03,13,14

Semiconductor Properties of Polymer Films Based on Nickel Complex with Salen-type Ligand

© Yu.A. Polozhentseva[1], E.V. Alekseeva[2], M.P. Karushev[1,¶]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] St. Petersburg State University,
St. Petersburg, Russia

¶ E-mail: mkarushev@mail.ioffe.ru

Received July 12, 2021
Revised September 9, 2021
Accepted September 9, 2021

Metal complexes of Schiff bases are considered as promising materials for energy storage and photovoltaic devices. In this work, the semiconducting properties of a polymer film of a nickel salen-type complex (poly-Ni(CH_3O-Salen)) were studied by spectrophotometric and electrochemical impedance spectroscopy methods. The Mott-Schottky analysis showed that the polymer film is a semiconducting material with a fairly narrow band gap, high charge carrier density and *p*-type conductivity. Using the method of electrochemical impedance spectroscopy, the limiting stage of the oxygen photoelectroreduction reaction, the process of charge transfer from the film to molecular oxygen, has been established.

Keywords: Schiff bases, Mott-Schottky analysis, photovoltaic devices, semiconductor properties.

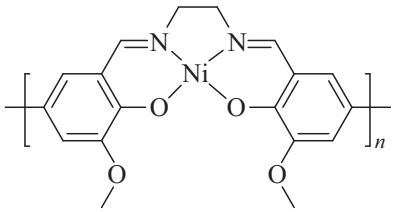
DOI: 10.21883/PSS.2022.01.52489.166

1. Introduction

Technologies for wide use of renewable energy sources are being actively developed at present. Among the available renewable energy resources, conversion of sunlight energy [1,2] attracts the most attention. Such photovoltaic devices can convert solar energy directly into electric or chemical energy without causing environmental damage. The chemical method of solar energy conversion is based on chemical reactions during which solar energy is stored, i.e. reaction products are substances richer in energy than the initial reagents. At present, solar energy converters use super-pure semiconductor materials, which makes the device much more expensive [3]. As an alternative, organic, inorganic and hybrid semiconductor materials are being widely studied; they can potentially replace the expensive materials in photoelectrochemical solar energy converters [4,5]. Though the use of organic materials is cheaper, their efficiency is yet insufficient for wide commercial application [6,7].

Complexes of transition metals with Schiff bases have a high stability, electrochemical activity, electric conductivity and can be considered as new semiconductor materials for photoelectric converters [8–10]. Such polymer films are conjugated systems. Electrons in them freely move along the polymer chain, which ensures efficient charge transport in the entire polymer volume. When irradiated by light or in the presence of electron-acceptor molecules, the film becomes *p*-doped: electrons are transferred from the film surface through the phase boundary, a positive charge forms on the film surface and is compensated by electrolyte solution ions. A Schottky barrier forms. The Mott–Schottky plot can be used to estimate the polymer film's semiconductor properties, such as conductivity type, band gap, charge carrier density etc.

In this paper we studied the semiconductor properties of a polymer film of a nickel complex with salen-type ligand, poly-Ni(CH_3O-Salen), its structure is shown in the diagram



An earlier paper [11] has shown the possibility to use the polymer poly-Ni(CH_3O-Salen) film in photoelectrocatalytic energy converters by oxygen photoelectroreduction reaction. This paper has established the limiting stage of the oxygen photoelectroreduction process by the method of electrochemical impedance spectroscopy. The Mott–Schottky theory was used to describe the electron emission into the solution of oxygenated supporting electrolyte.

2. Experimental part

The Ni(CH_3O-Salen) monomer was synthesized as per the procedure [12] using commercially available aldehyde and diamine.

All electrochemical studies, including measurements of electrochemical impedance, were performed using

the Bio-Logic potentiostat (BioLogic Science Instruments, France) in a three-electrode cell, the working electrode was a glass-carbon (GC)-plate ($2\,cm^2$); platinum foil served as an counter electrode. A non-aqueous Ag/Ag^+ electrode MF-2062 (Bio Analytical Systems, USA), filled with acetonitrile solution containing 0.005 M of $AgNO_3$ and 0.1 M of Et_4NBF_4, was used as a reference electrode for electropolymerization in the acetonitrile solution. An Ag/AgCl (KCl sat.) electrode was used for aqueous solutions. The system's impedance response was analyzed in Nyquist coordinates using the EC-Lab software (Bio-Logic, France).

