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***In situ* conductance studies of electrochemically doped polymer thin films based on nickel-salen complexes**

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Abstract. Modulation of the electron transport properties of metallopolymers based on nickel-salen complexes N,N'-bis(salicylidene)ethylenediaminonickel(II) and N,N'-bis(3-methoxysalicylidene)ethylenediaminonickel(II) upon electrochemical p-doping was studied by *in situ* conductance measurements in an organic electrochemical transistor configuration. Both polymers showed bell-shaped conductance profiles upon positive voltage bias; the results were interpreted using the mixed-valence conductivity model. The electrochemical doping of the methoxy-substituted polymer film resulted in a change in its electrical conductance by four orders of magnitude, which indicates its potential suitability as a channel material for electrochemical transistors. Electrochemical quartz crystal microbalance studies confirmed mixed ionic-electronic transport in this polymer film and revealed different regimes of ion and solvent transfer in the polymer at different doping levels.

Keywords: conducting metallopolymer, electrochemical doping, nickel-salen complex, *in situ* conductance measurements, electrochemical quartz crystal microbalance, organic electrochemical transistor

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Материалы конференции

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Исследование проводимости электрохимически легированных тонких полимерных пленок на основе salenовых комплексов никеля

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Аннотация. Влияние электрохимического легирования на особенности электронного транспорта в полимерных формах salenовых комплексов никеля N,N'-бис(салицилиден)этилендиаминоникель(II) и N,N'-бис(3-метоксисалицилиден)-этилендиаминоникель(II) исследовано *in situ* методом измерения проводимости на экспериментальной установке, моделирующей условия функционирования органического электрохимического транзистора. Для обоих полимеров получены колоколообразные кривые зависимости проводимости от напряжения. При электрохимическом легировании метокси-замещенной полимерной пленки ее проводимость увеличивается на четыре порядка величины, что указывает на принципиальную возможность использования этого материала в каналах электрохимических транзисторов. Методом электрохимических кварцевых микровесов подтвержден смешанный электронно-ионный транспорт в данном полимере, а также



обнаружены различные режимы переноса ионов и растворителя в пленках с различным уровнем легирования

Ключевые слова: проводящий полимерный металлокомплекс, электрохимическое легирование, саленовый комплекс никеля, *in situ* измерения проводимости, электрохимические кварцевые микровесы, органический электрохимический транзистор

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Introduction

Thin films of polymeric mixed ionic-electronic semiconductors have attracted a great deal of attention in the past few decades as functional materials for a broad range of promising applications in energy storage and conversion, electrocatalysis, smart displays, actuators for soft robotics, and organic electronics [1]. An interesting example of conducting polymer-based electronic devices is the organic electrochemical transistor (OECT) used in chemical sensors and biosensors, circuits, memory and neuromorphic systems, wearable and implantable devices [2, 3]. In contrast to more well-known field-effect transistors, an OECT polymer channel bridging the source and drain electrodes is permeable to the ions of the electrolyte layer between the channel and the gate electrode. The working principle of an OECT involves bulk electrochemical doping of the channel material. Upon application of a gate voltage, electrolyte ions are injected into the channel to compensate the charge carrier formation. The doping state and conductivity of the polymer film is modulated by the amount of injected ions throughout its entire volume [4].

To be able to support the switching and amplification functions of an OECT, the channel materials are required to demonstrate a significant (over several orders of magnitude), fast, and reversible change in electronic conductivity upon electrochemical doping. In order to do that, a competitive OECT channel material should exhibit fast electronic transport in the horizontal direction (between the source and the drain) and effective ion penetration in the vertical direction (from the electrolyte into the channel) [5]. However, electronic and ionic transport in most known organic semiconductors cannot be improved simultaneously, which makes it difficult to maximize the device performance [6]. There is an ongoing search for novel polymers that efficiently transport and couple ionic and electronic charge and exhibit drastic variation in conductivity upon electrochemical doping.

Polymeric nickel(II) complexes with salen-type ligands are main-chain metallopolymers, in which oligomers formed by covalently linked monomer units (Fig. 1) can assemble into supramolecular structures. Nickel-salen polymers are undoped in their pristine state and can be electrooxidized (p-doped) in a supporting electrolyte. Unlike many other metallopolymers bearing redox-active metal sites, the electroactivity of nickel-salen polymers is centered at phenolate moieties while nickel(II) ions act as redox-innocent sites that mediate the electronic coupling between the phenolates [7]. In this work, the effect of electrochemical doping on the electrical conductivity of polymer films derived from N,N'-bis(salicylidene)ethylenediaminonickel(II) (poly-[NiSalen]) and N,N'-bis(3-methoxysalicylidene)ethylenediaminonickel(II) (poly-[NiCH₃OSalen]) (Fig. 1) was investigated to preliminarily evaluate the suitability of these polymers as OECT channel materials.

