ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 10, pp. 1890−1893. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © M.A. Besedina, S.A. Krasikova, A.M. Timonov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 10, pp. 1738−1741.

MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Ionic Charge Transfer in Films of Polymeric Complexes of Transition Metals with Schiff

M. A. Besedina, S. A. Krasikova, and A. M. Timonov

Herzen Russian State Pedagogical University, St. Petersburg, Russia

Received April 1, 2009

Abstract—Transport of charge-compensating ions in redox transformations in films of polymeric complexes of nickel, copper, and palladium with tetradentate Schiff bases was studied by electrochemical quartz crystal microgravimetry.

DOI: 10.1134/S1070427209100279

Polymer films exhibiting conjugate electronic–ionic conductivity are promising materials for energy storage systems, membrane electrochemistry, polymer microelectronics, bioelectrochemistry, and selective electrocatalysis. The basic problem whose solution will determine further progress in the development and use of such polymeric materials is elucidation of relationships between their composition, structure, and properties.

Polymer films based on complexes of transition metals (M) with tetradentate Schiff bases (examples of the compounds are shown in Fig. 1a) are capable of functioning in both nonaqueous and aqueous solutions. They exhibit high mechanical strength and thermal stability.

In our previous studies we determined the structure of these materials (Fig. 1b) and found methods for controlling it on the nano- and molecular levels [1, 2]. An important characteristic of the polymers is also the rate of charge transfer in the polymer matrix [3].

In the general case, the most important interrelated steps of this process are as follows:

(i) electron transfer between the redox centers, which can occur by the mechanism of electron hopping;

(ii) introduction into the polymer, diffusion–migration transfer in the polymer, and exit from the polymer of charge-compensating ions, due to the need for compensating the volume charge arising in the polymer in the course of redox processes (concept of conjugate electron–ion flows);

(iii) introduction into the polymer, diffusion transfer in the polymer, and exit from the polymer of solvent molecules in the course of redox processes.

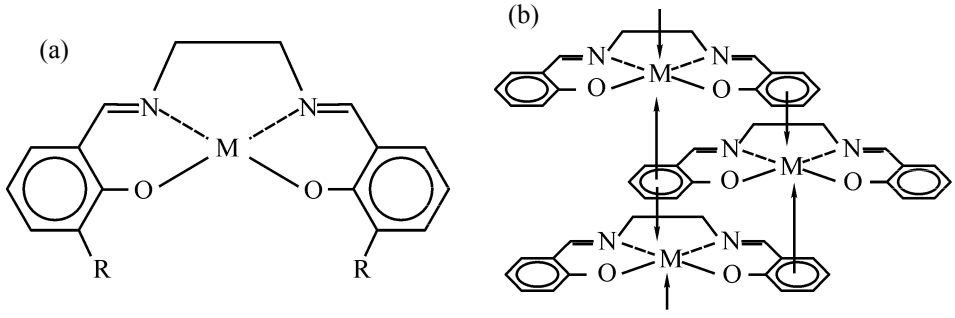

Fig. 1. (a) Scheme of the structure of the starting complexes [M(Schiff)] and (b) structure of the polymers poly-[M(Schiff)]. (a) M = Ni, Pd, Cu; R=H: [M(SalEn)] = *N,N*'-ethylenebis(salicylideniminato)metal(II); R=OCH_3: [M(CH_3O–SalEn)] = *N,N*'-ethylenebis(3-methoxysalicylideniminato)metal(II). (b) Polymers consist of stacks in which separate fragments are bonded by donor–acceptor interaction between the metallic center of one fragment and the ligand of another fragment.

In the majority of polymers, the limiting step of charge transport is motion of charge-compensating ions occurring in the electrolyte solution inside the film. Specifically this process determines the operation speed of devices based on these polymers, and therefore it requires further study. One of the most informative and advanced methods for studying the ionic charge transfer in polymers is in situ electrochemical quartz crystal microgravimetry (EQCMG) used in this study.

