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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Solid Polymeric Electrolyte Based on Poly(ethylene carbonate)–Lithium Perchlorate System

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Abstract—Interaction in the poly(ethylene carbonate)–lithium perchlorate system was studied by means of IR spectroscopy and differential-thermal and X-ray structural analyses. The electrical conductivity of the composites obtained was measured.

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A study of composites constituted by a polymer and a lithium salt is of interest in view of the development of solid polymeric electrolytes (SPE) for lithium and lithium-ion chemical power cells (CPCs) [1–3]. Replacement of a liquid nonaqueous electrolyte with a polymeric electrolyte makes it possible to design a completely solid-phase CPC and to obviate a number of technological and performance problems. Polyesters, polynitriles, polyamides, polysulfones, and other polymeric materials serve as polymeric matrices [4]. At present, wide use of SPE in CPCs is hindered by the low room-temperature conductivity of the electrolytes and instability of their electrochemical parameters in the course of time. Therefore, development of lithium-conducting polymeric electrolytes with good transport properties at ambient temperatures, stable phase composition, and satisfactory physicomechanical characteristics is a topical task.

It is known [2] that, in development of an SPE, the polymeric system should possess a rather high dielectric constant and solvating capacity with respect to various ions. These properties are characteristic of functional polymers whose molecules contain electron-donor and electron-acceptor groups. Aliphatic polycarbonates, e.g., poly(ethylene carbonate) (PEC) are of particular interest because units of this polymer (–CH_2–CH_2–O–CO–O–) are similar in their chemical nature to low-molecular-weight cyclic carbonates (ethylene carbonate and propylene carbonate), which are dipolar aprotic solvents with high dielectric constant, used to prepare nonaqueous lithium-conducting electrolytes. In addition, this PEC belongs to biodecomposable polymers [5], which simplifies its utilization.

This communication presents the results of a study of polymer–electrolyte systems based on PEC matrices with lithium perchlorate.

EXPERIMENTAL

The study was performed using IR spectroscopic, differential-thermal, X-ray diffraction techniques and the electrochemical-impedance method. As the polymeric matrix served PEC manufactured by Kaustic Open Joint-Stock Company (Volgograd). The polymer was in the form of white grains soluble in acetonitrile, methylene chloride, and acetone. The molecular mass of PEC was 152300, it contained no ether units, and had the following residual content of mineral impurities (ppm): ash 11.0, Zn 2.8, Fe 5.4, Ni < 1.0, and Cr < 1.0.

Before preparing a solution, the polymer was subjected to stepwise heating in a vacuum drying oven from 293 to 383 K in the course of 3 h and then was kept at 383 K for 3 h. Lithium perchlorate of chemically pure grade was dried at 403–423 K for 2 h, melted, and kept at 533–543 K for 3 h (under a vacuum during the last hour). Acetonitrile of chemically pure grade, dried and distilled with P_2O_5, served as a solvent. Polymeric films were produced by dissolution of calculated amounts of the polymer and dry lithium salt in acetonitrile to give a 15–20% solution. A homogeneous solution was cast onto a glass substrate. The resulting film was dried in a vacuum oven at 293–298 K for 24 h, then the temperature was elevated in steps to 373 K and the film was kept for a long time at the same temperature under dynamic vacuum

Table 1. Destruction onset point of PEC at varied content of $LiClO_4$ in the composite

PEC : $LiClO_4$ molar ratio	Destruction onset point, K
Pure polymer	463
50:1	453
20:1	428
10:1	413
6:1	403

conditions. The absence of water and the solvent in the SPE films was verified by IR spectroscopy. The resulting films were transparent and elastic, their thickness was 40–60 μm. Samples with the following molar ratios of the components, PEC and LiClO4, were fabricated ($[CO_3]$: $[Li]^+$): 50 : 1, 30 : 1, 20 : 1, 14 : 1, 12 : 1, 10 : 1, 8 : 1, and 6 : 1.

The thermal properties of the polymer and composite films were studied with a MOM derivatograph (Hungary). The sample mass was 0.2 g, and the heating rate, 2.5 deg min^{-1}. The IR spectral studies were carried out on a Specord-M82 instrument, with samples in the form of solutions in acetonitrile.

The X-ray structural analysis of the samples was made with a DRON-2 diffractometer with CuK_α radiation and an iron filter on samples in the form of 5-mm-thick plates. The electrical conductivity was measured by the electrochemical-impedance method in the frequency range from 12 Hz to 100 kHz with a Goodwill Instek LCR-819 immitance meter in a hermetically sealed two-contact cell with stainless steel blocking electrodes. All procedures for film deposition and sample preparation for analyses and measurements were performed under conditions ruling out ingress of moisture into the films.

