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High-conductivity organic metals as electrode materials

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Electrode properties of TCNQ (7,7,8,8-tetracyanoquinodimethane) and BEDT-TTF (bis-(ethylenedithio)tetrathiafulvalene) derivatives are considered. The BEDT-TTF-based organic electrode materials were produced by electrochemical technique. Electrodes with TCNQ salts were obtained by thermal or evaporation method. Polarization and impedance investigations have shown the high electrode activity of the BEDT-TTF based materials in irreversible electrochemical processes. TCNQ-based OM sensitivity to pH as well as electrode surface resistance vary depending on gaseous phase composition. The latter circumstance is quite prospective for applications of organic metals in analytical control devices.

Key words: *TCNQ molten salts; H-function; impedance spectroscopy; evaporation technique; electrochemical synthesis*

1. Introduction

Extensive data on highly conducting organic substances [1, 2] are accumulated at present. A lot of fundamental papers describe synthesis technique, structural characteristics, physical and chemical properties of the organic metals (OM). These fundamental investigations provide a basis for the development of advanced technologies. The key element of the instruments and devices used in such a technique is a single electrode, or electrode system containing modern materials. Therefore, the analysis of the performance of the OM electrode under various conditions is of a special interest. It permits to make a step from theoretical investigations to creation and testing the compounds of desired properties.

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A strong electron acceptor, 7,7,8,8-tetracyano-quinodimethane (TCNQ), and electron donor, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET), derivatives forming radical anion and cation salts, respectively, whose properties have been thoroughly investigated [3], are used as electrode materials in the present research.

Usually the solid phase of an electrode where the electrochemical reactions occur [4] is considered as the electrode material. The stationary potential formation and complex character of processes at the OM electrode are caused by the presence of interfaces of various nature.

2. Experimental

The electrode material structure and the electrode properties are determined by their processing. We employed electrochemical, thermal (melting) and evaporation methods. The electrochemical method consists in forming the OM phase at a conducting substrate under oxidizing or reduction potentials. The thermal method was employed for TCNQ salts whose decomposition process at melting point is essentially limited [5]. We used the TCNQ salts tendency to be dissolved in organic solvents with a high volatility (particularly in chloroform) for production of thin-film electrodes. The OM film of given thickness was formed during the solvent evaporation from the solution applied on a substrate.

The galvanostatic method [6] is widely used for the OM single crystal synthesis, but we preferred more valid potentiostatic regime. Let us consider the electrode material at the moment of appearance of the potential forming phase at the inert substrate/electrolyte interface. The synthesis was carried out on the platinum wire in an airproof glass cell under argon atmosphere at 293 K. The counter electrode was a platinum wire separated from the working one by low-porosity glass frit, the reference was a standard calomel electrode (SCE). The electrolyte contained the organic solvent (dimethylformamide, DMF), $N(CH_3)_4ClO_4$ (0.1 M), ET (2×10^{-3} M) and $(N(C_4H_9)_4)_2Mo_6O_{19}$. The voltage was provided with an electrochemical battery supplied by a potential stabilizing device. Polarization measurements were carried out using the pulse potentiostatic device with a programmed output signal. The electrode impedance frequency distribution was obtained by the automatic alternating current bridge in a cell with the coaxial electrodes.

OM was thermally deposited at constant temperature of the salt melting point in an inert atmosphere or under vacuum up to a complete melting of salt. The following quenching in environmental conditions leads to adherent OM layer formation on the substrate.

The modification of a melting method is the substrate warming by Joule heat obtained from electrical current that was passed through a wire with a high specific resistance. As a result, we obtained solid phases of TCNQ salts completely covering the substrate.

3. Results and discussion

Electrosynthesized conducting OM phase. OM potentiostatic synthesis (350 hours from the electrolyte containing $Mo_6O_{19}^{2-}$ and ET) results in needle-like crystals $(ET)_2Mo_6O_{19}$ with the orientation of their main axes in the direction of the electric field applied [6].

The stationary potential of the working electrode became more positive after electrosynthesis of the cation-radical salts that indicated formation of the active phase of the electrode. In particular, the $(ET)_2Mo_6O_{19}$ formation on a platinum substrate was attended by the electrode stationary potential increase exceeding 0.2 V. Rather high rate of the main exchange process

$$\mathrm{ET} - \mathrm{e} \rightarrow \mathrm{ET}^{+}$$

which is characterized by exchange current density of 2.0×10^{-3} A/m^2 (polarization resistance is of 1.2×10^{5} ohm×cm^2), was estimated from polycrystalline needle electrode current-voltage dependences.

Similar studies were carried out on the same solid phase in sulfuric acid aqueous solution (0.05 M) (Fig. 1). They have shown the stationary potential to be more positive (0.50 V by SCE) due to the change in the nature of exchange processes.

