

Article

In-Situ EC-AFM Study of Electrochemical P-Doping of Polymeric Nickel(II) Complexes with Schiff base Ligands

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Abstract: Conductive electrochemically active metallopolymers are outstanding materials for energy storage and conversion, electrocatalysis, electroanalysis, and other applications. The hybrid inorganic–organic nature of these materials ensures their rich chemistry and offers wide opportunities for fine-tuning their functional properties. The electrochemical modulation of the nanomechanical properties of metallopolymers is rarely investigated, and the correlations between the structure, stiffness, and capacitive properties of these materials have not yet been reported. We use electrochemical atomic force microscopy (EC-AFM) to perform in-situ quantitative nanomechanical measurements of two Schiff base metallopolymers, poly[NiSalphen] and its derivative that contains two methoxy substituents in the bridging phenylene diimine unit poly[NiSalphen(CH₃O)₂], during their polarization in the electrolyte solution to the undoped and fully doped states. We also get insight into the electrochemical p-doping of these polymers using electrochemical quartz crystal microgravimetry (EQCM) coupled with cyclic voltammetry (CV). Combined findings for the structurally similar polymers with different interchain interactions led us to propose a correlation between Young's modulus of the material, its maximum doping level, and ion and solvent fluxes in the polymer films upon electrochemical oxidation.

Keywords: schiff base metal complexes; metallopolymer; poly[NiSchiff], p-doping; electrochemical quartz crystal microbalance; electrochemical atomic force microscopy; Young's modulus



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1. Introduction

Nickel(II) complexes with tetradentate N₂O₂ Schiff base ligands are used as monomers in the preparation of polymeric functional materials poly[NiSchiff] for advanced electrochemical energy storage cells, electrocatalytic systems, sensors, and electrochromic devices [1–6]. A detailed understanding of the fundamental properties and functionality of these polymers is key to designing materials with excellent performance characteristics. Much research has been devoted to elucidating relationships between the structure and electrochemical properties of metallopolymers obtained from Ni(II) Schiff base complexes [1,2], whereas their mechanical properties have been rarely assessed. It has been however acknowledged that understanding the factors affecting the mechanical integrity of redox active conducting polymers is an essential prerequisite in realizing their applications in electrochemical devices.

The p-doping of poly[NiSchiff] materials has been used as the basis of the majority of their applications in electrochemical cells. Polymer-modified electrodes undergo repeated charging/discharging accompanied by the ingress/egress of charge compensating anions and often solvent to maintain the electroneutrality of the polymer network. Polymeric Schiff base transition metal complexes show substantial swelling on anodic cycling due to the counter ion and solvent uptake [7]. Constant changes in the film thickness can negatively

affect the mechanical durability of the film and hence the stability of its electrochemical performance. The procedure for screening these metallopolymer as functional materials should therefore include not only the evaluation of electrochemical parameters such as doping level, charge transfer rate, mass transfer regimes, etc., but also the assessment of the ability of the polymer network to withstand multiple cycles of swelling/shrinking. The latter is expected to be defined by the composition, morphology, and nanomechanical properties of poly[NiSchiff] materials such as stiffness, hardness, plasticity, etc. It is also critically important to establish the relationship between the electrochemical performance and nanomechanical properties of conducting polymers.

Electrochemical quartz crystal microbalance (EQCM) is a valuable method for studying ion transport processes in polymer films. It allows us to follow mass changes during polymer switching between neutral and p-doped states. EQCM has been successfully used to estimate the maximum achievable p-doping levels in poly[NiSchiff] films [8] and to assess ion and solvent exchange between the polymer and the electrolyte solution upon redox cycling [9–11].

Atomic force microscopy (AFM) offers a unique opportunity to map surface mechanical properties of functional materials. The previous use of AFM in the research of Schiff base polymer films [12–16] has been largely limited to the standard imaging modes that provide high-resolution topographic information of the surface of the polymer film without any quantitative information regarding its nanomechanical properties. The nanoscale maps of stiffness, elastic modulus, adhesion force and other critical mechanical parameters of the material can be obtained using advanced AFM tapping modes such as PeakForce™ [17] and HybriD™ [18]. Both approaches are based on measuring the tip-sample force as a function of the tip-sample distance (an indentation curve). The analysis of the nanomechanical properties may be performed by calculating the value of directly measured contact stiffness from the slope of the indentation curve and using it to estimate the Young's modulus by applying one of the tip-sample contact models (Hertz, DMT, JKR). The HybriD™ mode enables fast recording of the force-distance curves (more than 1000 curves per second) because they are collected at the kHz rate as oscillatory motion of a sample is actuated by sine voltage wave. This allows real-time Quantitative nanomechanical measurements (QNM) that yield high spatial resolution maps of nanomechanical properties of the studied samples.