Materials and Methods

Monomeric complexes [NiSalen] and [NiCH₃OSalen] were synthesized as previously reported [8]. Polymer films were obtained by oxidative electropolymerization of corresponding monomers. The electrodeposition of polymers and subsequent measurements were performed in an argon atmosphere in three-electrode setups with a working electrode (WE), a glassy carbon counter electrode and a non-aqueous Ag/Ag⁺ reference electrode (+0.3 V versus Ag/AgCl/sat'd NaCl, which

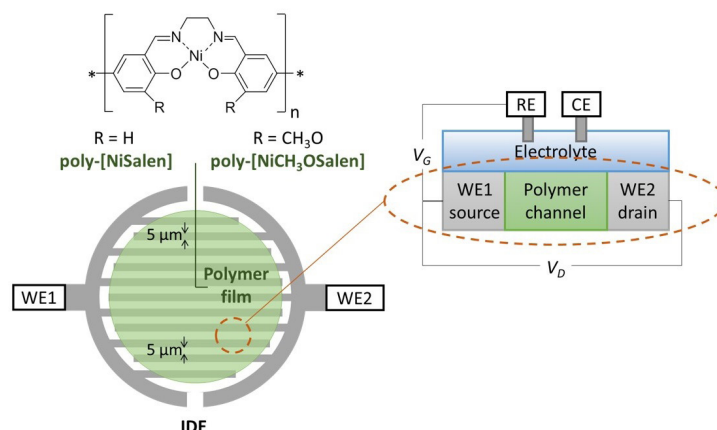


Fig. 1. The structures and abbreviations of the polymers, schematic representation of an interdigitated electrode (IDE), and an OEECT-like experimental setup

is used to report the values of electrode potentials in this study) operated by the VSP potentiostat (BioLogic Science Instruments). Two-terminal platinum interdigitated electrodes (IDE) with a comb distance of $5\ \mu\text{m}$ (MicruX Technologies) or platinum-coated quartz crystal substrates were used as working electrodes. A $0.1\ \text{M}$ solution of tetraethylammonium tetrakisfluoroborate (Et_4NBF_4) in acetonitrile (MeCN) was used as an electrolyte. The electropolymerization was performed by scanning the WE potential between $0.0\ \text{V}$ and $+1.6\ \text{V}$ at $10\ \text{mV/s}$ using $1\ \text{mM}$ monomer solution in $0.1\ \text{M}\ \text{Et}_4\text{NBF}_4/\text{MeCN}$.

In situ conductance measurements were performed on polymer-coated IDEs; two IDE combs constituted two working electrodes (WE1 and WE2) (Fig. 1). By using the potentiostat in a bipotentiostat mode, the working electrode potentials were biased with respect to the RE at a constant rate of $10\ \text{mV/s}$, while keeping a $10\ \text{mV}$ difference between WE1 and WE2. The currents on each WE were monitored and used to calculate the conductance of the polymer from Ohm's law as described in [9].

Electrochemical quartz crystal microbalance measurements were performed using a QCM100 (Stanford Research Systems) equipped with an MXC-1600 frequency counter (Metex). A positive bias sweep between $0.0\ \text{V}$ and $+1.6\ \text{V}$ at a $10\ \text{mV/s}$ rate was applied to the polymer-modified crystal as the working electrode. The change in the frequency of the crystal oscillation was converted to a change in mass using the Sauerbrey equation [10].

Results and Discussion

To evaluate electronic transport properties of poly-[NiSalen] and poly-[NiCH₃OSalen] films, their conductance was measured *in situ* [11] in an OEECT-like setup shown in Fig. 1. In this configuration, two platinum terminals of a polymer-coated IDE (WE1 and WE2) constitute the source and drain electrodes. The drain bias V_D is defined as the constant potential difference maintained between WE1 and WE2. The combination of a counter electrode (CE) and a reference electrode (RE) constitute the gate. The gate voltage V_G is the potential of the source electrode versus the reference so it is equal in magnitude but opposite in sign to the gate voltage in the solid state field-effect transistors. In this contribution, the data are presented using the V_G scale relative to Ag/AgCl.

