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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Behavior of 4-Methyl-2-phenyl-5,6-tetramethylenethiopyrilium Perchlorate at the Interface with β-Alumina

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Abstract—Dependences of the current density of electrochemical reduction of 4-methyl-2-phenyl-5,6-tetramethylenethiopyrilium perchlorate on the potential, rate and duration of cathodic polarization, and content of carbon black in the electrode were studied.

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A large group of ionic crystals with predominantly electronic conduction is formed by so-called "organic metals", salts of cation radicals whose representatives are salts of tetrathiofulvalene and its derivatives and of their selenium-containing analogs with various halide, complex fluoride, and organic anions. Compounds of this kind have high conductivity at room temperature and lower temperatures; some of these compounds may pass to the superconducting state upon a decrease in temperature. A fundamental area of research into the electrochemistry of these salts consists in describing the equilibrium and transport properties of these materials in terms of ion–ion and ion–lattice interactions.

The application field of electrically active organic materials based on heterocyclic compounds extends beyond a simple replacement of metals and includes the use of these materials as conductors, super-conductors, semiconductors, batteries, transistors, sensors, light-emitting diodes, and related electro-chromic materials, which is of particular commercial importance [1, 2].

A search for new electrochemical systems for development of high-efficiency miniature solid-phase chemical power cells (CPCs) is an important task. Promise is shown by electrochemical systems with alkaline metals (lithium, sodium) as the working substance of the anode; solid electrolyte based on β-alumina, with conduction by alkali metal ions; and ionic organic salts as the cathode [3–8]. Compounds of the type of β-alumina, $Na_2O{\cdot}nAl_2O_3$ ($n = 5–11$), belong to superionics. The ionic transport in their hexagonal layered crystal lattice occurs along the planes in which sodium and oxygen ions are localized, because only one third of positions accessible to cations is occupied. The parallel planes are surrounded by spinel-like oxide-aluminum fragments. The electrical conductivity of β-alumina (~1 S m^{-1} at 273 K) increases upon doping with various cations or appearance of small displacements of sodium cations relative to the plane in which lie oxygen atoms bonded to these ions, with the 2D nature of conduction preserved [9].

Ionic organic salts belong to organic semiconductors and are charge-transfer complexes. In these complexes, organic cations of thioxanthilium, thiochromilium, or thiopyrilium are combined via ordinary exchange reactions with various inorganic anions (Cl^-, ClO_4^-, $FeCl_4^-$, BF_4^-, I^-, $H_2PO_4^-$, $H_2PO_3^-$) [3–8]. Many of these salts and their derivatives have found use as biologically active substances, medicinal preparations, valuable dyes, indicators, and sensitizers. The specific distribution of the electron density of a heteroatom over the aromatic ring system and the specific crystal structure provide transport of both electrons and ions in compounds of this type [8, 10–12]. The high electrochemical activity and the conductivity on the order of 10^{-2}–10^{-6} S cm^{-1} make it possible to regard these compounds as promising cathode materials for energy converters and information processing devices.

Models adequately describing mechanisms of processes occurring in solid-phase systems constituted by an alkali metal, solid electrolyte, and organic semiconductor have almost not been reported in the literature. According to [3–8], the cathodic reduction of organic salts of the type under consideration occurs in two stages corresponding to an irreversibly intra- and intermolecular charge transfer, followed by a chemical reaction. To substantiate the two-electron mechanism of charge transfer, followed by a chemical transformation, it is necessary to accumulate new data and to systematize evidence concerning the electrochemical properties of these compounds.

Preliminary studies have shown [13–15] that the electrical characteristics of cathodes based on organic salts strongly depend on the nature and concentration of an additive contained in the working substance of the cathode and on the polarization rate and duration of an open-circuit storage. The reasons for these effects are unclear. The lack of systematic studies in this area gives no way of passing to the solution of technological problems in development of electrodes based on ionic organic salts for solid-phase chemical power cells. Therefore, studying the electrochemical properties of salts of thiopyrilium and its derivatives at the interface with a solid electrolyte and finding the relationship between the potential, current density, and composition of the cathode material are of scientific value and practical importance.