A combination of AFM and electrochemical techniques (EC-AFM) makes it possible to in situ monitor the changes in the electrode surface topology and nanomechanical properties during electrochemical reactions, which offers new opportunities in the characterization of redox-active functional materials [19]. In a recent study [20], atomic force microscopy in the PeakForce™ Quantitative Nanomechanical Mapping mode run under electrochemical conditions was used to monitor variations in nanomechanical properties of a redox-active film belonging to the family of poly[NiSchiff] polymers (poly[*meso*-N,N'-bis-(salicylidene)-2,3-butanediaminonickel(II)], or poly(*meso*-Ni-SaldMe)) caused by the ongoing oxidation-reduction. This method was combined with electrochemical piezoelectric microgravimetry at EQCM for in-depth characterization of the polymer film under electrochemical conditions.

In the present paper, we use EQCM and in-situ EC-AFM in the HybriD™ QNM mode (EC-HD QNM AFM) in combination with cyclic voltammetry (CV) to investigate the relationship between electrochemical and nanomechanical properties of poly[NiSchiff] films critical to their practical applications, namely the maximum achievable p-doping level, ion dynamics and stiffness of the polymer in different oxidation states in the electrolyte solution. We focus on two polymers with aromatic imine bridges electrosynthesized from the complexes [NiSalphen] and [NiSalphen(CH₃O)₂] (Figure 1). The synthesis and chemical structure of [NiSalphen] have been previously reported [21–24]. [NiSalphen(CH₃O)₂] is a novel complex that we recently synthesized and investigated [25]. The polymers with *Salphen* type ligands have not been as widely studied as their *Salen* type analogues with aliphatic imine bridges. However, adding another six-membered aromatic ring to the monomer structure could be the key to multielectron redox behavior of corresponding

metallopolymers [8,26,27], which is a desirable material property in many application areas [28,29]. The electrochemical synthesis and p-doping of poly[NiSalphen] has been described in previous studies [8,26,30], whereas poly[NiSalphen(CH₃O)₂] is a novel polymer that we electrosynthesized from the respective monomer to investigate the effect of introducing two strongly electron donating methoxy substituents in the bridging phenylenediimine unit on the functional properties of poly[NiSchiff] films.

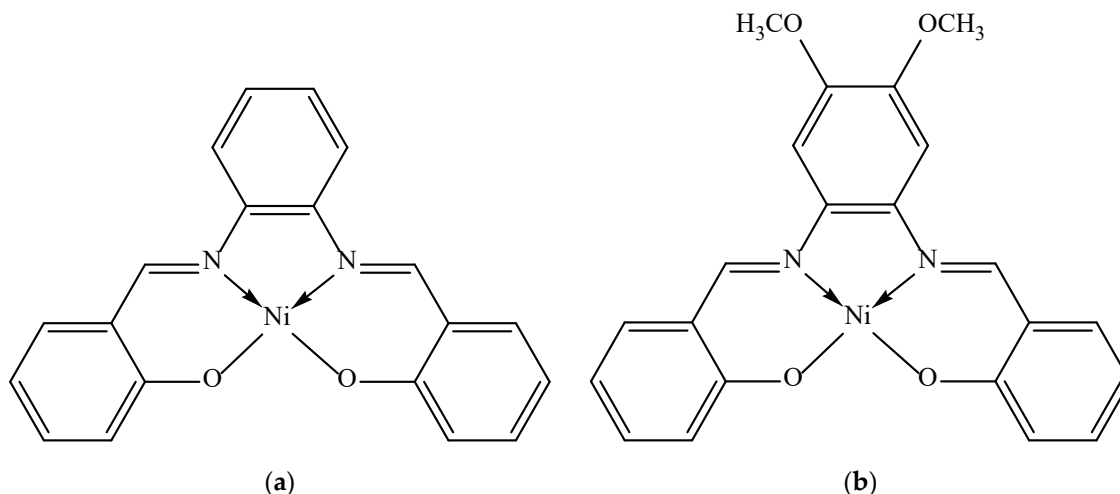


Figure 1. Molecular structures of [NiSalphen] (a) and [NiSalphen(CH₃O)₂] (b).

2. Results and Discussion

2.1. Electrochemical Synthesis of Polymer Films

The polymer films poly[NiSalphen] and poly[NiSalphen(CH₃O)₂] were synthesized by oxidative electrochemical polymerization of corresponding monomers on the Pt-plated quartz crystals and ITO electrodes that were later used for EQCM and EC-HD QNM studies, respectively. The electropolymerization was performed under potentiodynamic conditions (i.e., by cycling the potential of the working electrode in the monomer solution) as they favor more reproducible growth of the polymer layers as compared to potentiostatic electrode polarization [31]. The electrodeposition proceeded in a similar fashion on both electrodes (albeit a small anodic shift of polymerization potentials) so the discussion below is limited to the polymer growth on the platinum surface.

The starting monomers (Figure 1) differ only within the structure of the diimine bridge: the novel complex [NiSalphen(CH₃O)₂] contains two strongly electron-donating substituents in the bridging aromatic ring. The CH₃O- substituents introduced into the phenyl rings of the ligand have been previously shown to significantly affect the parameters of the electrodeposition process and electrochemical properties of the resulting poly[NiSchiff] films [8,32]. The effect of placing methoxy groups on the aromatic diimine bridge has not been reported.

