

07.2;13.3

## Gate-source voltage dependence of the electrical conductivity of nickel-salen polymers in the electrochemical transistor

© E.A. Smirnova, I.A. Chepurayana <sup>†</sup>

Ioffe Institute, St. Petersburg, Russia

<sup>†</sup> E-mail: ichepurayana@mail.ioffe.ru

Received August 19, 2021

Revised August 19, 2021

Accepted September 14, 2021

For the first time, polymeric forms of the complexes N,N'-bis(salicylidene)ethylenediaminonickel(II) and N,N'-bis(3-methoxysalicylidene)ethylenediaminonickel(II) have been investigated as functional materials for the conducting channels of organic electrochemical transistors. The dependence of the electrical conductivity of the polymers on the electrolyte anion-doping level has been established. The polymer film conductance versus gate voltage curve parameters have been shown to depend on the molecular structure of the complex and the nature of the electrolyte solvent.

**Keywords:** organic electronics, electrochemical transistor, nickel-salen polymer, conductivity, doping.

DOI: 10.21883/0000000000

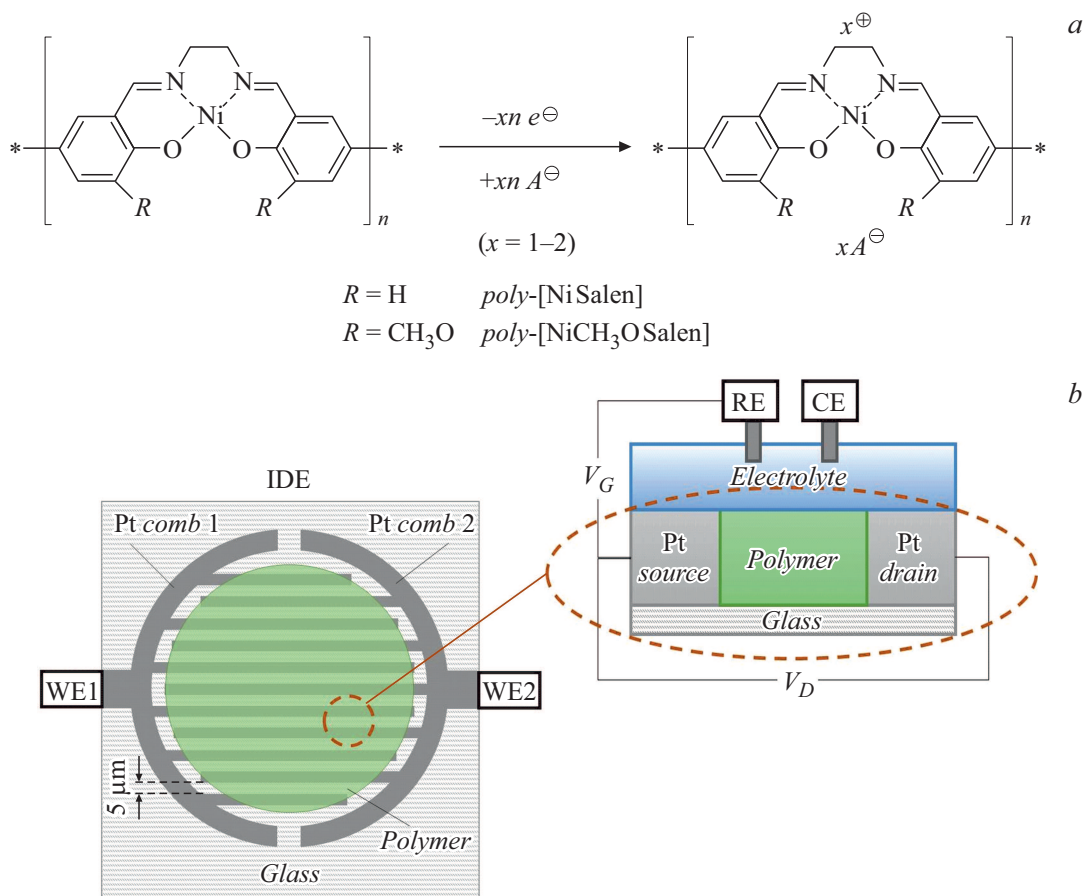
Among various molecular electronic devices employing coatings based on polymer semiconductors, most interesting are organic electrochemical transistors (OECT) [1–3]. Contrary to widely known organic field-effect transistors, the OECT gate is electrically connected to the polymer-semiconductor-based conducting channel through the electrolyte system. The OECT operation is based on the injection of electrolyte ions into the channel at the moment the control voltage is applied to the gate. Therewith, the channel conductivity is governed by the concentration and mobility of charge carriers generated in the polymer as a result of oxidation-reduction transformations.