EXPERIMENTAL

As starting compounds for preparing polymeric complexes poly-[M(Schiff)] we used complexes of Cu(II), Ni(II), and Pd(II) with Schiff bases. Their structure is shown in Fig. 1. The general procedure for preparing the starting complexes [M(Schiff)] is described in [4]. By this procedure, using commercially available ligands H_2(SalEn) (Aldrich) and H_2(CH_3O–SalEn) (Aldrich), we synthesized the complexes [M(SalEn)] and [M(CH_3O–SalEn)]. The complexes were identified by electronic absorption spectra [5, 6]. For preparing supporting electrolyte solutions we used tetraethylammonium tetrafluoroborate $(Et_4N)BF_4$ (Merck, 97%). Before preparing solutions, the salt was dried at 125°C for 12 h in an inert atmosphere. As solvent we used acetonitrile (AN) (Kriokhrom, grade 0).

The use of electrochemical quartz crystal microbalance (EQCM) allows recording of electrochemical characteristics of the system in the course of polymer formation and testing simultaneously with recording of the polymer weight on the electrode. An installation for microgravimetric studies includes the complex QCM100 Quartz Crystal Microbalance Analog Controller + QCM25 Crystal Oscillator (Stanford Research Systems, USA) and an Epsilon2 potentiostat (BAS, USA). Variation of the crystal vibration frequency (eigenfrequency 5 MHz) caused by variation of the polymer weight on the electrode was recorded automatically with a Metex MXC 1600 frequency meter (Korea).

The holder with the working electrode was placed in a hermetically sealed 100-ml glass cell. The working electrode was a quartz piezoelectric crystal with a platinum layer sputtered onto it (working surface area 1.37 cm^2), the auxiliary electrode was a glassy carbon plate of size 10 × 30 mm, and the reference electrode was MF-2062 (BAS, USA), Ag^+/Ag in 0.1 M $(Et_4N)BF_4$/AN. The potential of the reference electrode is +0.34 V relative to the silver chloride electrode filled with a saturated aqueous solution of sodium chloride. All the potentials are given vs. this silver chloride electrode.

Determination of the polymer weight on the electrode surface by the method of electrochemical quartz crystal microbalance is based on the dependence of the crystal vibration frequency on the electrode weight (Sauerbrey equation) [7]:

$$\Delta f = -C_f \Delta m,$$

where Δm is the change in the electrode weight; Δf, the corresponding change in the resonance frequency of the crystal; and C_f, crystal sensitivity factor.

The crystal sensitivity factor is a constant characteristic of a quartz crystal. It does not take into account the properties of the film being deposited and amounts to 56.6 Hz cm^2 μg^{-1} at room temperature. Estimation of the contribution of viscoelastic interactions of the crystal with the film and electrolyte solution to changes in the crystal vibration frequency showed that this contribution is negligible compared to the effect exerted on the frequency by changes in the polymer weight.

The number of replicate runs in each experiment with EQCM was no less than three; the reproducibility of the results was no less than 90%.

Previously [3], using cyclic chronovoltammetry, we determined the charge diffusion coefficients in the polymers examined in this study. We also determined the limiting steps of the charge transport process: For the nickel- and palladium-containing polymers, the limiting step is the motion of ions in the polymer matrix, and for the copper-containing polymers, motion of electrons over polymer stacks. A change in the nature of the limiting step in the polymeric copper complexes is associated with the fact that fragments of the polymer in these complexes are linked via the oxygen atom in the Schiff base, which drastically decreases the rate of electron motion along the polymer chain [3]. The charge diffusion coefficients in the polymers under consideration are given in the table.

In going from polymeric complexes of nickel to those of palladium with similar ligand surrounding, the metal d orbitals become more diffuse, and the donor–acceptor bonds between polymer fragments become stronger and shorter, which leads to the formation of denser polymer films and to a decrease in the rate of the ion transport in the system.