In the first potential scan, the cyclic voltammetry (CV) curve of the working electrode in [NiSalphen] solution (Figure 2a) displays two overlapping oxidation waves with peak potentials at 1.09 V, and 1.18 V and a broad reduction peak at 0.85 V. In the second potential scan, a new anodic wave appears in the potential range from about 0.80 to 0.98 V while the peak current of the other waves increases. An increase in current continues through the third cycle, which indicates that a conducting polymer film is deposited on the platinum surface. The shape of the CV curves recorded in [NiSalphen(CH₃O)₂] solution (Figure 2b) is overall similar to the potentiodynamic curves of the oxidative electropolymerization of [NiSalphen]. The onset of oxidation is cathodically shifted with respect to the one of [NiSalphen] and so is the first oxidation peak observed at 1.00 V. The peak potentials of the second oxidation waves are identical (1.18 V). The cathodic peak is found at 0.80 V.

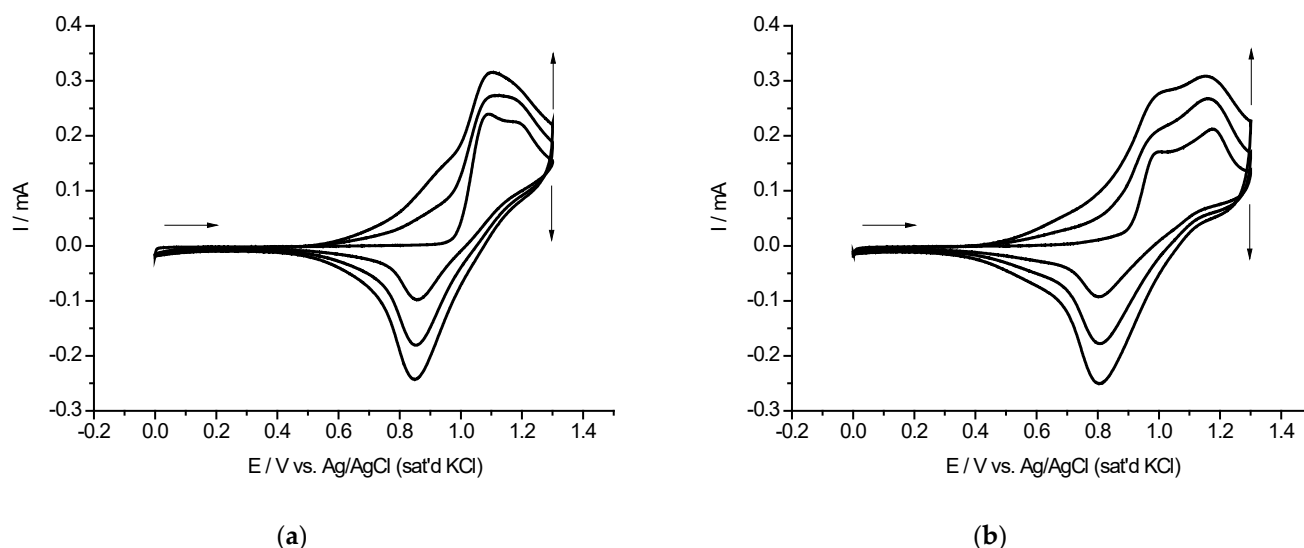


Figure 2. Cyclic voltammograms showing polymerization of [NiSalphen] (a) and poly[NiSalphen(CH₃O)₂] (b) at a Pt-coated quartz crystal electrode (1.37 cm²) at a scan rate of 0.05 V s^{−1} in 3·10^{−4} monomer/0.1 M Et₄NBF₄/CH₃CN. C.

Voltammetric responses of electrochemically active species undergoing electropolymerization are often quite complex, which makes it challenging to unambiguously identify the nature of redox processes associated with the observed redox waves. The first anodic peak in the CV curves of [NiSchiff] can be ascribed to the monomer oxidation. As seen in Figure 2a,b, the first oxidation peak of [NiSalphen(CH₃O)₂] is shifted to more negative potentials versus [NiSalphen] in accordance with the electron-donating nature of CH₃O-groups in the aromatic bridge.

The three voltammetric cycles of the working electrode in the [NiSalphen] and [NiSalphen(CH₃O)₂] solutions in the potential range from 0 to 1.3 V resulted in the deposition of similar polymer masses on the electrode surface (about 5 µg as determined by microgravimetric measurements) (Table 1). The thickness of the polymer films was in the 30–50 nm range. The obtained polymer layers completely covered the electrode surface, maintained mechanical integrity through testing, and displayed sufficiently uniform morphology and a rather smooth surface. No large globules or irregularly shaped domains were observed on top of the continuous polymer layers, which allowed to ascribe the differences in the electrochemical and nanomechanical properties of the two studied polymers to the different structure of their repeat units.