Fig. 2 shows the conductance (G) versus gate voltage characteristics for poly-[NiSalen] and poly-[NiCH₃OSalen] (curve 1 in Fig. 2, *a*, and curve 1' in Fig. 2, *b*, respectively) in OEECT-like setups operated in $0.1\ \text{M}\ \text{Et}_4\text{NBF}_4$ in MeCN at $V_D = 10\ \text{mV}$. In both cases, the pristine polymer film is virtually non-conductive (*OFF* state). Upon application of a positive gate bias, the polymer conductance sharply increases at a threshold voltage V_T , reaches a maximum at V_M (*ON* state), and then decreases, i.e. both films show rather bell-shaped conductance profiles. Simultaneously with conductance measurements, the current flowing between the working and counter electrodes I_w was also monitored as a function of gate voltage (curve 2 in Fig. 2, *a* and curve 2' in Fig. 2, *b*

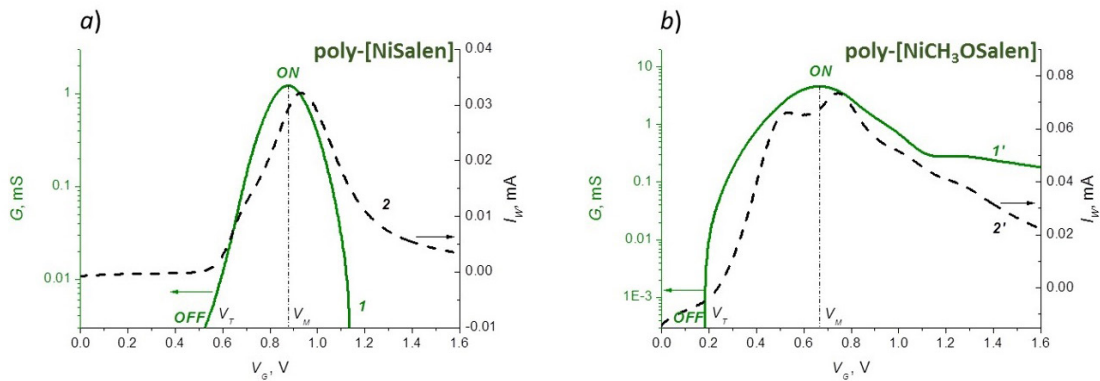


Fig. 2. Variation of conductance G (curves 1 and 1') and current I_w (curves 2 and 2') with gate voltage for poly-[NiSalen] (a) and poly-[NiCH₃OSalen] (b)

for poly [NiSalen] and poly-[NiCH₃OSalen], respectively). This current primarily arises from the electrochemical oxidation of the polymer film resulting in its conversion from the charge-neutral to the p-doped form. The $I_w = f(V_G)$ curves show several broad redox processes with oxidation onsets closely matching the values of V_T , and the oxidation current peaks associated with the conductance maxima. Depicted changes in conductance therefore result from the electrochemical doping of polymer films at $V_G > V_T$.

The conductance changes with gate voltage obtained for both polymers do not exhibit a sigmoidal shape typical for highly conjugated intrinsically conducting polymers; rather, they are reminiscent of bell-shaped conductance profiles observed for redox systems and organic oligomer networks [11]. Taking into account the small length of poly-[NiSalen] and poly-[NiCH₃OSalen] chains [12], it is feasible to apply the mixed-valence conductivity model [13] for the analysis of the experimental results. According to this model, the electronic transport in electrochemically doped polymers can be described as electron hopping between isoenergetic sites of the overlapping redox states available in the polymer film. The conductivity is proportional to the ratio of the occupied and unoccupied sites of a redox state and should reach a maximum when half the sites are charged. The main conductance maxima in $G = f(V_G)$ plots (curves 1 and 1' in Fig. 2) are reached at gate voltages equal to the half-wave potentials of the redox couples exhibiting the highest oxidation current peaks in $I_w = f(V_G)$ curves (curves 2 and 2' in Fig. 2). Based on the literature data [7], this conductivity regime can be attributed to the polymer conversion from the neutral to the radical cation state. For both polymers, the conductance increases in the voltage range between V_T and V_M following an increase in the concentration of mobile charge carriers generated in the polymer backbone. After reaching the maximum value, the conductance decreases due to the smaller number of sites available for hopping. In a highly doped poly-[NiSalen] film, the values of G quickly drop below 10^{-3} mS, which points out to the limited amount of redox states in the polymer. On the contrary, the $G = f(V_G)$ plot obtained for the methoxy-substituted film features several shoulders at $V_G > V_M$, which are indicative of the generation of additional (e.g., dicationic [7]) overlapping redox states, which contribute to a non-negligible (above 10^{-1} mS) polymer conductance at high doping levels.