Impedance measurements on Pt and Pt|OM electrodes were analyzed in terms of the electrochemical system described by the Ershler–Randls circuit [4]. Double layer capacity values (C_d) on platinum electrodes and Pt|OM ones were calculated from the capacitance-frequency dependences (Fig. 2)

Table. Double layer capacity (C_d)
for Ershler–Randls circuit in different electrolytes

Solution	$10^7 C_d$, F	
	Pt	Pt|$(ET)_2Mo_6O_{19}$
H_2SO_4	13.0	1.6
DMF, $N(CH_3)_4ClO_4$, ET, $(TBA)_2Mo_6O_{19}$	1.6	0.4

The essential effect of steric factor on C_d (Table) was established from the experimental data on assumption of the double layer described by the parallel-plate capacitor model. The double layer capacity decreases with the increase of charged particles distance from a metal surface in organic solvent with molecules larger than those of water. At the same time the ratio of the double layer thickness on platinum in DMF and in aqueous solution (3.7) is higher than the same parameter for electrodeposited OM (1.8). It is probably caused by peculiarities of solvation and by the interaction of solvent molecules with the solid phase surface giving rise to an increase of double layer thickness on OM in comparison with a platinum electrode. The result obtained characterizes the structural peculiarities of the double layer on $(ET)_2Mo_6O_{19}$. This substance diminishes the selectivity of the interaction of the liquid phase components with the substrate. Thus, impedance measurements are useful for revealing the electrode material nature and composition optimization. Complex exchange processes at the interface influence essentially the response formation in different OM based devices.

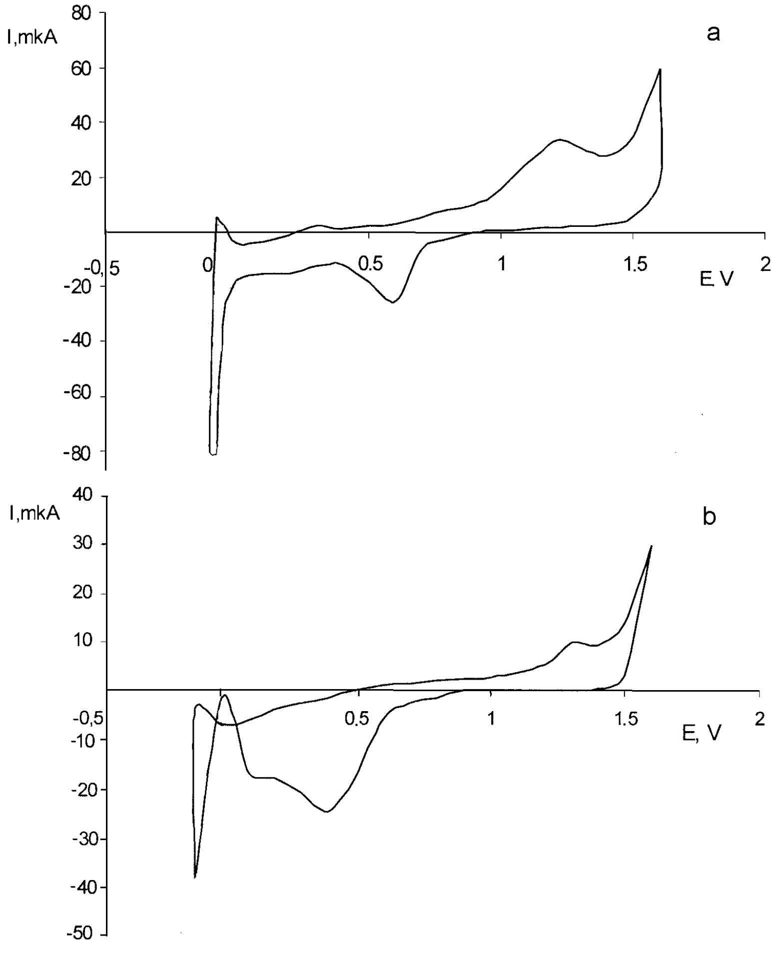

Fig. 1. Cyclic polarization of the Pt|$(ET)_2Mo_6O_{19}$ (a) and Pt (b) electrodes in H_2SO_4 (0.05 M.)

The Faraday reaction resistance of the Pt(OM)|(synthesis solution) electrode was estimated from the capacitance–frequency dependence (Fig. 2). This value (60 ohms) in comparison with the value obtained from the current–voltage dependence (5×10^4 ohms) points to the electrode surface increase under alternating current polarization caused by electrode reaction irreversibility. The phase angle (β)–circular frequency ($\omega^{1/2}$) dependence (Fig. 3) allows us to discuss a mixed diffusion and charge-transfer control of electrode reaction [7].