Table 1. The number of electrons exchanged by each repeat unit of the polymer film in the p-doping/dedoping in 0.1 M Et₄NBF₄/PC, values of the effective molar mass of the electrolyte species, and their proposed composition.

Polymer	Mass of Dry Polymer Film, m, µg (±0.1)	Number of Electrons Exchanged by Each Monomer Unit, n (±0.1)	Effective Molar Mass of the Electrolyte Species, M (±10), g mol ^{−1}	Proposed Composition of the Electrolyte Species
poly[NiSalphen]	5.1	1.2	190	BF ₄ [−] + PC
poly[NiSalphen(CH ₃ O) ₂]	4.9	1.5	245	BF ₄ [−] + 1.5 PC

2.2. Cyclic Voltammetry and EQCM Measurements

To gain a better understanding of electrochemical p-doping/dedoping of poly[NiSalphen] and poly[NiSalphen(CH₃O)₂] and to identify the type of electrolyte species that contribute to the redox charge balancing, the polymer films electrosynthesized on the Pt-plated quartz

crystals were tested by a combination of CV and EQCM in 0.1 M Et_4NBF_4 solution in propylene carbonate (PC), which matches the electrolyte solution used in EC-HD QNM studies.

Figure 3 shows the CV responses of poly[NiSalphen] (curve 1, Figure 3a) and poly[NiSalphen(CH_3O) $_2$] films (curve 1, Figure 3b) attributable to their electrochemical switching between neutral and p-doped states. The cyclic voltammograms of both polymers show a pair of pronounced redox peaks. The oxidation peaks appear at 1.12 V for poly[NiSalphen] and 1.09 V for poly[NiSalphen(CH_3O) $_2$]. The reduction peaks are located at 0.90 V and 0.88 V for poly[NiSalphen] and poly[NiSalphen(CH_3O) $_2$], respectively. Contrary to the oxidation of the monomers, there appears to be very little effect of CH_3O - groups in the bridging unit on the position of redox peaks and the shape of the voltammetric curves. The peak potentials of poly[NiSalphen(CH_3O) $_2$] are slightly shifted to more negative values, which reflects the overall higher electron density of the polymer containing electron-donating groups in the main chains. At the same time, as shown below, methoxy-substituents influence the maximum doping level achievable in the investigated polymer films.

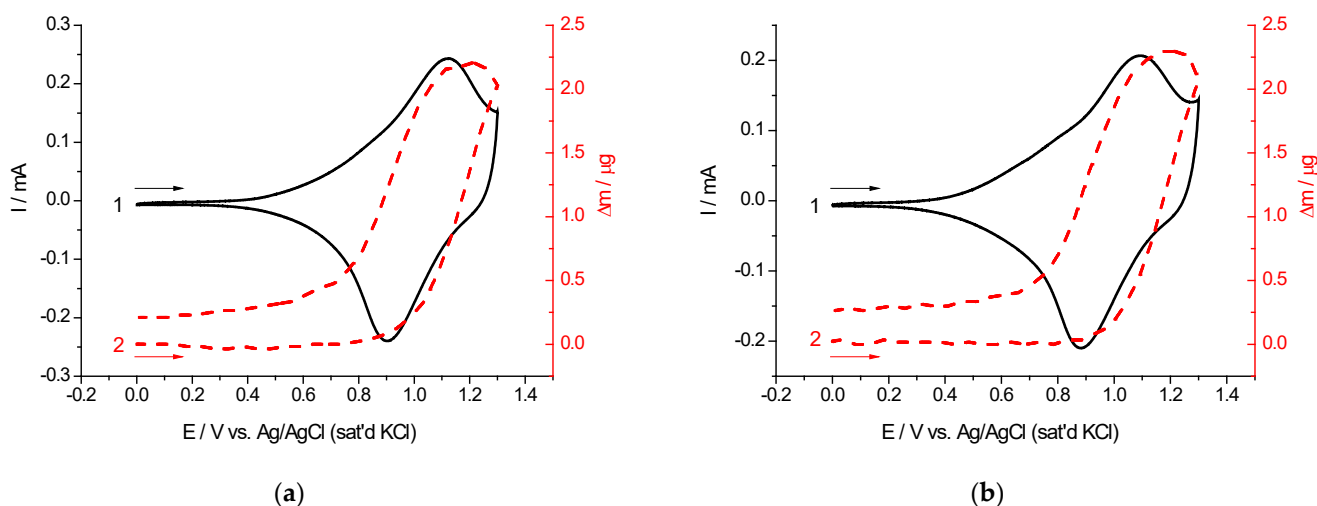


Figure 3. Cyclic voltammograms of a Pt-coated quartz crystal electrode (1.37 cm^2) modified with poly[NiSalphen] (a, black curve 1) or poly[NiSalphen(CH_3O) $_2$] (b, black curve 1) at a scan rate of 0.05 V s^{-1} in 0.1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ and the corresponding electrode mass variation vs. potential during the CV cycle of poly[NiSalphen] (a, red curve 2) or poly[NiSalphen(CH_3O) $_2$] (b, red curve 2).

