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Tuning the conductivity of nickel-salen polymers in the channels of electrochemical transistors

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The conductivity of polymeric complexes of nickel (II) with N,N'-bis(salicylidene)ethylenediamine ligand and its substituted analogues (poly-[NiSalen], poly-[NiCH$_3$Salen], poly-[NiCH$_3$OSalen]) was investigated in the channels of organic electrochemical transistors. The conductance characteristics of the polymers during scanning the gate voltage were found to depend on the molecular structure of the complexes and the upper limit of the electrochemical doping level of the polymeric material in the channel. The ratio of poly-[NiCH$_3$Salen] conductance in the ON and OFF states exceeded 10^4.

Keywords: organic electronics, electrochemical transistor, nickel-salen polymer, conductance.

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An organic electrochemical transistor (OECT) is a unique combination of an amplification device, a switch and a sensor for use in neural interfaces, analog and logic circuits, bioelectronics, and sensor devices [1,2]. The OECT is structurally similar to an organic electrolytic transistor: in both devices the polymer semiconductor channel between the drain electrode and the source electrode is separated from the gate electrode by an electrolyte layer. The key difference lies in the nature of the processes occurring in the system when control voltage is applied to the gate. In the electrolytic transistor double electrical layers are formed at the semiconductor/electrolyte and electrolyte/gate interfaces. In OECT the main process is the transfer of electrolyte ions across the polymer/electrolyte interface and electrochemical doping of the polymer channel material (the introduction of ions into the polymer layer during its oxidation-reduction transformations). In this case, the polymer transits between low- and high-conducting states, which leads to the appearance or disappearance of the drain current in the channel. Like the electrolytic transistor, OECT can operate at low voltages, but is characterized by a higher transconductance due to the high channel specific capacitance, which provides advantages of this device over other types of transistors [2].

Promising materials for OECT channels should demonstrate a rapid and reversible change in electrical conductivity by several orders of magnitude when the transistor transits between ON and OFF states, while providing low threshold voltages. Traditionally, organic polymer semiconductors are used in OECT [3]. The incorporation of metal ions into the molecular structure of organic polymers provides additional opportunities for more flexible control of their functional characteristics [4] and can provide a number of significant advantages to electrochemical transistors based on them, in particular, in sensor applications. However, only a few examples of OECTS are known, OECTs based on polymeric conductive metal-organic structures [5,6].

We previously showed that polymers with nickel (II) ions integrated at the molecular level into a three-dimensional matrix based on salen ligands can be used in OECT channels [7]. During electrochemical oxidation (doping with electrolyte anions) in acetonitrile solutions, the conductance of these materials increases by at least three orders of magnitude, while the maximum conductance is observed at gate voltage that ensures doping of the polymer to a level of 50%. The search of tools to control the conductivity of nickel-salen polymers during electrochemical doping is a topical task, as it will significantly increase the efficiency of final devices based on them.

The purpose of this paper was to study the influence of the maximum level of doping of nickel-salen type polymers with electrolyte anions, determined by the scanning range of the gate-source voltage, on the nature of changes in the conductivity of these materials in the channels of electrochemical transistors. Polymer complexes of nickel (II) with the ligand N,N'-bis(salicylidene)ethylenediamine (poly-[NiSalen]) and its methyl- and methoxy-substituted analogues (poly-[NiCH$_3$Salen] and poly-[NiCH$_3$OSalen]) were selected for this study (Figure 1, *a*). The electrical conductivity of polymers poly-[NiSalen] and poly-[NiCH$_3$OSalen] was investigated earlier in the paper [7], but the measurements were carried out in the electrolyte with lower ionic strength and only in one control voltage range. The conductivity of the polymer complex poly-[NiCH$_3$Salen] under the selected conditions was studied for the first time in this paper.

The electrical conductance of polymers was measured in the *operando* mode on samples and under conditions simulating OECT operation. The architecture of the studied samples is presented in Figure 1, *a*. The source

