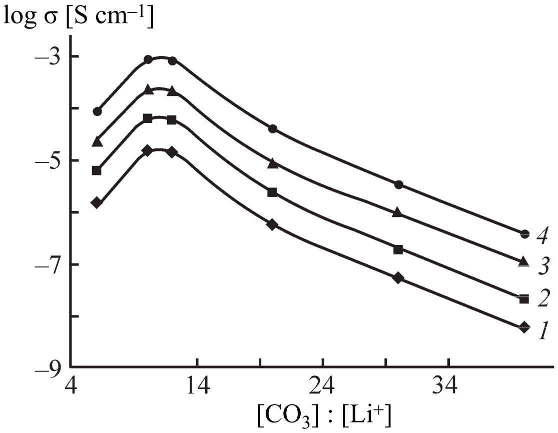

**Fig. 4.** Specific electrical conductivity σ of the PPC–$LiClO_4$ system as a function of the $[CO_3] : [Li^+]$ molar ratio. *T*, K: (*1*) 298, (*2*) 313, (*3*) 333, and (*4*) 353.

cations interact with lone electron pairs of oxygen atoms of carbonyl groups to form the complexes. Such interaction can lead to dissociation of lithium perchlorate in the polymeric composite. The formation of complexes in the PPC–$LiClO_4$ system is confirmed by the results of X-ray diffraction analysis, according to which the degree of crystallinity of the composites as a function of the salt content passes through a minimum (Fig. 3).

Initially introducing the salt into the polymer, causes the decrease in the relative amount of the crystalline phase. Thus, the degree of crystallinity of the polymer is 36%. As the $LiClO_4$ content is increased to the $[CO_3] : [Li^+]$ molar ratio of 10 : 1, the degree of crystallinity sharply decreases, reaching 19%, which indicates that the relative amount of the amorphous phase in the polymeric composite considerably increases. This can be favorable for the conductivity. Further increase in the salt concentration leads to a monotonic increase in the degree of crystallinity of the composite. These trends are apparently associated with the fact that addition of the first portions of lithium perchlorate leads to a decrease in the degree of association of macromolecular chains. Then, as the salt concentration is increased further, another kind of ordering of structural elements arises. The new elements are, apparently, lithium ions surrounded by the carbonate groups –O–CO–O– of the macromolecules, like a chelate complexes.

The results obtained are well consistent with the concept formulated in [8] that the SPE conductivity increases as the content of amorphous components in the matrix is increased or as low-molecular-mass additives are introduced. In our case, the mobility of the monomeric segment increases, the coordination of –O–CO–O– groups with the lithium ion is facilitated, and the transport and hence the electron density conductivity in the composite matrix are enhanced.

The results of measuring the specific electrical conductivity of the electrolytes in the temperature interval 298–353 K at the $[CO_3] : [Li^+]$ molar ratios from 30 : 1 to 6 : 1 are shown in Fig. 4.

The isotherms of the concentration dependences of the specific electrical conductivity of the electrolytes pass through a maximum. The maximal conductivity is observed for the composites of the composition $[CO_3] : [Li^+] = 10 : 1$ at all the examined temperatures. At 298 K, the conductivity of the system is $2.45 \times 10^{-5}$ S cm$^{-1}$. Further increase in the lithium salt content leads to a decrease in the specific electrical conductivity. At temperatures higher than 298 K, the concentration dependences are similar. At 353 K, the maximal conductivity of the system is $1.45 \times 10^{-3}$ S cm$^{-1}$.

The presence of a maximum at a certain ratio of the components is apparently due to the fact that the decreased degree of crystallinity of the composite of the composition $[CO_3] : [Li^+] = 10 : 1$, suggesting increased content of the amorphous phase in the system, facilitates the ion transport. As a result, the electrical conductivity of the SPE increases [9]. The electrical conductivity of the SPE based on poly(propylene carbonate) is somewhat higher than that of the composites based on poly(ethylene carbonate) [6]. The higher branching of the PPC macromolecule, leading to the decreased degree of crystallinity, facilitates the charge transport in the matrix. In addition, the presence of $–CH_3$ group in the poly(propylene carbonate) macromolecule can facilitate the dissociation of lithium perchlorate in the polymeric matrix.