We combined the results of electrochemical studies with the data on the mass of the dry uncharged polymer film obtained by microgravimetric measurements to determine the number of electrons n reversibly exchanged by repeat units of poly[NiSalphen] and poly[NiSalphen(CH_3O) $_2$] films during redox switching using the following equation [8]:

$$n = \frac{Q \times M}{F \times m}$$

where Q is the amount of charge passed in electrochemical reduction of a polymer film (C); M is the molar mass of a repeat unit (g mol^{-1}); F is the Faraday constant ($96,485 \text{ C mol}^{-1}$); and m is the mass of a dry polymer film (g).

As shown in Table 1, both poly[NiSalphen] and poly[NiSalphen(CH_3O) $_2$] films are able to exchange more than one electron per a monomer unit in the oxidation/reduction processes. Each monomer possesses several redox-active sites, which justifies the discovered multielectron redox processes in respective polymer films. A higher doping level is achieved in the more electron-rich polymer poly[NiSalphen(CH_3O) $_2$].

The EQCM responses accompanying p-doping/dedoping of poly[NiSalphen] (curve 2, Figure 3a) and poly[NiSalphen(CH₃O)₂] (curve 2, Figure 3b) show non-monotonic variation of electrode mass Δm with potential. In both cases, the polymer mass increases during the oxidation and decreases during the reduction of the polymer film. The data are consistent with the overall uptake of electrolyte species by the polymer network in the charging process and their expulsion during discharging. Figure 4 shows the mass change versus charge plots determined from the CV/EQCM measurements of the two polymer films (the mass changes are quite symmetrical in the forward and backward scans so the data for the reduction half-cycle are omitted for clarity). The linear segments of these curves are used to calculate the effective molar mass M of the electrolyte species exchanged during redox switching [9–11]. The Δm – ΔQ plots in Figure 4 show several linear segments. In the context of this research, the ones corresponding to the ion dynamics at more anodic potentials are of particular interest. As shown in previous studies [7], the transition of poly[NiSchiff] materials into highly doped states may be accompanied by dramatic volume changes (expansion on oxidation and contraction on the reduction). So the uncharged and charged polymer films are expected to display most pronounced differences in the nanomechanical properties. With respect to that, the values of M were calculated from the slopes of the linear segments of Δm – ΔQ plots in the potential range from 0.9 to 1.3 V. The obtained data shown in Table 1 are consistent with the transfer of a BF₄[−] anion (86.81 g mol^{−1}) and a PC molecule (102.09 g mol^{−1}) into the poly[NiSalphen] film, and one BF₄[−] anion and 1.5 molecules of propylene carbonate into the poly[NiSalphen(CH₃O)₂] film upon oxidation of high anodic potentials.

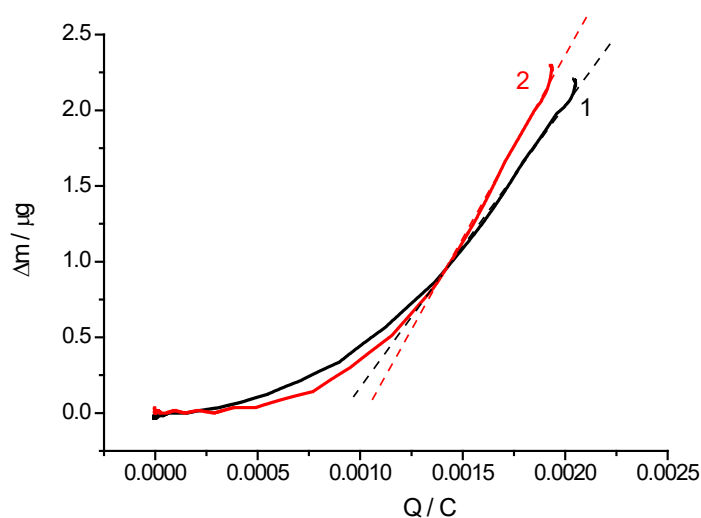


Figure 4. An oxidation mass-charge plot of a Pt-coated quartz crystal electrode (1.37 cm²) modified with poly[NiSalphen] (black curve 1) or poly[NiSalphen(CH₃O)₂] (red curve 2) at 0.05 V s^{−1} in 0.1 M Et₄NBF₄/PC.

As follows from Table 1, there is a correlation between the maximum achievable doping level and the amount of solvent ingress into the polymer network. The nanomechanical properties of the polymer film should enable the reversible structural changes upon counter ions and solvent exchange for stable electrochemical performance.

2.3. In-Situ Electrochemical Atomic Force Microscopy Measurements

Stiffness is an important parameter of a functional conducting polymer material as it refers to its resistance to deformation. The material stiffness is directly proportional to Young's modulus: stiff materials have high Young's moduli and vice versa. An EC-HD QNM mode of AFM was used to investigate the changes in the elastic modulus of the studied polymer films induced by p-doping/dedoping.