As promising materials for the OECT channels, both the electroconductive organic polymers (e.g., polyethylenedioxithiophene doped with polystyrene sulfonate) [3] and conductive polymer materials based on metal-organic and coordination compounds [4] were proposed. Interesting representatives of metallopolymers with intrinsic conductivity are nickel-salen polymers (polymeric complexes of nickel (II) with the N<sub>2</sub>O<sub>2</sub> Schiff bases of the salen type) that are thin film matrices immobilized on current-conductive substrates, in which chain macromolecules with covalently bound aryl fragments (Fig. 1, *a*) are combined into three-dimensional supramolecular structures [5]. The simplicity of modular synthesis, good stability, and possibility of achieving high electrophysical and electrochemical characteristics provide a wide range of practical applications of these polymeric metal complexes, for instance, energy generation and storage devices, sensors and electrocatalytic cells [6]. Earlier it was revealed that varying the electrode substrate potential ensures the material transition from the non-charged state to the oxidized one. The excess positive charge generated in the polymer film is stabilized due to doping with the background electrolyte anions (Fig. 1, *a*) [5]. Thus,

the nickel-salen polymers are potentially able to provide the OECT functioning in the accumulation mode.

In order to more accurately assess the possibility of using nickel-salen polymers in OECT, it is necessary to elucidate the influence of the molecular and structural (supramolecular) arrangement of the polymer matrix and electrolyte medium composition on changes in the material electrical conductivity upon electrochemical doping. Electrical conductance of individual representatives of these polymeric metal complexes was earlier studied in [7]. However, those experiments were performed in the electrolyte composition for lithium-ion batteries containing high concentration of lithium ions able to specifically coordinate to ligand heteroatoms. Such interactions significantly affect the electron density distribution governing the charge carrier generation and transport in the polymer [8]. The goal of this work was to study the influence of the polymer molecular composition and electrolyte solvent nature on the conductivity of nickel-salen polymer films upon electrochemical doping in solutions that do not contain lithium ions.

Polymer films *poly*-[NiSalen] and *poly*-[NiCH<sub>3</sub>OSalen] (Fig. 1, *a*) were obtained on the surface of a platinum interdigitated electrode (IDE) (MicruX Technologies) (Fig. 1, *b*) by oxidative electropolymerization of complexes N,N'-bis(salicylidene)ethylenediaminonickel (II) and N,N'-bis(3-methoxysalicylidene)ethylenediaminonickel (II), respectively. Two interdigitated systems of microelectrodes (IDE combs) applied on a glass substrate were used as working electrodes (WE1 and WE2) of an electrochemical cell controlled by means of bipotentiostat VSP (BioLogic Science Instruments). The cell also comprised a glassy carbon plate used as an auxiliary electrode (AE) and non-aqueous reference electrode Ag/Ag<sup>+</sup> (MW-1085, BASi) (RE) characterized by the potential of -0.3 V relative to the standard silver/silver chloride reference



**Figure 1.** *a* — structural formula of macromolecules of nickel-salen polymers, general scheme of their electrochemical doping with the background electrolyte anions, and designations of the polymers studied in this work. *b* — schematic sketch of an interdigitated electrode and an electrochemical transistor based on it.