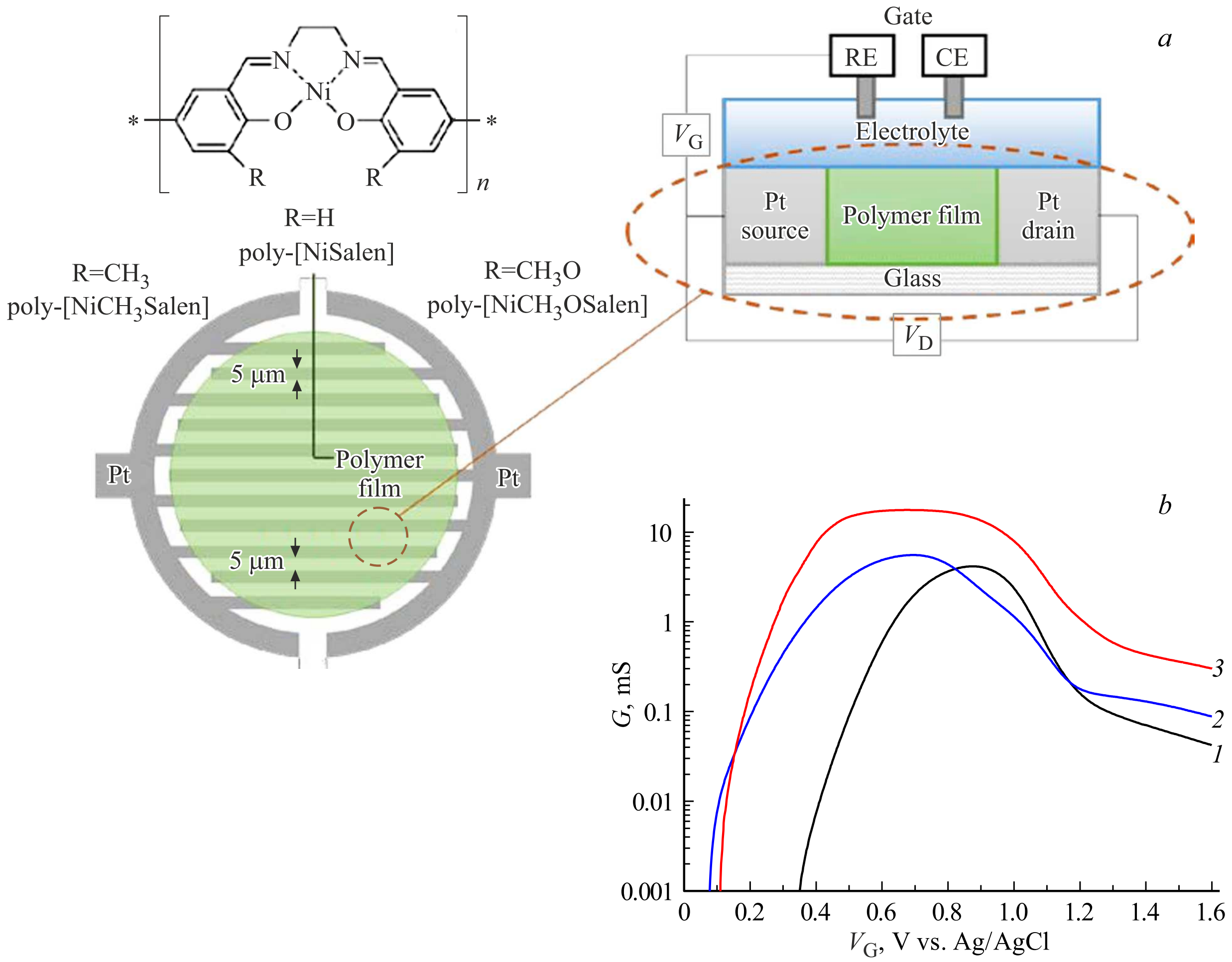

Figure 1. Architecture of OECT samples based on IDE electrodes, general structural formula and symbols of the polymers studied in the paper (*a*) and dependence of the polymer comductance G on the gate–source voltage V_G for OECT with a polymer channel poly-[NiSalen] (curve *1*), poly-[NiCH$_3$OSalen] (curve *2*) and poly-[NiCH$_3$Salen] (curve *3*) (*b*).

and drain electrodes were platinum microelectrodes of an interdigitated structure (IDE) deposited on a glass substrate, the gap between which was 5 μm. The gate was formed by an auxiliary electrode (carbon plate) and a non-aqueous Ag/Ag$^+$ reference electrode (+0.3 V relative to the standard silver / silver chloride electrode Ag/AgCl, NaCl(saturated)). The electrolyte was 0.1 M Et$_4$NBF$_4$/CH$_3$CN. The electrodes were immersed in the electrolyte solution in a cell controlled by VSP bipotentiostat (BioLogic Science Instruments). To deposit polymer layers the cell was filled with the electrolyte additionally containing 0.001 mol $\cdot$ l^{-1} of monomer complex. The control voltage V_G in the range 0–1.6 V was applied to the IDE with a scan rate of 10 mV $\cdot$ s^{-1} (the number of cycles varied from five to seven, depending on the nature of the complex). As a result, oxidative electrochemical polymerization of the complexes occurred, and the gaps between IDE microelectrodes were filled with polymer. Next, in the electrolyte containing no monomer, CVC of the samples were recorded in different voltage ranges V_G at a fixed drain–source voltage $V_D = 10$ mV. The obtained drain current values were used to calculate the conductance of polymers G according to Ohm's law [7].