Young's modulus maps were obtained for poly[NiSalphen] (Figure 5) and poly[NiSalphen(CH₃O)₂] (Figure 6) in the undoped and p-doped states. Due to data variation across the scanned areas, the average values of Young's modulus were recalculated from the data of the probe-sample contact stiffness signal using the nominal value of the probe curvature $R_T = 10$ nm (Table 2). For both polymers, they are in the hundreds of MPa range, which agrees well with the previously published data [20].

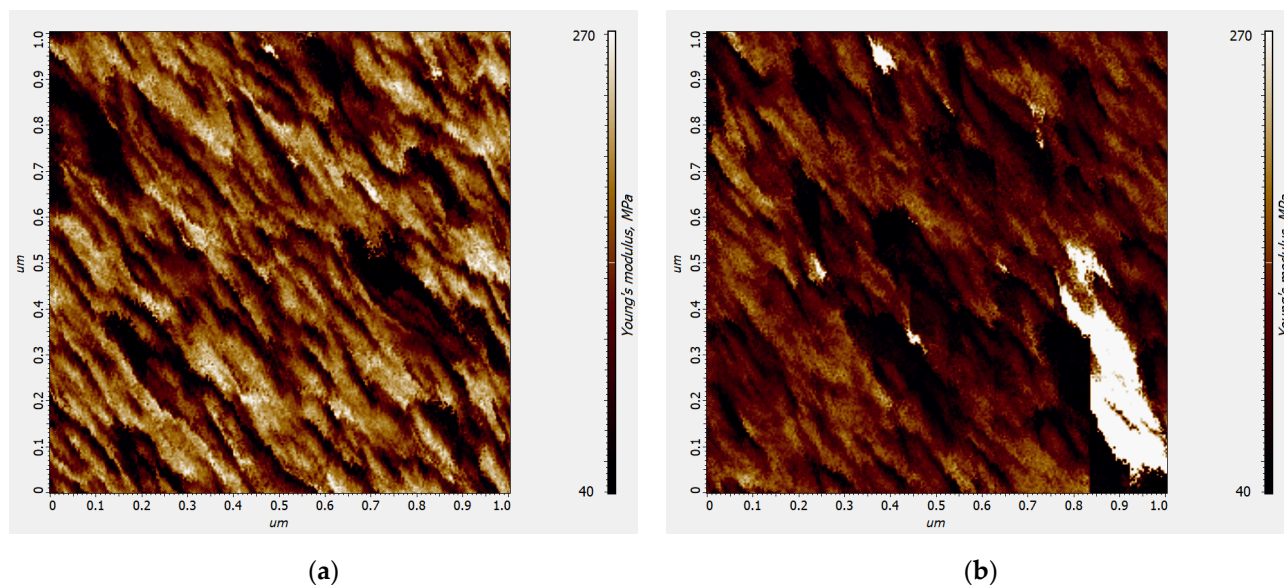


Figure 5. The maps of Young's modulus of the poly[NiSalphen] film in 0.1 M Et₄NBF₄/PC in the uncharged (a) and charged (b) states acquired by EC-HD QNM AFM.