Because phase equilibria in the system constituted by a polymer and a lithium salt predetermine, on the whole, the transport properties of polymeric electrolytes, the limiting solubility of $LiClO_4$ in PEC at 298 K was determined by means of X-ray structural analysis and optical microscopy. It was found that, at a lithium perchlorate content of the polymer exceeding $[CO_3]$: $[Li]^+ = 6 : 1$, a free salt phase appears in the system, which thereby ceases to be homogeneous. This markedly impairs the physicomechanical properties of the polymeric film and makes inappropriate their study.

The differential-thermal and thermogravimetric analytical methods were used to assess the stability of the SPE under study against thermo-oxidative destruction at different salt contents of the electrolyte. The results obtained are listed in Table 1.

It was found that the PEC containing no lithium perchlorate is stable against thermal destruction up to 463 K. Introduction of $LiClO_4$ into the polymeric matrix results in a chemical interaction of the oxidizing agent with the polymer, which substantially diminishes the thermal stability of the composite. Raising the lithium perchlorate content of the composite to the maximum possible value (6 : 1) at which the system still remains homogeneous results in that the destruction temperature of the polymer decreases to 403 K. The thermal stability of PEC-based electrolytes is poorer than that of composites with polyethylene oxide or poly(trimethylene carbonate) [6]. However, PEC matrices have stability required for CPCs working at, or near, the ambient temperatures.

To analyze the physicochemical interaction of PEC with lithium perchlorate, IR spectroscopic studies were carried out in a wide range of concentrations. An analysis of the resulting IR spectra of the PEC–$LiClO_4$ system demonstrated that introduction of lithium perchlorate changes the intensity and characteristic frequencies of vibrations of some atomic groups. This indicates that there is a physicochemical interaction of the polymer with the salt. Particular attention was given to vibrations of the carbonyl group and C–O–C ester bond in PEC, which can enter into coordination interactions with positively charged ions [7] because of the lone electron pairs of oxygen atoms. It was found that the positions of the absorption bands associated with the C–O–C bond of the ester group in IR spectra of both the pure polymer and composites containing lithium perchlorate are nearly identical and independent of the amount of the salt, with the intensities of the absorption bands associated with the bond remaining unchanged. Another pattern is observed in the case of stretching vibrations of the carbonyl group of PEC. For PEC samples containing no lithium salt, the characteristic band associated with stretching vibrations of the carbonyl group is observed at 1748 cm^{-1}. Introduction of lithium perchlorate into the polymeric matrix results in that the band splits in two, with a second band appearing at 1630–1650 cm^{-1} (Table 2).

An increase in the salt content of the system results in that the intensity of the first absorption band at ~1750 cm^{-1} gradually decreases and its position is somewhat shifted to smaller wave numbers. At the same time, the intensity of the second absorption band increases and its position is shifted to higher frequencies.

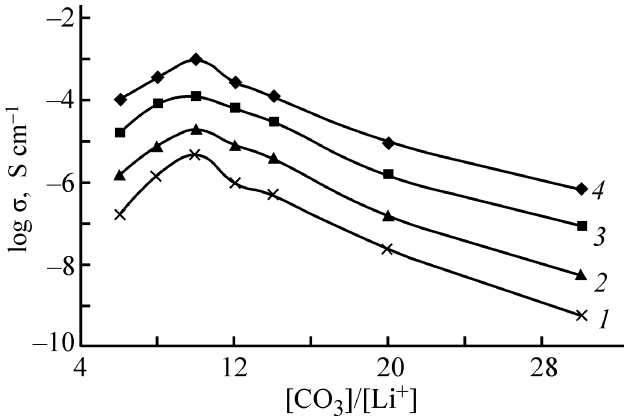
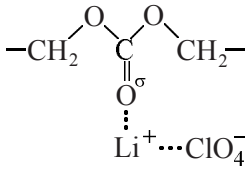


Fig. 1. Electrical conductivity σ of the PEC–$LiClO_4$ system vs. the salt content. ($[CO_3]$: $[Li]^+$) Molar ratio. *T* (K): (*1*) 298, (*2*) 313, (*3*) 333, and (*4*) 353.

This apparently indicates that lithium cations enter into interaction with the lone electron pairs of oxygen atoms in carbonyl groups to give complexes of the type



This interaction leads to dissociation of lithium perchlorate in the polymeric composite. The formation of complexes in the PEC–$LiClO_4$ system is confirmed by X-ray diffraction analysis [8].

It was found that the dependence of the crystallinity of the composites on the content of lithium perchlorate has an extremum. Initially, introduction of the salt into the polymer leads to a decrease in the content of the crystalline phase. The crystallinity of the composites reaches the minimum values when the polymer contains $LiClO_4$ in molar ratios $[CO_3]$: [Li]+ of 12 : 1 and 10 : 1 and then, as the salt content is raised further, substantially increases. Apparently, this occurs because there are no transverse C–C bonds between the macromolecular chains of this polymer and, after small amounts of lithium perchlorate is introduced, the degree of association of the macromolecular chains decreases. Then, as the content of lithium perchlorate is raised, there appears another arrangement of structural elements, whose centers are, apparently, lithium ions framed, as in "chelate complexes, by –O–CO–O– carbonate groups contained in the macromolecule.