EXPERIMENTAL

As objects of the study served electrodes made of an ionic organic salt, 4-methyl-2-phenyl-5,6-tetramethylenethiopyrilium perchlorate, with addition of carbon black and a β-alumina (sodium polyaluminate $Na_2O \cdot nAl_2O_3$) solid electrolyte with conduction by sodium ions and high cationic conductivity, which is the reason why a ceramic on its basis is promising as a solid electrolyte for CPCs with various electrochemical systems [16–18]. 4-Methyl-2-phenyl-5,6-tetramethylenethiopyrilium perchlorate was synthesized using the procedure described in [19]. For this purpose, a suspension of 0.04 mol of a diketone in 50 ml of glacial acetic acid was saturated with hydrogen sulfide for 1.5–2 h at a constant feed rate and 20–25 ml of 70% perchloric acid was added dropwise in the course of 2 h. After the whole amount of $HClO_4$ was added, hydrogen sulfide was passed for additional 2 h. The reaction mixture was allowed to stand for 24 h and then was diluted with ethyl ether. Crystalline 4-methyl-2-phenyl-5,6-tetramethylenethiopyrilium perchlorate was filtered off and reprecipitated. The yield of the product was 67%. To prepare electrodes, the salt in the form of a finely crystalline powder was mixed with a graphitized thermal carbon black of Sterling MT brand with a specific surface area $S_{sp} = 7.6$ m^2 g^{-1} and particle diameter of 0.16–0.20 mm.

According to its structure and physicochemical properties [19], the ionic organic salt under study must possess an electrochemical activity and can be used as a cathode in solid-electrolyte CPCs. Here, the thiopyrilium cation acts as a charge carrier. The composition of the salt synthesized was determined by elemental analysis. Electrochemical studies were performed with a P-5848 potentiostat combined with a KSP-4 self-recorder. The discrepancy between the currents and potentials in parallel runs did not exceed 3 and 5%, respectively. In cases of a poorer reproducibility, the number of runs was raised to six.

Potentiodynamic curves were measured at potentials of 0 to 4 V (relative to a sodium reference electrode at linear potential sweep rates of 80, 40, 20, 8, 4, and 2 mV s^{-1}). Galvanostatic measurements were made at current densities of 15, 25, 45, and 65 μA cm^{-2}. The ionic organic salt (working substance of the cathode) was thoroughly ground in a porcelain mortar for 15–20 min to a homogeneous state, mixed with carbon black in a prescribed ratio, and again thoroughly ground for 30 min. The resulting homogeneous mass was placed in the cell. The following ratios between the thiopyrilium salt and graphitized carbon black in the working substance of the cathode were used: 95 : 5, 90 : 10, 85 : 15, 80 : 20, 70 : 30, 50 : 50, and 30 : 70 (wt %). The solid electrolyte was prepared for an experiment as follows. Edge surface of a β-alumina pellet were mechanically polished to mirror shine, wiped with cotton cloth, and calcined in air at a temperature of 800°C for 2 h. Then the pellet cooled to 80–100°C was transferred into a box filled with dry argon, in which the cell was assembled.

As the auxiliary electrode served a plate of metallic sodium. As the reference electrode was used an electrode cut in the form of a “wire” from metallic sodium. The electrode was introduced into the electrolyte pellet from the lateral side through an opening in the cell and fixed with a holddown screw. The pellet of sodium β-alumina was placed in a cell case made of polymethyl methacrylate [GOST (State Standard) 10667–63], sealed with a fluoroplastic ring,