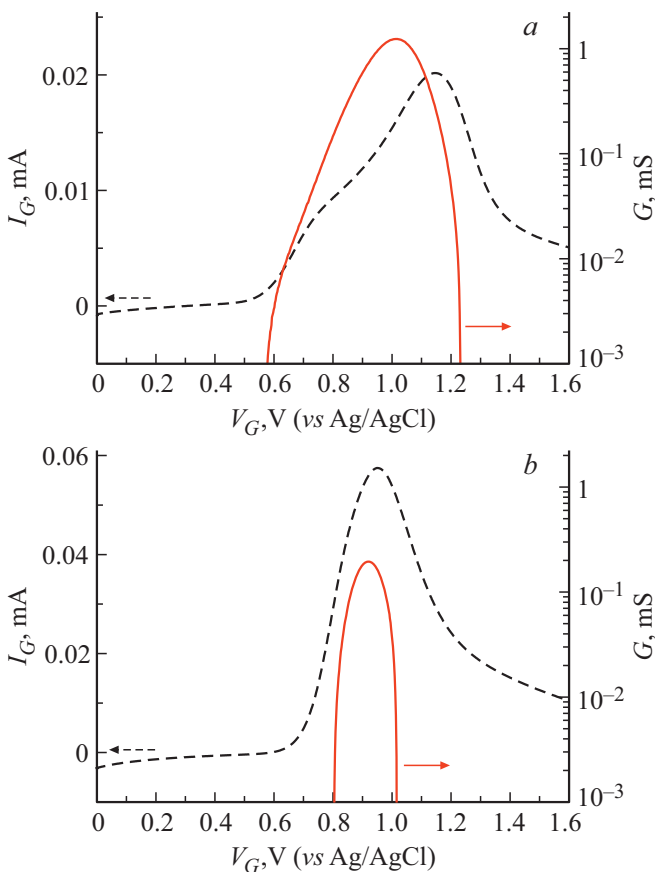
electrode Ag/AgCl, NaCl (saturated), with respect to which all the electrode potentials are presented in this work. The cell was filled with electrolyte composition containing  $0.05 \text{ mol} \cdot \text{l}^{-1}$  of tetraethylammonium tetrafluoroborate ( $\text{Et}_4\text{NBF}_4$ ) and solvent (1,2-dichloroethane (DCE) or acetonitrile (AN)), as well as  $0.001 \text{ mol} \cdot \text{l}^{-1}$  of monomer  $[\text{NiSalen}]$  or  $[\text{NiCH}_3\text{OSalen}]$  synthesized according to a standard procedure [9]. The complex was polymerized on the IDE surface in the mode of multiple potential cycling in the range of 0 to 1.6 V with the rate of  $10 \text{ mV} \cdot \text{s}^{-1}$  (the polymer synthesis procedure is described in details in [7]). The polymer-modified electrode was rinsed, dried and set into the cell with the electrolyte composition identical to the polymerization solution but free of the monomer.

Two neighboring interdigitated microelectrodes interconnected with the nickel-salen polymer may be regarded as an electrochemical transistor with a polymer channel (Fig. 1, *b*). The gate is formed by combination of the auxiliary electrode and reference electrode in the electrolyte solution. The gate-source voltage ( $V_G$ ) is equivalent to the preset potential difference in the circuit of the working and reference electrodes. Using the bipotentiostat, voltage  $V_G$  was increased from 0 to 1.6 V with the rate of  $10 \text{ mV} \cdot \text{s}^{-1}$ .

Constant potential difference  $V_D = 10 \text{ mV}$  was maintained between IDE combs ensuring the drain current flow through the polymer channel. Electric current ( $I_G$ ) was measured in the circuit of the working and auxiliary electrodes for WE1 and WE2; based on the difference in the obtained values ( $\Delta I_G$ ), polymer conductance ( $G$ ) was calculated as in [7]:

$$G = \frac{\Delta I_G}{2V_D}. \quad (1)$$

Experimental dependences  $I_G = f(V_G)$  and  $G = f(V_G)$  for  $\text{poly-}[\text{NiSalen}]$  are presented in Fig. 2, those for  $\text{poly-}[\text{NiCH}_3\text{OSalen}]$  are given in Fig. 3. In all the studied cases, the polymers are non-conductive ( $G < 10^{-3} \text{ mS}$ ) in the non-charged state (at  $V_G = 0 \text{ V}$ ). When  $V_G$  is shifted to above the threshold, different values of currents  $I_G$  are detected which evidence the presence of oxidation processes in the nickel-salen polymer channel. The polymer conductances increase sharply with the electrochemical doping level, reach the maxima and then decrease. The obtained  $G = f(V_G)$  curves with one (for  $\text{poly-}[\text{NiSalen}]$ ) or two (for  $\text{poly-}[\text{NiCH}_3\text{OSalen}]$ ) maxima differ significantly from the sigmoidal curves of the conductance versus voltage dependence characteristic of conjugated organic polymer