The results obtained when measuring the electrical conductivity of the electrolytes in the temperature range

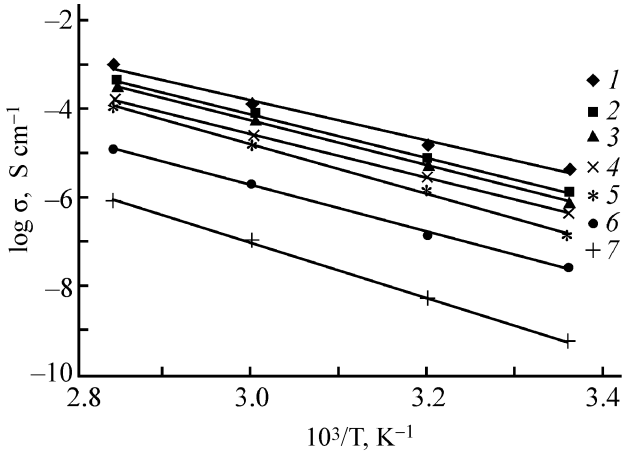


Fig. 2. Electrical conductivity σ of the PEC–$LiClO_4$ system vs. temperature *T*. $[CO_3]$: $[Li]^+$: (*1*) 10 : 1, (*2*) 8 : 1, (*3*) 12 : 1, (*4*) 14 : 1, (*5*) 6 : 1, (*6*) 20 : 1, and (*7*) 30 : 1.

298–353 K with composite samples with $[CO_3]$: [Li]+ molar ratios in the range from 30 : 1 to 6 : 1 are presented in Fig. 1. The isotherms of the concentration dependences of the electrical conductivity of the electrolytes have an extremum. The maximum conductivity is observed for electrolytes with $[CO_3]$: $[Li]^+$ = 10 : 1 in the entire temperature range studied. At 298 K, the conductivity of this system has a value of 4.93×10^{-6} S cm^{-1}. Further increase in the content of the lithium salt to $[CO_3]$: $[Li]^+$ = 6 : 1 leads to a decrease in the electrical conductivity to 1.86×10^{-7} S cm^{-1}. At temperatures higher than 298 K, the run of the concentration dependences remains the same. The highest conductivity of the system under study at 353 K is 9.62×10^{-4} S cm^{-1}.

The maximum is apparently observed at a certain molar ratio because the decrease in the crystallinity for systems with $[CO_3]$: $[Li]^+$ of 10 : 1 and 12 : 1, indicating that the amount of the amorphous phase in the system

Table 2. Characteristic absorption bands associated with stretching vibrations of >C=O in IR spectra of the system constituted by poly(ethylene carbonate) and lithium perchlorate

PEC : $LiClO_4$ molar ratio	Vibration frequency, cm^{-1}
Individeal polymer	1748
50:1	1748; 1628
20:1	1746; 1630
12:1	1744; 1633
10:1	1744; 1636
8:1	1752; 1644
6:1	1748; 1652

increases, favors the ionic transport and leads to a higher electrical conductivity of SPEs [9].

It follows from the data in Fig. 2 that the temperature dependence is described by the Arrhenius equation $\sigma = A/T \exp(-E_a/RT)$ for all of the composites studied. The graphically calculated activation energy of electrical conductivity, E_a, varies with the concentration of the lithium salt in the polymeric matrix. The lowest activation energy of 83.88 kJ mol^{-1} is observed for the system with $[CO_3] : [Li]^+ = 10 : 1$, which has the highest electrical conductivity. A decrease in the salt concentration in the polymeric matrix makes the activation energy of electrical conductivity higher, 116.93 kJ mol^{-1} for the composite with $[CO_3] : [Li]^+ = 30 : 1$. However, the activation energy is also high for composites with high content of the salt: 101.34 kJ mol^{-1} at $[CO_3] : [Li]^+ = 6 : 1$.

The difference in the values of the activation energy of conductivity may indicate that the ionic structure of the polymeric electrolytes under study varies with the salt content of the polymeric matrix. Local structures formed in SPEs in various concentration and temperature ranges of the polymer–salt system are determined by ion solvation and association processes. Different structures of the macromolecular ionic solution may give rise to different mechanisms of ion transport, which, in turn, determines the total conductivity of the electrolyte.

It has been found previously [10] that, as the salt concentration in the polymolecular matrix (SKN-40) increases, the ionic structure of the solid polymeric electrolyte regularly varies: full dissociation, then appearance of ion pairs, steep increase in their number (at medium salt concentrations), and, further, formation of high-order ionic associates and gradual appearance of a separate salt phase (at high concentrations). Apparently, the existence of concentration ranges with different types of ion association and, consequently, with different ion transport mechanisms is natural for solid polymeric electrolytes based on composites of this kind.

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