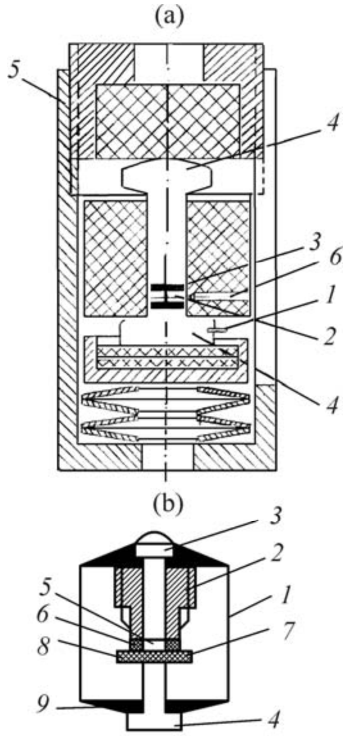


Fig. 1. Schematic of the electrochemical cell. (a) (*1*) Current leads, (*2*) electrode, (*3*) electrolyte, (*4*) die, (*5*) "bomb" case, (*6*) reference electrode; (b) (*1*) case, (*2*) nut, (*3, 4*) titanium die, (*5*) anode mass, (*6*) fluoroplastic seal, (*7*) electrolyte membrane, (*8*) cathode mass, and (*9*) sealant.

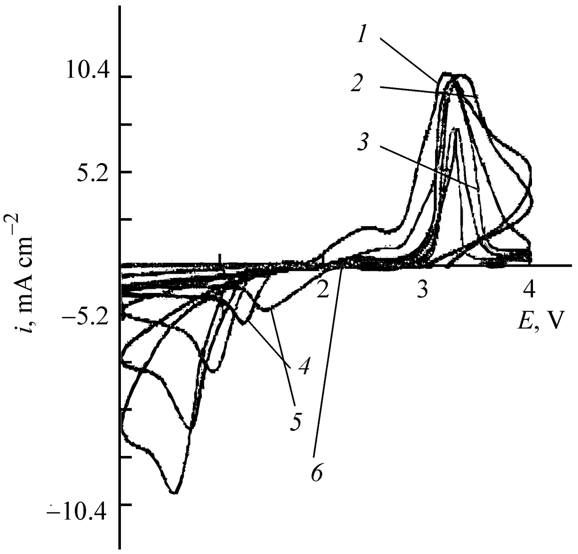


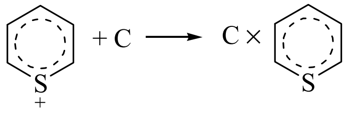
Fig. 2. Cyclic potentiodynamic curves of the electrode under study at different potential sweep rates. Carbon black content 30 wt %, compaction pressure 10 kg cm^{-2}. (*i*) Current density and (*E*) potential; the same for Fig. 3. Potential sweep rate (mV s^{-1}): (*1*) 80, (*2*) 40, (*3*) 20, (*4*) 8, (*5*) 4, and (*6*) 2.

and tightened with a nut. Then, a finely ground homogeneous mixture of the ionic organic salt and carbon black was compacted onto one side of the electrolyte pellet, and a metallic sodium plate was pressed to the other side of the pellet with the second die. The assembled cell was embedded in a sealant of the following composition (wt %): rosin 49, paraffin 49, and natural rubber the rest, and mounted in a compression device providing a clamping pressure of 9.81×10^6 Pa. The electrochemical cell is shown schematically in Fig. 1.

The temperature of 20°C was maintained with a *T* 2/77 thermostat. To create a dry atmosphere, a vessel with a water-absorbing substance was placed in the box and the box was thoroughly sealed and filled with dry argon. Phosphorus pentoxide was used as the water-absorbing substance. The appearance of moisture in the box was judged from the onset of melting of phosphorus pentoxide, which occurs as a result of its interaction with water. The following techniques were used in the study: chronovoltammetry with a linear potential sweep, method of galvanostatic curves, and electron spin resonance (ESR) spectroscopy. All the potentials are given relative to the sodium reference electrode. An X-ray diffraction analysis was made on a DRON-3.0 diffractometer in order to study phase transformations occurring as a result of the electrochemical treatment.