It follows from Fig. 5 that the temperature dependence of the conductivity is described by the Arrhenius equation $\sigma = (A/T)\exp(-E_a/RT)$ for all the composites studied. The activation energy of the electrical conductivity, $E_a$, varies depending on the lithium salt concentration in the polymeric matrix. The system of the composition $[CO_3] : [Li^+] = 10 : 1$, having the maximal specific electrical conductivity, is characterized by the lowest activation energy, 62.74 kJ mol$^{-1}$. As the salt concentration in the polymeric matrix is decreased, the activation energy of the specific electrical conductivity increases, reaching 67.01 kJ mol$^{-1}$ for the composite of the composition $[CO_3] : [Li^+] = 30 : 1$.

The difference in the activation energies of the conductivity suggests changes in the ionic structure of the polymeric electrolytes with variation of the salt content of the polymeric matrix. The local structures formed in the SPE in different concentration and temperature intervals of the polymer–salt system are determined by the ion solvation and association processes. Different structures of the macromolecular ionic solution can generate different mechanisms of ionic transport, which, in turn, determines the overall conductivity of the electrolyte [10].

## CONCLUSIONS

(1) Solid polymeric electrolytes based on poly(propylene carbonate) exhibit better conducting properties compared to those based on poly(ethylene carbonate).

(2) The dependences of the degree of crystallinity and specific conductivity of the composites on the lithium perchlorate content pass through extrema. Composites of the composition poly(propylene carbonate) : $LiClO_4$ = 10 : 1 exhibit the highest conductivity.

(3) The temperature dependence of the electrical conductivity of the composites is described by the Arrhenius equation. The activation energies of the conductivity for all the composites were calculated, and their dependence on the lithium perchlorate concentration was determined.

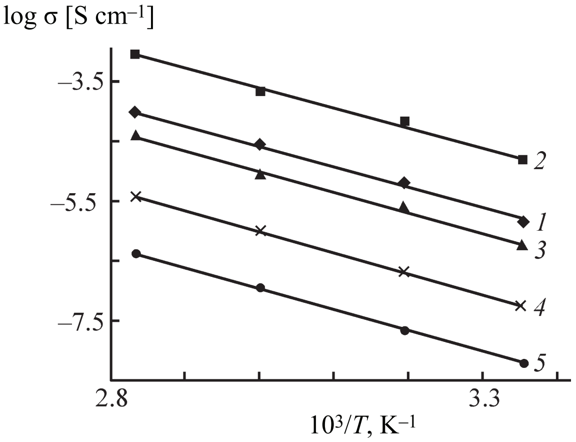

**Fig. 5.** Specific electrical conductivity σ of the PPC–$LiClO_4$ system as a function of temperature *T*. $[CO_3] : [Li^+]$: (*1*) 6 : 1, (*2*) 10 : 1, (*3*) 20 : 1, (*4*) 30 : 1, and (*5*) 40 : 1.

## REFERENCES

1. Baskakova, Yu.V., Yarmolenko, O.V., and Efimov, O.N., *Russ. Chem. Rev*., 2012, vol. 81, no. 4, p. 367.
2. Hallinan, D.T. and Balsara, N.P., *Annual Rev. Mater. Res*., 2013, vol. 43, pp. 503–525. DOI: 10.1146/annurev-matsci-071312–121705.
3. Kolosnitsyn, V.S., Dukhanin, G.P., Dumler, S.A., et al., *Russ. J. Appl. Chem*., 2005, vol. 78, no. 1, pp. 1–18.
4. Yarmolenko, O.V. and Khatmullina, K.G., *Al'tern. Energet. Ekol*., 2010, no. 3, pp. 59–76.
5. Scrosati, B., *Applications of Electroactive Polymers*, New York: Chapman & Hall, 1993.
6. Dukhanin, G.P., Dumler, S.A., Sablin, A.N., et al., *Russ. J. Appl. Chem*., 2009, vol. 82, no. 2, pp. 243–246.
7. Wendlandt, W.W.M., *Thermal Methods of Analysis*, New York: Wiley–Interscience, 1974.
8. Chebotarev, V.P., Smirnov, S.E., and Komkov, V.A., *Plast. Massy*, 2003, no. 11, pp. 7–9.
9. Zhukovskii, V.M., Bushkova, O.V., Lirova, B.I., et al., *Ross. Khim. Zh*., 2001, vol. 45, no. 4, pp. 35–41.
10. Manning, Y. and Frech, R., *Polymer*, 1992, vol. 33, pp. 3487–3490.