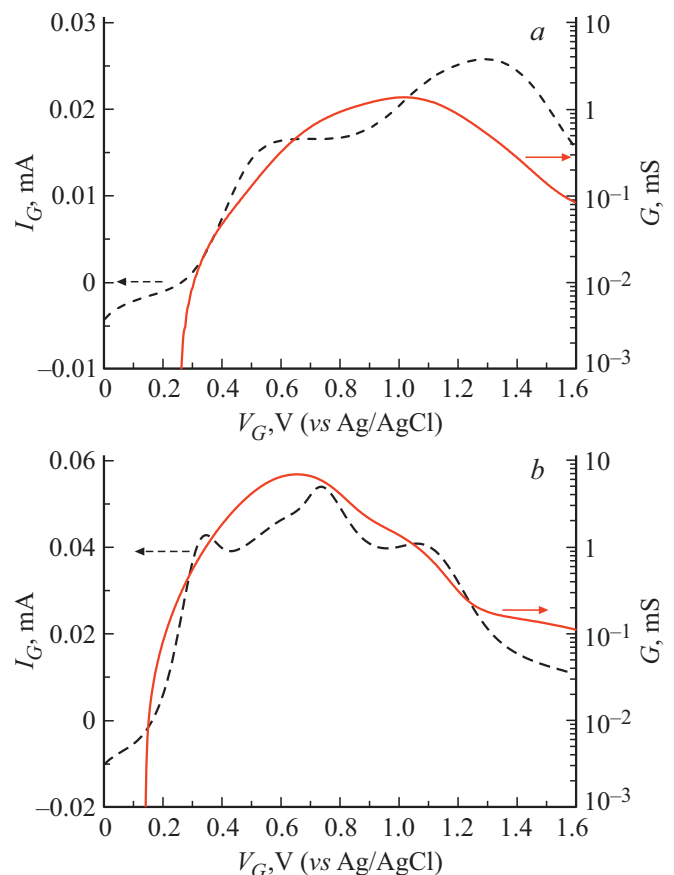
**Figure 2.** Gate current  $I_G$  (dashed line) and conductance  $G$  (solid line) versus gate-source voltage  $V_G$  for OEET with the  $poly$ -[NiSalen] polymer channel in electrolyte based on 1,2-dichloroethane (a) and acetonitrile (b).

films. Vice versa, they are similar to curves  $G = f(V_G)$  recorded for redox-polymers or conductive matrices with local conjugation areas between which charge is transported according to the hopping mechanism [10]. Earlier it was found out that oxidation of the system of phenyl rings of nickel-salen polymer ligands leads to sequential generation of two types of charge carriers in the film: radical cations and dications [5]. It is possible to assume that in the case of polymer  $poly$ -[NiCH<sub>3</sub>OSalen] the curve  $G = f(V_G)$  maxima are observed when equal particle concentrations are reached in the mixed-valent systems "neutral fragment/radical cation" and "radical cation/dication", respectively. In the case of  $poly$ -[NiSalen], formation of dications is hindered [5], thus each of the relevant curves exhibits only one conductance maximum.

The threshold gate-source voltage is significantly lower in  $poly$ -NiCH<sub>3</sub>OSalen than in  $poly$ -[NiSalen], which is obviously caused by easier oxidation of macromolecules with electron donating CH<sub>3</sub>O groups in the ligand structure. The transition from the non-conductive to conductive state is accompanied by an increase in  $G$  by two or three orders of magnitude in the case of  $poly$ -[NiSalen] and three or four orders of magnitude in the case of  $poly$ -

[NiCH<sub>3</sub>OSalen] depending on the solvent type. In transition from AN to DCE, both polymers exhibit a shift of the main conductance maximum towards higher  $V_G$ . After reaching the maximum, the  $poly$ -[NiSalen] conductance decreases rapidly to  $G < 10^{-3}$  mS. Values of  $G$  in a highly doped  $poly$ -[NiCH<sub>3</sub>OSalen] polymer film decrease relative to the maximal ones (by two orders of magnitude in AN and one order of magnitude in DCE) but remain of about  $10^{-1}$  mS at  $V_G = 1.3$  V. Thus the voltage range corresponding to the  $poly$ -[NiCH<sub>3</sub>OSalen] film conductive state (conductivity window) varies from 1.35 to 1.45 V (in electrolyte systems based on DCE and AN, respectively). The conductivity window width for polymer  $poly$ -[NiSalen] is less than values obtained for  $poly$ -[NiCH<sub>3</sub>OSalen] and stronger depends on the solvent nature, being 0.6 V in the 1,2-dichloroethane-based electrolyte and 0.2 V in the acetonitrile solution.