Initially, a cyclic chronovoltammetry of 4-methyl-2-phenyl-5,6-tetramethylenethiopyrilium perchlorate at the interface with sodium β-alumina was performed. Figure 2 shows potentiodynamic curves (chronovoltammograms) of 4-methyl-2-phenyl-5,6-tetramethylenethiopyrilium perchlorate at different potential sweep rates at the interface with sodium β-alumina. It can be seen from the run of the potentiodynamic curves that the electrochemical reduction of the thiopyrilium salt is characterized by the maximum current in the cathodic half-cycle. After the current reversal in the cathodic region, the peak disappears; however, there is a bend in the reverse curve at the potential of this peak. In the anodic range of potentials, a second peak is recorded in the anodic half-cycle of the potentiodynamic curve, to which a bend also corresponds in the reverse curve. Thus, a single cathodic process occurs under cathodic polarization at potentials ranging from 0 to 2.2 V. The ESR spectra reported in [13] demonstrate that an organic cation radical of 4-

methyl-2-phenyl-5,6-tetramethylenethiopyrilium is formed at the cathode under these conditions. Upon a current reversal in the anodic direction, a reverse process occurs, in which the product formed in the cathodic reaction is oxidized to the starting cation. In the anodic range of potentials, carbon black s oxidized to give an intercalation compound with an organic cation.



The formation of the intercalation compound was found already in the absence of a current, by a simple mechanical grinding. The intercalation compound facilitates the cathodic reduction of the organic salt and transfers this processes to the diffusion mode. This is confirmed by the fact that the dependences of the peak current Imax on a square root of the potential sweep rate $\sqrt{v_{sw}}$ are linear. The run of the cyclic potentiodynamic curves of electrodes compacted at a pressure of 12.5–15 kg cm^{-2} is similar to that shown in Fig. 2. The only difference is that the rate of the electrochemical process increases with the electrode compaction pressure.

This understanding of the experimental data is consistent with the dependence of the run of cyclic potentiodynamic curves on the amount of carbon black in the electrode (Fig. 3), found in the next stage of the study. As the amount of carbon black increases from 10 to 50 wt %, the current density at the peaks of the potentiodynamic curves in the cathodic and anodic half-cycles grows. The decrease in the current density at the electrode at a higher content of carbon black can be attributed to supersaturation of the salt structure with carbon black particles. Thus, carbon black plays an important part in solid-phase transformations at the electrode made of the ionic organic salt: it not only facilitates the electric current transport, but also exerts a catalytic influence on the process of reduction of the ionic organic salt through the formation of an intercalation compound being formed. From this standpoint, the increase in the current density at the electrode in multiple cycling (>10 cycles) can be attributed to accumulation of the intercalation compound and to an increase in its formation rate because of the rise in the number of surface defects as a result of such a cathodic–anodic treatment of the electrode. The results of the potentiodynamic study are in agreement with the potentiostatic data (Fig. 4a).

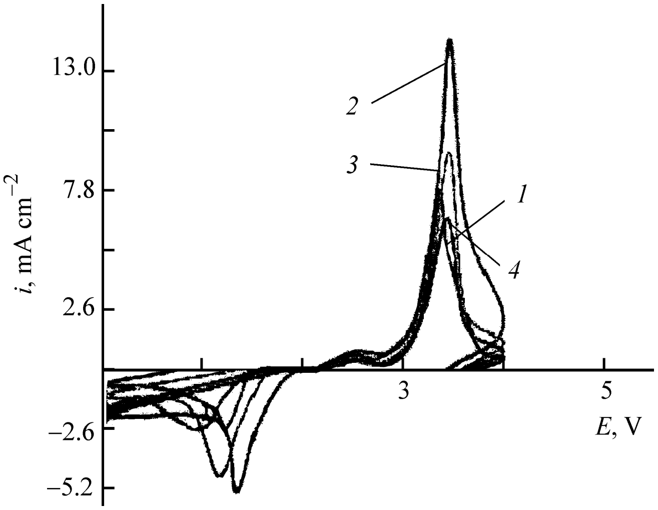


Fig. 3. Cyclic potentiodynamic curves of the electrode under study. Potential sweep rate 8 mV s^{-1}. Content of the thiopyrilium salt (wt %): (*1*) 30, (*2*) 50, (*3*) 85, and (*4*) 90.