The polymer composition has a pronounced effect of the parameters of $G = f(V_G)$ curves (Table 1). Compared to poly-[NiSalen], the poly-[NiCH₃OSalen] film shows lower threshold voltage and wider conductivity window (the voltage range in which the polymer is in the conductive state) due to the presence of electron-donating methoxy substituents in the ligand phenyl rings that increase the overall electron density in the polymer backbone and apparently enable charge carrier mobility over extended voltage range. Poly-[NiCH₃OSalen] demonstrates a conductance modulation by four orders of magnitude between ON and OFF states upon electrochemical doping, which indicates its potential suitability as an OECT channel material. For this polymer film, the variation of the conductance with gate voltage is reversible and stable for V_G in the range from 0 V to $V_M = 0.67$ V, which is the voltage range of interest for OECT applications. If the polymer is biased above V_M , a hysteresis in the conductance response and a gradual decrease in the G values are observed upon doping-dedoping.

Table 1

Parameters of $G = f(V_G)$ curves for studied polymers

Polymer	V_T (V)	V_M (V)	Conductivity window (V)	G_{ON}/G_{OFF}
poly-[NiSalen]	0.52	0.88	0.62	$\sim 10^{-3}$
poly-[NiCH ₃ OSalen]	0.18	0.67	1.42	$\sim 10^{-4}$

Table 2

Apparent dopant masses during oxidation of poly-[NiCH₃OSalen]

V_G range (V)	Apparent mass (g/mol)
0.18 – 0.70	38
0.70 – 0.97	93
0.97 – 1.18	170
1.18 – 1.35	260
1.35 – 1.6	80

The in situ conductance studies of poly-[NiCH₃OSalen] were complemented by electrochemical quartz crystal microbalance (EQCM) measurements to gain more insight into the ion uptake process during electrochemical doping of the polymer. A positive voltage bias was applied to the polymer film on the surface of a Pt-coated quartz crystal in the same V_G range and at the same rate as in the in situ conductance tests. A continuous non-monotonic increase in the polymer mass was observed, which may be indicative of the charge-compensating electrolyte ions (BF_4^-) moving into the polymer film upon its oxidation. To confirm this assumption, the apparent molar mass of the dopant counterions was calculated from the EQCM data, as previously described [14]. The results summarized in Table 2 show that the mechanism of charge compensation is voltage dependent. In the V_G ranges for which the apparent molar mass of the dopant is significantly smaller than the molar mass of the pure BF_4^- anion (87 g/mol), the dopant entry apparently requires concurrent solvent transfer in the opposite direction. And vice versa, values of the apparent dopant mass greater than 87 g/mol are consistent with simultaneous ingress of ions and solvent into the polymer film. Comparison of the data presented in Table 2 with the results of in situ conductance measurements (Fig. 2, *b*) indicates that the initial increase in the poly-[NiCH₃OSalen] conductance results from the doping of solvated polymer domains and is accompanied by solvent egress from the polymer film whereas the decrease in the conductance at high polymer doping levels is associated with excessive solvent uptake.

The integration of current with respect to time in EQCM measurements shows that when the poly [NiCH₃OSalen] film is biased to V_M , the amount of charge consumed in the doping process is nearly equal to the amount of charge extracted during the dedoping process and corresponds to half the total charge that can be extracted from the fully doped polymer. It confirms that the main conductance maximum is observed at equal concentrations of neutral and charged redox sites of the polymer film.

Conclusions

In this work, we presented a study on the electronic conductivity of nickel-salen type metallopolymers poly-[NiSalen] and poly-[NiCH₃OSalen]. The electrochemical doping of these polymer films in an OECT-like setup gives bell-shaped conductance profiles. Experimental results can be explained by mixed-valence conductivity between isoenergetic sites of redox states generated in the polymers, with the main conductance maxima observed at equal concentration of occupied and unoccupied sites in a neutral-radical cation mixed-valence systems. The poly-[NiCH₃OSalen] film shows a threshold voltage of 0.18 V, a wide conductivity window (over 1.4 V), and a conductance modulation by four orders of magnitude upon increasing the gate bias voltage, which makes it a preferred candidate for OECT applications. Electrochemical quartz



crystal microbalance studies confirm mixed-ionic electronic transport in this polymer film and reveal different regimes of ion and solvent transfer in the polymer at different doping levels. The elucidated structure-property relationships for mixed ionic-electronic transport in nickel-salen polymers can also be useful to other potential applications of these materials, for example, in the field of energy storage.

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