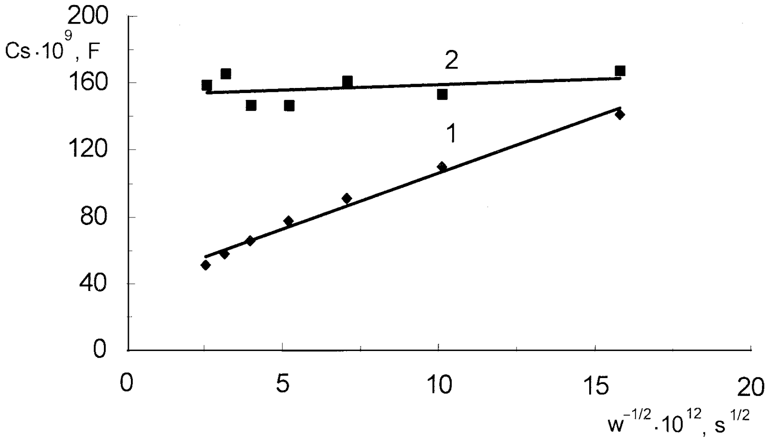

Fig. 2. Frequency dependence of the electrodes capacity:
1 – Pt|$(ET)_2Mo_6O_{19}$|synthesis solution, 2 – Pt| synthesis solution

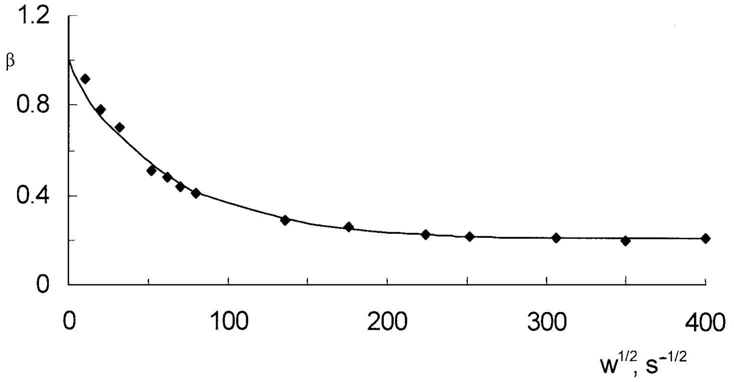

Fig. 3. The phase angle frequency dependence (*β*) of electrode Pt|$(ET)_2Mo_6O_{19}$

Behaviour of molten salts electrodes. The organic metal [N-C_6H_{13}-isoQn] $(MeTCNQ)_2$ layer[*] synthesized by the thermal method on the aluminum wire was polarized in sulfuric acid aqueous solution (0.05 M) up to potentials exceeding solvent decomposition ones (from –4.0 to 4.0 V). The current density in the potential range did not exceed 0.1 mA/cm^2 testifying the appearance of a dielectric film on the substrate.

The capacitance-frequency dispersion of [N-C_4H_9-isoQn] $(MeTCNQ)_2$ deposited by melting on previously oxidized aluminum is caused by the change of the system conductivity mechanism in comparison with aluminum oxide film [7] (Fig. 4).

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[*] [N-C_nH_{2n+1}-isoQn] denotes N-alkyl-isoquinolinium.

Investigation of the electrodes with solid phases [N-C_3H_7-isoQn](MeTCNQ)$_2$ and [N-C_4H_9-isoQn](MeTCNQ)$_2$ exhibits their sensitivity to pH drop the a point of equivalence. The character of dependence of the indicator electrode potential change on the factor of equivalence α (α is the mol-equivalent ratio of a titrant amount to the initial titrated component amount in a probe) corresponds to the Nernst equation. It allows one to use TCNQ salts as a basic material for sensitive elements or indicator electrodes of liquid environment acidity.

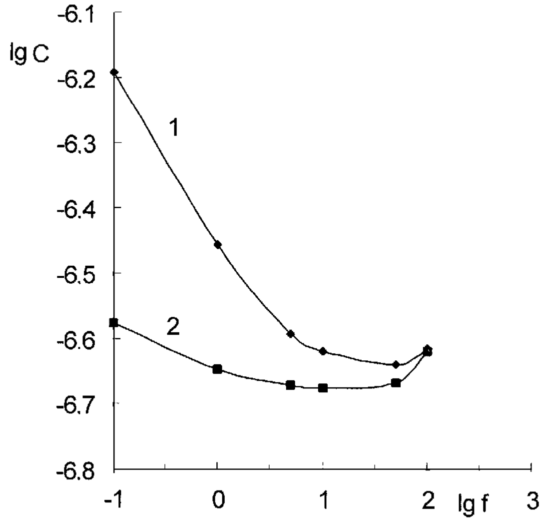

Fig. 4. Frequency dependence of capacitance of the systems: 1 – Al | Al_2O_3, 2 – Al | Al_2O_3 | [N (C_6H_{13})-isoQn](MeTCNQ)$_2$. f is frequency expressed in s^{-1}, C is capacitance expressed in F