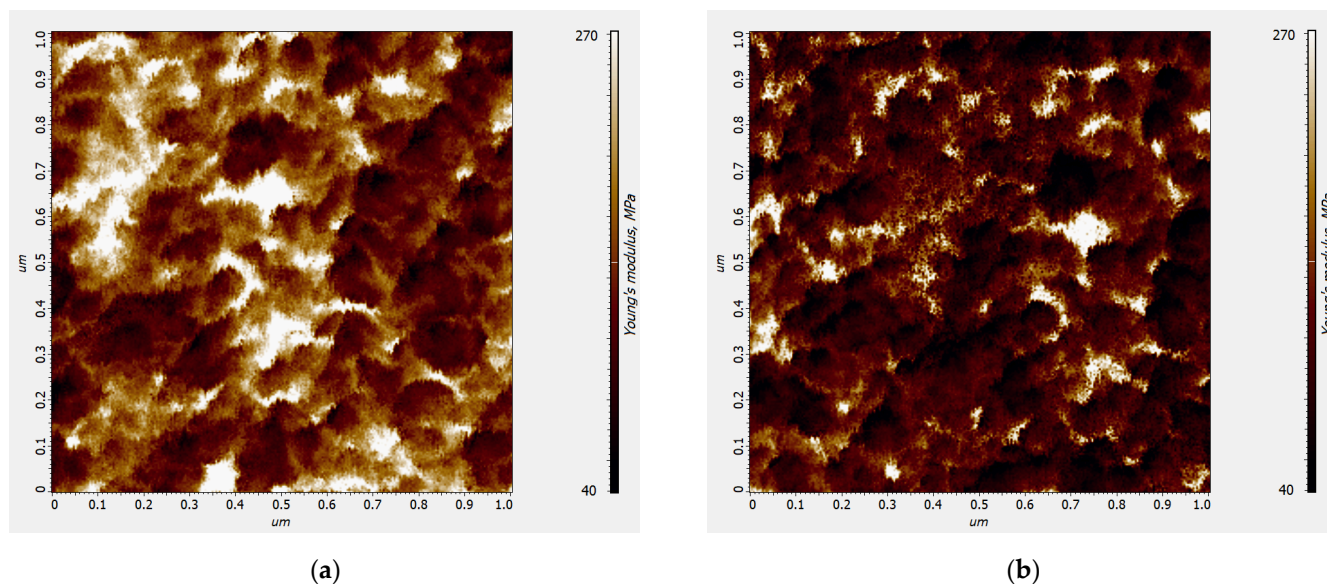


Figure 6. The maps of Young's modulus of the poly[NiSalphen(CH₃O)₂] film in 0.1 M Et₄NBF₄/PC in the uncharged (a) and charged (b) states acquired by EC-HD QNM AFM.

Table 2. Average Young's modulus of polymer films in uncharged and charged states in 0.1 M Et₄NBF₄/PC.

Polymer	Average Young's Modulus, MPa	
	Uncharged State	Charged State
poly[NiSalphen]	175 ± 8	108 ± 4
poly[NiSalphen(CH ₃ O) ₂]	145 ± 5	95 ± 4

As follows from Table 2, the uncharged poly[NiSalphen(CH₃O)₂] is softer than the poly[NiSalphen] film. The decrease in Young's modulus of the polymer upon introducing two CH₃O- substituents into the aromatic bridges of their repeat units can be explained by inhibited interchain interactions due to steric hindrance created by bulky methoxy groups. In both cases, the polymer stiffness decreases upon electrochemical p-doping due to the ingress of charge compensating anion and solvent into the space between polymer chains: the Young's modulus decreases by 38% for poly[NiSalphen] and by 34% for poly[NiSalphen(CH₃O)₂]. The relative changes in the elastic modulus upon polymers p-doping are similar, so the oxidized poly[NiSalphen(CH₃O)₂] film remains softer than poly[NiSalphen], but the difference between the two doped polymers is less dramatic than in the neutral (uncharged) state. Ultimately, the polymer stiffness depends on its composition and doping level; the changes in the Young's modulus of the polymer are caused by ingress and egress of electrolyte species associated with the transfer of electric charge.

The discussed EQCM/CV and in-situ EC-HD QNM AFM results suggest that the changes in the polymer nanomechanical properties, ion dynamics, and pseudocapacitive behavior with the state of charge are interrelated. It appears that softer polymers can accommodate higher additional electrolyte volume so they can be reversibly charged to higher doping levels. Poly[NiSalphen(CH₃O)₂] has 17% lower Young's modulus in the uncharged state, higher apparent molar mass of transferred electrolyte species at anodic cycling (higher solvent uptake), and 25% higher number of electrons exchanged by each repeat unit in the electrochemical switching than poly[NiSalphen]. The discovered relationship between the Young's modulus of the polymer film and its pseudocapacitive properties is a novel structure-property finding that could be as essential to designing advanced functional materials for energy storage applications as the relationship between the material stiffness and its durability in multiple charge/discharge cycles. Combined EQCM/CV and in-situ EC-AFM studies of various series of poly[NiSchiff] films are currently under way in our laboratory to further confirm the revealed relationships between their electrochemical and nanomechanical properties.

3. Materials and Methods

3.1. Chemicals

1,2-phenylenediamine (Aldrich), 1,2-dimethoxybenzene (Aldrich), salicylaldehyde (Aldrich), nickel(II) acetate (Aldrich), J.T.Baker[®] BIOANALYZED[™] acetonitrile (Avantor Performance Materials), and propylene carbonate (anhydrous, electrochemical grade) (Sigma-Aldrich) were used as received without further purification. Tetraethylammonium tetrafluoroborate Et₄NBF₄ (Sigma-Aldrich, 99%) was recrystallized from isopropyl alcohol and dried at 65 °C for 72 h before use. The monomeric complexes [NiSalphen(CH₃O)₂] and [NiSalphen] were synthesized according to the previously described standard procedure [33]. It involved the condensation of salicylaldehyde with appropriate diamine to obtain the free ligand, which was then reacted with nickel(II) acetate to yield the final product. The obtained complexes were recrystallized from ethanol and dried at 60 °C for several hours. The details of [NiSalphen] synthesis and its structure verification by IR spectroscopy, ¹H NMR spectroscopy, and elemental analysis are described in [24]. The details of [NiSalphen(CH₃O)₂] synthesis and its structure determination by X-ray diffraction analysis, IR, ¹H and ¹³C NMR spectroscopy are reported in [25].