It follows from the data in Table 1 that, as the potential sweep rate increases, the current density in

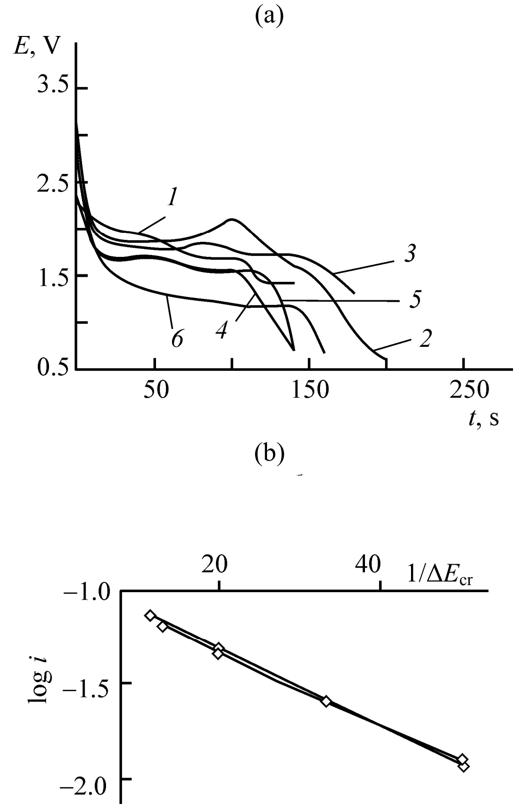


Fig. 4. (a) Variation of the potential E (V) with time t for the electrode under study and (b) log i–$1/\Delta E_{cr}$ dependence. (a) Current density 0.065 mA cm^{-2}. Salt content of the cathode (wt %): (*1*) 30, (*2*) 50, (*3*) 70, (*4*) 80, (*5*) 85, and (*6*) 90. (b) Carbon black content of the cathode 30 wt %.

Table 1. Current density i_{max} and potential E_{max} in the cathodic half-cycle for the electrode made of an ionic organic salt at varied content of carbon black and different potential sweep rates ν_{sw}

ν_{sw}, mV s^{-1}								
	30		50		80		90	
	i_{max}, mA cm^{-2}	E_{max}, V	i_{max}, mA cm^{-2}	E_{max}, V	i_{max}, mA cm^{-2}	E_{max}, V	i_{max}, mA cm^{-2}	E_{max}, V
2	0.91	1.08			0.39		1.30	1.12
4	2.34	0.95			1.89	1.41	1.89	1.14
8	2.60	0.80	5.2	1.3	2.65	1.22	2.60	0.75
20	5.20	0.61			4.68	0.95	4.94	0.50
40	7.70	0.46			7.54	0.74	7.49	0.35
80	12.5	0.48			10.40	0.52	9.75	0.40

Table 2. Current density i_{max} and potential E_{max} at peaks of the potentiodynamic curves in current reversal in the anodic potential range (2.5–4 V) for an electrode made of the ionic organic salt at 20°C and varied content of carbon black in relation to the potential sweep rate ν_{sw}

ν_{sw}, mV s^{-1}	Content of carbon black in the electrode, wt %							
	30		50		85		90	
	i_{max}, mA cm^{-2}	E_{max}, V	i_{max}, mA cm^{-2}	E_{max}, V	i_{max}, mA cm^{-2}	E_{max}, V	i_{max}, mA cm^{-2}	E_{max}, V
2	0.160	3.19	0.018	3.18	0.121	3.19	0.014	3.20
4	0.122	3.35	0.024	3.32	0.127	3.35	0.018	3.32
8	0.028	3.50	0.032	3.50	0.038	3.48	0.020	3.50
20	0.030	3.68	0.040	3.70	0.047	3.69	0.023	3.70
40	0.032	3.80	0.045	3.79	0.053	3.80	0.025	3.78
80	0.034	4.07	0.048	4.06	0.060	3.99	0.026	4.06

the cathodic half-cycle grows and reaches the maximum value at 50% of carbon black in the electrode. At the same time, upon current reversal, an increase in the content of carbon black has nearly no effect on the process rate (Table 2). In the anodic range of potentials, from 2.5 to 4 V, the same effect is observed.

Now, the nature of the slow stage of the electrochemical reduction of 4-methyl-2-phenyl-5,6-tetramethylenethiopyrilium at the interface with β-alumina is considered.