The observed changes in the curve  $G = f(V_G)$  parameters in transition from 1,2-dichloroethane to acetonitrile may be caused by differences in their donor ability (donor numbers are 0.0 for DCE and 14.1 for AN) and dielectric permeability (dielectric constants are 10.36 for DCE and 38.0 for AN). These characteristics of electrolyte solvents used for synthesizing and subsequent electrochemical doping of nickel-salen polymers can essentially affect the factors



**Figure 3.** Gate current  $I_G$  (dashed line) and conductance  $G$  (solid line) versus gate-source voltage  $V_G$  for OEET with the  $poly$ -[NiCH<sub>3</sub>OSalen] polymer channel in electrolyte based on 1,2-dichloroethane (a) and acetonitrile (b).

defining the charge carrier concentration ( $n$ ) and mobility ( $\mu$ ) in the films and, hence, their conductance ( $G \propto n\mu$ ). For instance, those factors are: 1) the macromolecule chain length and interchain distances in the polymer matrix; 2) charge states of metal centers in highly doped polymers; 3) intrachain and intermolecular electrostatic interactions in the films at different doping levels. The effect of the solvent nature on the above mentioned factors may be different for polymers with different ligand electronic structures. Evidently, this explains the absence of consistent patterns of variations in the curve  $G = f(V_G)$  parameters for polymers *poly*-[NiSalen] and *poly*-[NiCH<sub>3</sub>OSalen] upon varying the electrolyte solvent.

Thus, the work has shown the possibility of controlling parameters of the gate voltage dependence of electrical conductance of the nickel-salen polymers by varying the polymer film molecular composition and nature of the electrolyte system solvent. It has been established that the *poly*-[NiCH<sub>3</sub>OSalen] film in acetonitrile solution is characterized by a wide electrical conductivity window and can be converted to the conductive state at low threshold voltage; therewith, the electrical conductance varies within four orders of magnitude. This allows us to tentatively attribute this polymer to promising materials for channels of organic electrochemical transistors.

### Conflict of interests

The authors declare that they have no conflict of interests.

### References

- [1] P.R. Paudel, J. Tropp, V. Kaphle, J.D. Azoulay, B. Lüssem, *J. Mater. Chem. C*, **9** (31), 9761 (2021). DOI: 10.1039/D1TC01601F
- [2] D. Tu, S. Fabiano, *Appl. Phys. Lett.*, **117** (8), 080501 (2020). DOI: 10.1063/5.0012599
- [3] E. Zeglio, O. Inganäs, *Adv. Mater.*, **30** (44), 1800941 (2018). DOI: 10.1002/adma.201800941
- [4] M.T. Nguyen, R.A. Jones, B.J. Holliday, *Coord. Chem. Rev.*, **377**, 237 (2018). DOI: 10.1016/j.ccr.2018.08.004
- [5] I.A. Chepurayna, M.P. Karushev, E.V. Alekseeva, D.A. Lukyanov, O.V. Levin, *Pure Appl. Chem.*, **92** (8), 1239 (2020). DOI: 10.1515/pac-2019-1218
- [6] C. Freire, M. Nunes, C. Pereira, D.M. Fernandes, A.F. Peixoto, M. Rocha, *Coord. Chem. Rev.*, **394**, 104 (2019). DOI: 10.1016/j.ccr.2019.05.014
- [7] E.V. Beletsky, Yu.A. Volosatova, S.N. Eliseeva, O.V. Levin, *Elektrokhimiya*, **55** (4), 500 (2019) (in Russian). DOI: 10.1134/S0424857019030034
- [8] I. Kiersztyn, L. Neto, A. Carneiro, J. Tedim, C. Freire, A.R. Hillman, *J. Solid State Electrochem.*, **16** (9), 2849 (2012). DOI: 10.1007/s10008-012-1698-3
- [9] P. Pfeiffer, E. Breith, E. Liibbe, T. Tsumaki, *Justus Liebigs Ann. Chem.*, **503** (1), 84 (1933). DOI: 10.1002/jlac.19335030106
- [10] G. Salinas, B.A. Frontana-Urbe, *ChemElectroChem.*, **6** (16), 4105 (2019). DOI: 10.1002/celec.201801488.