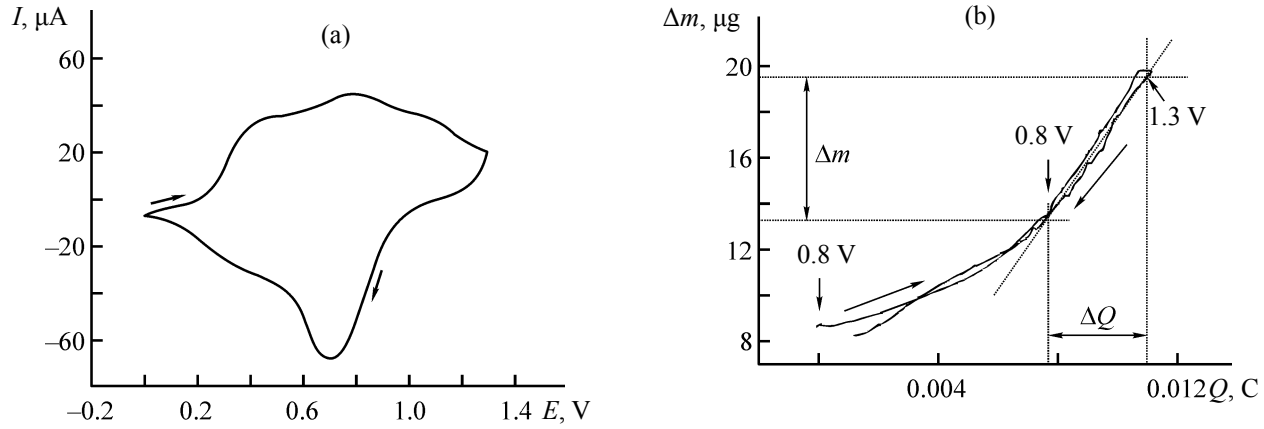

Fig. 2. (a) Voltammogram of poly-[Ni(CH_3O–SalEn)] and (b) polymer weight as a function of the charge spent for its oxidation/reduction. (a) (I) current and (E) potential; film thickness 0.5 μm, V_s = 0.05 V s^{-1}, 0.1 M (Et_4N)BF_4/AN. (b) (Δm) weight change, (E) potential, and (Q) amount of electricity; 0.1 M (Et_4N)BF_4/AN, V_s = 0.01 V s^{-1}.

This assumption was proved by in situ electrochemical microgravimetry. Namely, we determined the composition of species participating in the charge transport in oxidation/reduction of polymers in supporting electrolyte solutions. As seen from Fig. 2a, oxidation of the polymer is accompanied by an increase in its weight due to introduction of charge-compensating ions and solvent molecules into the film, and the reduction is accompanied by exit of the corresponding species from the film. From the ratio $\Delta m/\Delta Q$ (Fig. 2b), it is possible to determine the molar weight of charge-transferring species participating in the oxidation and reduction of the polymer film (see the table):

$$M = nF(\Delta m/\Delta Q),$$

where n is the absolute value of the ion charge (n = 1), and F is the Faraday constant.

In poly-[Ni(CH_3O–SalEn)], the polymer oxidation is accompanied by introduction into the film of the BF_4^- ion and two acetonitrile molecules per polymer fragment.

In poly-[Pd(CH_3O–SalEn)], the molecular weight of charge-transferring species is 60 ± 3 g mol^{-1}, which can be accounted for as follows: the BF_4^- ion entering into the film in the course of oxidation displaces from it one acetonitrile molecule. In going from poly-[Ni(CH_3O–SalEn)] to poly-[Pd(CH_3O–SalEn)], the weight of charge-transferring species decreases, which may be due to formation of a denser structure of the film.

In going from poly-[M(SalEn)] to poly-[M(CH_3O–SalEn)], the molar weight of the charge-transferring species increases, i.e., the polymer density decreases. Apparently, methoxy groups, like methyl groups [8], enhance repulsive interactions in the polymer, favoring a decrease in its density and an increase in the rate of the ion transport.