It can be seen from the run of the galvanostatic curves describing the variation of the electrode potential with time (Fig. 4a) that the potential sharply falls at the initial instant of time and a small peak is formed. In 20–30 s, the potential again grows and, in the case of a longer polarization, remains constant. This shape of the potential–time curve may indicate that the nucleation of a new phase is hindered. The differences of the potentials at the peak and on the plateau of the E–t curve at different cathodic current densities are listed in Table 3. This potential difference E_{cr} can be taken to be the crystallization overvoltage.

The dependence of log i on $1/\Delta E_{cr}$ can be used to make a conclusion about the mechanism of nucleation and growth of the new phase. As follows from Fig. 4b, this dependence is represented by a straight line, which is an argument that the process occurs by the mechanism in which 2D nuclei are formed and grow over the surface to give a solid layer. As the surface is covered with a solid layer of the new phase, the cathodic process starts to be limited by the diffusion stage. Because of the localization of the electron

Table 3. Potential differences between the peak and plateau of *E–t* curves at different current densities of the cathodic polarization of the ionic organic salts with carbon black added in an amount of 30 wt %

i_c, mA cm^{-2}	Potential E, V (relative to Na/Na$^+$)		
	E_{peak}	$E_{plateau}$	ΔE_{cr}
0.015	1.75	1.725	0.02
0.025	1.60	1.570	0.03
0.045	1.52	1.470	0.05
0.065	1.35	1.280	0.07
0.075	1.27	1.190	0.08
0.085	1.18	1.080	0.10

charge on the (S, O) heteroatom, the thiopyrilium cation has the structure of the unstable pentadienyl cation. The electron charge delocalization energy for thiopyrilium cation is 192.46 kJ mol–1 and correlates with the empirically found resonance energy [13–15]. The higher degree of the charge density delocalization for the lone pair of π-electrons in the heterocycle of the thiopyrilium cation is also confirmed by the bond orders. Thus, it can be assumed that the salts under consideration are highly sensitive to the action of the electric current. This opens wide prospects for the use of these substances as the working substance of cathodes in solid-phase chemical power cells.

It can be stated on the basis of the results of this study that the specific features of the electrochemical reactions at the interface with the solid electrolyte are largely determined by various surface states localized at the semiconductor–electrolyte interfaces and at the heterointerface. It can be assumed that the reason for the appearance of surface states are structural defects, impurities and distortions of the periodic variation of the potential in surface cells of the crystal lattice.

The accumulated experimental evidence suggests that the cation of the organic salt is electrochemically converted at the cathode to the cation radical, with its subsequent dimerization. The new phase is formed by the mechanism of 2D nuclei. Because of the growth of these nuclei to form a monolayer, the reaction occurs at the internal interface between the product phase and cathode material.

In some cases, the chemisorption of carbon atoms on the semiconductor surface may occurs with partial or full electron charge transfer from the semiconductor to the carbon atom of carbon black to give adatoms, which can further lose electrons to become ad-ions. Levels of donor energy states are involved in the formation of adatoms, ad-ions, and clusters of carbon black. These processes facilitate the cathodic reduction of the organic salt cation and promote its transition to the diffusion mode. This interpretation of the process mechanism is well consistent with the results of the potentiostatic measurements and with the linear dependence of the potential and current density at the peak of the potentiodynamic curves on the square root of the potential sweep rate ν_{sw}.

Thus, the rate of electrochemical transformations at the interface between the ionic organic salt and the solid electrolyte must be largely determined by the state of this interface. The pattern observed is in good agreement with the results obtained in a study of the interface between the organic salt and solid electrolyte in the potentiostatic mode.

CONCLUSIONS

(1) It was experimentally confirmed that the rate of electrochemical transformations on the electrode made of an ionic organic salt of the thiopyrilium series at the interface with sodium β-alumina is the highest when the electrode contains 50 wt % carbon black. This composition of the electrode can be recommended for use in further technological development of solid-phase chemical power cells.

(2) It was demonstrated that the electrochemical reduction of 4-methyl-2-phenyl-5,6-tetramethylene-thiopyrilium perchlorate at the interface with a solid electrolyte conducting by sodium ions occurs via formation of 2D nuclei.

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