3.2. Electrochemical Synthesis of Poly[NiSalphen] and poly[NiSalphen(CH₃O)₂]

The films were deposited onto ITO electrodes or Pt-plated quartz crystals by oxidative electropolymerization from 0.1 mol L⁻¹ Et₄NBF₄/CH₃CN solutions containing 0.0003 mol L⁻¹ monomeric complex by three potentiodynamic cycles in the potential range from 0.0 to 1.3 V vs. Ag/AgCl (sat'd KCl) at a scan rate of 0.05 V s⁻¹. A customized three-electrode electrochemical cell was used for the electropolymerization. After polymerization, the polymer-modified electrode was rinsed with the acetonitrile and dried for 30 min before further use.

3.3. Combination of Cyclic Voltammetry and EQCM Measurements

Electrochemical syntheses and examinations of the polymer films were performed using VSP potentiostat-galvanostat (Bio-Logic Science Instruments, France). A 5 MHz QCM100 Quartz Crystal Microbalance (Stanford Research Systems Inc., USA) connected to an MXC 1600 frequency counter (Metex, Korea) was used to determine the mass of the films deposited on the electrode.

The customized electrochemical cell was a closed single compartment three-electrode cell, equipped with a platinum-plated quartz crystal (electrode area 1.37 cm²) as the working electrode, a glassy carbon plate (12.5 cm²) as the counter electrode, and a non-aqueous Ag/Ag⁺ reference electrode (MW-1085, BASi) filled with a 0.005 mol L⁻¹ AgNO₃ solution in 0.1M Et₄NBF₄/CH₃CN. The potential of this reference electrode was +0.3 V vs. an Ag/AgCl (sat'd KCl). The numerical values all potentials are referred to the Ag/AgCl (sat'd KCl) reference electrode. All the experiments were performed at ambient temperature.

The oscillation frequency of the dry crystal was measured before and after polymerization. In the latter case, the polymer-modified electrode was dried until the crystal reached a constant oscillation frequency (for about 30 min). The mass of the dry film was then calculated by using the Sauerbrey equation [34], which relates the mass change per unit area at the electrode surface to the observed change in the oscillation frequency of the crystal.

The cyclic voltammetry and EQCM characterization of the films was performed in a 0.1 mol L⁻¹ Et₄NBF₄/propylene carbonate solution in the range of potentials from 0.0 V to 1.3 V at 0.05 V s⁻¹.

3.4. In-Situ EC-HD QNM AFM

In-situ EC-HD QNM AFM measurements were performed using an Ntegra Aura atomic force microscope (NT-MDT, Russia) and Epsilon potentiostat/galvanostat (BASi, USA). The experimental setup consisted of a three-electrode cell (NT-MDT, Russia) equipped with a polymer-modified ITO glass plate (1 cm²) as the working electrode, a platinum wire (length 3 cm, diameter 1 mm) as the counter electrode and a Ag/AgCl wire (length 3 cm, diameter 1 mm) as the reference electrode. The cell was filled with a deaerated 0.1 mol L⁻¹ Et₄NBF₄/propylene carbonate solution.

The mapping of the nanomechanical properties of a polymer film was carried out with a high resolution high accuracy AFM probe HA_NC_B (NT-MDT, Russia) with nominal spring constant $k_C = 4$ N/m and nominal tip radius $R_T = 10$ nm. The cantilever spring constant was calibrated by thermal noise and Sader methods [35] before each measurement. During the electrochemical experiment the probe was completely covered with electrolyte.

The polymer surface was scanned vertically over the area of 1 $\mu\text{m} \times 1 \mu\text{m}$ with a scanning rate of 0.5 Hz, 256 points per line. The initial AFM image of the polymer surface was captured at OCV (−0.03 V), the position of the polymer surface in this experiment was set as a fixed scanning position. The following AFM images were captured with the same set of parameters as the initial image.

The electrode was polarized at a constant potential of 0.0 V vs. Ag/AgCl, KCl(sat) to capture the AFM image of the undoped polymer film. After that, the polymer was charged by linear sweep voltammetry at 5 mV/s scan rate from 0.0 V to 1.0 V, followed by anodic polarization at a constant potential of 1.0 V to capture the AFM image of the doped polymer

film. After that, the polymer film was discharged to 0.0 V at 5 mV/s. The procedure was repeated for at least 3 times. All experiments were performed at ambient temperature.

The images were post-edited by Gwyddion modular program, version 2.61 (<http://gwyddion.net/> accessed: 7 June 2022). Images of 256×256 pixels were acquired at the area of $1 \times 1 \mu\text{m}$, thus collecting a total of 65,536 force curves. Based on each curve, the tip-sample contact stiffness k_s was calculated using the measured force curve slope S as: $k_s = k_c S / (S_0 - S)$ (S_0 is the slope of the force curve on a solid substrate without a polymer film). After that, the Young's modulus, E , for every pixel of the image was evaluated as $E = k_s / R_T$ and average values of Young's modulus were calculated for uncharged and charged polymer films.

A tip-scratch method was used to measure the thickness of the polymer films on the electrode surface.

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