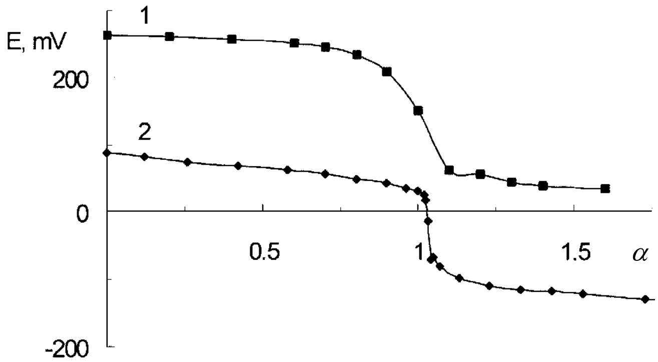

Fig. 5. Acidic-alkaline titration curves (H-function) of the systems C_3H_7-isoQn(MeTCNQ)$_2$ (1) and C_4H_9-isoQn(MeTCNQ)$_2$ (2)

Evaporated OM films as the sensitive elements of the gases detectors. The dynamic parameters of a film resistance stipulated by surface phenomena, in particular by adsorption, increase with decreasing thickness and increasing integrity of the film. Evaporation method becomes more appropriate for fabricating thin-film OM electrodes. The resistance of such film is caused by the exchange adsorption processes rate in different gaseous solutions. It is shown that the resistance of such electrode depends on concentration of NO_x, CO_2, CO, H_2S, SO_2, NH_3 and on the presence of water vapour (Fig. 6) in the environment.

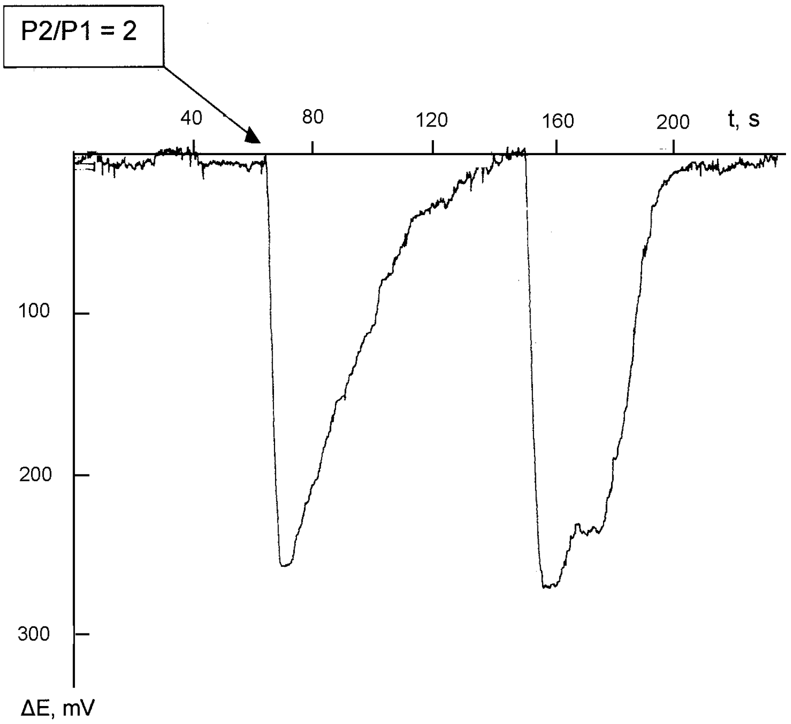

Fig. 6. Response of the system Cu|CuH_9-isoQn$(MeTCNQ)_2$|Cu to partial vapour pressure change (wetting function). P1 is the initial value of vapour partial pressure, P2 is vapour partial pressure after wetting

The electrodes obtained exhibit high sensitivity and low transient time. The output signal value exceeds the input one more than an order of magnitude. The delay time is in the range of 1–2 s, the time constant – 0.1–0.5 s, the relaxation time – 10–20 s.

4. Conclusions

- The implementation of technological methods for OM electrodes formation is possible due to physicochemical properties of precursors and ion radical salts.
- The detailed study of OM as electrode materials can be performed by classical electrochemical analysis methods.

The usage of the OM-based electrodes, in particular as the electronic engineering elements base and analytical instrument production, is a prospective technical direction. Such approach will allow creating original devices with extended spectrum of working parameters.

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