The dependence of the conductance of polymeric complexes on the gate-source voltage in the range $V_G = 0–1.6$ V is presented in Figure 1, *b*. At the voltage of 0 V all polymers are undoped and exhibit conductance less than 10^{-3} mS. As the control voltage increases, the increase in the channel current is observed due to electrochemical doping of the polymer. As the doping level increases, the conductance of polymers increases, reaches maximum values and then significantly decreases. The threshold voltage values V_T vary from 0.11 ± 0.04 V to 0.37 ± 0.03 V, and the maximum conductance voltage V_M — from 0.68 ± 0.02 V to 0.88 ± 0.02 V depending on the nature of the polymeric complex. The highest maximum conductance values G_M were found for poly-[NiCH$_3$Salen] (15 ± 2 mS).

Analysis of the data in Figure 1, *b* shows that the sample transition between the OFF and ON states is possible in the V_G range from 0 V to V_M. In the second series of experiments, $G = f(V_G)$ curves were recorded on as-formed samples by repeatedly scanning the gate voltage in the range

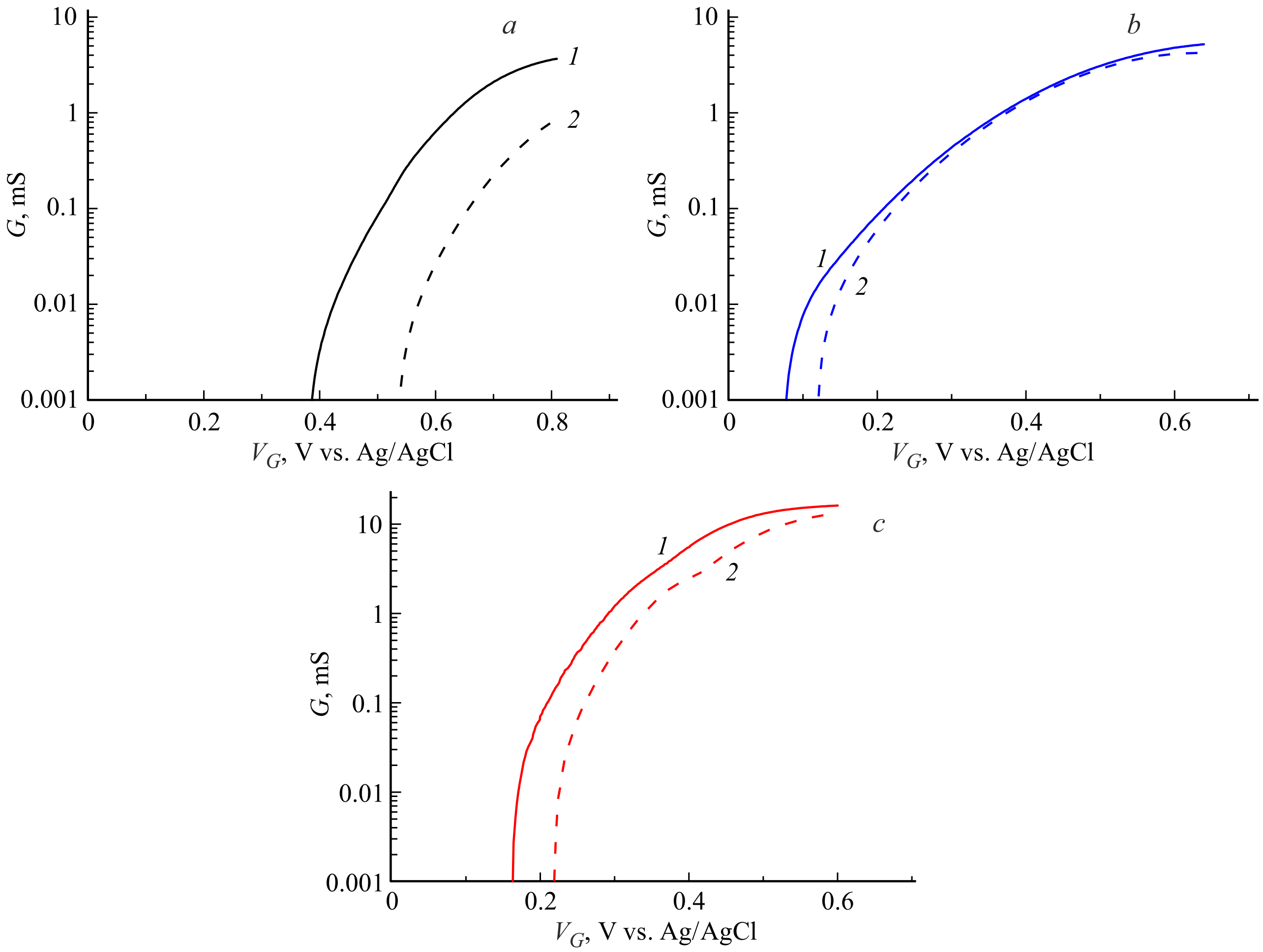

Figure 2. Dependence of polymer conductance G on gate-source voltage V_G for OECT with polymer channel poly-[NiSalen] (*a*), poly-[NiCH$_3$OSalen] (*b*) and poly-[NiCH$_3$Salen] (*c*) for as-formed samples (solid curves *1*) and after a single voltage scan in the range $V_G = 0-1.6$ V (dashed curves *2*).

of 0 V (OFF) to voltage that ensured the conductance values of about 95% of G_M (ON). The obtained dependences $G = f(V_G)$(curves *1*, Figure 2) closely match the ascending part of the curves in Figure 1, *b*. The ratio of polymer conductance in the ON and OFF states is more than 10^3 for poly-[NiSalen] and poly-[NiCH$_3$OSalen] and more than 10^4 for poly-[NiCH$_3$Salen]. In successive ON/OFF cycles, the maximum conductance values G_{ON} do not change significantly (Figure 3), other characteristic parameters of the curves $G = f(V_G)$ do not change either, which indicates stable operation of the samples at voltages that ensure the doping level of the material below 50% of the maximum ($V_G < V_M$).