Charge diffusion coefficients D, limiting steps of charge transport processes, and molar weights of charge-compensating species in polymeric films of poly-[M(Schiff)]. Polymer preparation conditions: five cycles of scanning in the potential range 0–1.3 V at a rate V_s = 50 mV s^{-1} in solution containing 1 mM [M(Schiff)] and 0.1 M (Et_4N)BF_4/AN

Polymer	$D \times 10^{10}$, cm^2 s^{-1}	Limiting step (i, transport of ions; e, transport of electrons)	Molar weight and composition of species compensating polymer charge
Poly-[Ni(SalEn)]	2.0 ± 0.2	i	135 ± 3 (BF_4^- + 1 AN)
Poly-[Ni(CH_3O–SalEn)]	4.0 ± 0.2	i	180 ± 5 (BF_4^- + 2 AN)
Poly-[Pd(SalEn)]	1.0 ± 0.2	i	50 ± 3 (BF_4^- – 1 AN)
Poly-[Pd(CH_3O–SalEn)]	1.7 ± 0.2	i	60 ± 3 (BF_4^- – 1 AN)
Poly-[Cu(SalEn)]	0.2 ± 0.2	e	130 ± 3 (BF_4^- + 1 AN)
Poly-[Cu(CH_3O–SalEn)]	0.3 ± 0.2	e	140 ± 5 (BF_4^- + 1 AN)

In poly-[Cu(Schiff)] complexes, if the process mechanism were preserved, the molar weights of charge carriers would correspond to the diffusion coefficient of the BF_4^- ions, i.e., would be of the order of (2–4) × 10^{-10} cm^2 s^{-1}. However, actual charge diffusion coefficients are lower by an order of magnitude, which confirms a change in the nature of the limiting step of the charge transport. Furthermore, this example shows that a combination of voltammetry with EQCMG allows estimation of the rate of transport of charge-compensating ions even in the case when this step is not limiting in the overall charge transport in the polymer.

CONCLUSIONS

(1) The method of in situ quartz crystal microgravimetry allows monitoring of changes in the composition and density of poly-[M(Schiff)] films in the course of redox transformations of the polymers.

(2) In oxidation of poly-[Ni(SalEn)] and poly-[Ni(CH_3O–SalEn)], compensation of polymer charge with BF_4^- ions is accompanied by introduction into the film of one acetonitrile molecule per polymer fragment. Oxidation of poly-[Pd(SalEn)] and poly-[Pd(CH_3O–SalEn)] is accompanied by introduction into the film of one BF_4^- ion and exit from the film of one acetonitrile molecule per polymer fragment.

(3) Replacement of Ni as metallic center by Pd leads to a considerable increase in the density of polymer films and to a twofold decrease in the rate of transport of charge-compensating BF_4^- ions.

(4) Introduction of methoxy groups into the ligand surrounding of poly-[M(Salen)] leads to a decrease in the polymer density and an increase in the rate of transport of BF_4^- ions.

REFERENCES

1. Tchepurnaya, I.A., Vasilieva, S.V., Logvinov, S.A., et al., *Langmuir*, 2003, vol. 19, no. 21, pp. 9005–9012.
2. Rodyagina, T.Yu., Gaman'kov, P.V., Dmitrieva, E.A., et al., *Elektrokhimiya*, 2005, vol. 41, no. 10, pp. 1224–1233.
3. Rodyagina, T.Yu., Chepurnaya, I.A., Vasil'eva, S.V., and Timonov, A.M., *Zh. Prikl. Khim*., 2005, vol. 78, no. 9, pp. 1416–1422.
4. Pfeiffer, P., Breith, E., Lubbe, E., and Tsumaki, T., Justus Liebigs Ann. Chem., 1933, vol. 503, p. 84.
5. Vasil'eva, S.V., Balashev, K.P., and Timonov, A.M., *Elektrokhimiya*, 1998, vol. 34, no. 10, pp. 1090–1096.
6. Vasil'eva, S.V., Balashev, K.P., and Timonov, A.M., *Elektrokhimiya*, 2000, vol. 36, no. 1, pp. 85–89.
7. Sauerbrey, G.*, Z. Phys*., 1959, vol. 155, pp. 206–222.
8. Dmitrieva, E.A., Logvinov, S.A., Kurdakova, V.V., et al., *Elektrokhimiya*, 2005, vol. 41, no. 4, pp. 433–441.