The increase in the level of electrochemical doping of polymers above 50%, which is achieved at $V_G > V_M$, in all studied cases leads to change in the dependence the conductance of the channel material on the control voltage. In particular, after a single scan in the range $V_G = 0-1.6$ V, the curves $G = f(V_G)$ recorded in a narrower range (curves *2*, Figure 2) show an increase in the values of V_T and a decrease in the values of G_{ON} are observed, which leads to a decrease in the parameter G_{ON}/G_{OFF} and means a decrease in the efficiency of the end device. After heavy doping the characteristics of samples based on poly-[NiSalen] change most significantly (Figure 2, *a*). This may be a consequence of both the presence of a large number of charge traps in fully oxidized forms of the given polymer, and irreversible structural changes in the material due to overoxidation at high voltages [8]. Polymers with electron-donating substituents in the ligand environment of complexes (poly-[NiCH$_3$OSalen] (Figure 2, *b*) and poly-[NiCH$_3$Salen] (Figure 2, *c*)) appear to be characterized by a lower charge trap density and/or greater resistance to overoxidation, which makes them less sensitive to doping to high levels.

Thus, the paper shows that the parameters of changes in the conductivity of nickel-salen polymers in OECT channels are determined not only by the nature of the polymer material, but can also be controlled by the range of gate-source voltages determining the level of the polymer doping with electrolyte anions. The data obtained confirm the previously made conclusion [7] that the polymer poly-[NiCH$_3$OSalen]

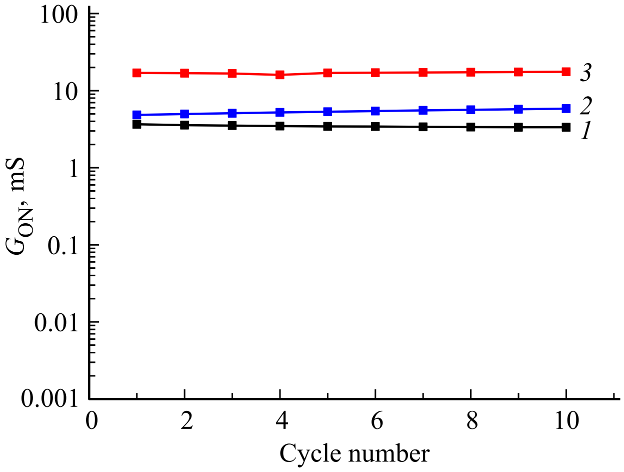

Figure 3. Change in maximum conductance in successive scanning cycles of gate-source voltage in the ranges indicated in Figure 2, for OECT with polymer channel poly-[NiSalen] (curve *1*), poly-[$NiCH_3OSalen$] (curve *2*) and poly-[$NiCH_3Salen$] (curve *3*).

is promising for electrochemical transistors. At the same time, the possibility of achieving high conductance and G_{ON}/G_{OFF} values exceeding 10^4 in channels based on poly-[$NiCH_3Salen$] determines the need for further work systematic studies the of doping of this polymer material and searching for ways to increase its stability to create a new generation of OECTs and other practically significant electrochemical devices.

Conflict of interest

The authors declare that they have no conflict of interest.

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