Prior to each experiment, the GC-electrode was thoroughly ground, washed with isopropyl alcohol and deionized water, and then dried at 120°C.

The polymer was deposited onto the GC-electrode by electrooxidative polymerization with the potential of 1 V vs Ag/AgCl from the acetonitrile solution containing 0.001 M of Ni(CH_3O-Salen) and 0.1 M of Et_4NBF_4 as supporting electrolyte. After passing of a certain charge ($10\,mC/cm^2$), the electrode was held at the potential of 0 mV for 5 min to fully reduce the polymer film that formed on its surface.

A light source for photoelectrochemical experiments was a blue light-emitting diode (470 nm), with the power of 12 W, distance from the light-emitting diode to the working electrode was 5 cm. Radiation power was estimated as $100\,mW/cm^2$. Experiments for photoelectrical oxygen reduction were carried out in 0.05 M aqueous solution of phosphate buffer (pH = 6.86).

Impedance was measured in the frequency range of 0.1 Hz–100 kHz at different potentials. The alternating voltage amplitude was 10 mV. The film was preliminarily held for 2 min at each potential value to attain the steady-state condition. Mott–Schottky measurements were performed at the fixed frequency of 10 kHz in the potential range of −0.15–0.4 V (rel. Ag/AgCl) with the interval of 50 mV. Measurements were performed without irradiation and with light irradiation both in argon atmosphere and in oxygen atmosphere.

Spectrophotometric studies were carried out using the SF-2000 spectrophotometer (Russia) in argon atmosphere. The polymer film was deposited on glass covered with conductive oxides (ITO), the film spectrum was recorded in an acetonitrile solution containing 0.1 M of Et_4NBF_4 as supporting electrolyte, the potential being 0 V.

3. Discussion of results

When semiconductors are irradiated with light, photoinduced current is sometimes observed in the circuit of the illuminated electrochemical cell [13,14]. Illumination causes electron transition to a higher energy level, valence-band electrons go to the conduction band, leaving positively charged holes in the valence band. The possibility of such processes in the poly-Ni(CH_3O-Salen) film was studied by the voltammetric method.

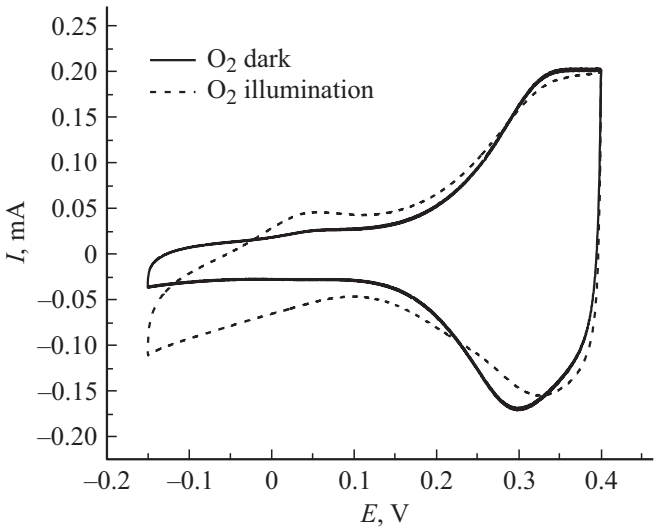


Figure 1. Cyclic voltammetric diagram of the polymer poly-Ni(CH_3O-Salen) film, recorded in oxygenated solution of phosphate buffer (pH = 6.86) with and without irradiation; scanning rate is 50 mV/s.

Voltammetric measurements were carried out in the potential range of −0.15–0.4 V in oxygenated aqueous solution of phosphate buffer (pH = 6.86) with and without irradiation by light. In this potential range, the polymer poly-Ni(CH_3O-Salen) film was electrochemically stable (Fig. 1).

In the potential range of 0.1–0.4 V the polymer film is electrochemically active, the voltammogram has waves that characterize the oxidation and reduction processes in the film volume. Without irradiation, at potentials below 0.1 V, the polymer film is electrochemically inactive, the voltammogram has no polymer oxidation/reduction waves. Electroreduction of dissolved oxygen on the film does not occur at this potential values the current flow corresponds to the background values. When irradiated with light, the polymer film starts acting as a photocathode, currents of oxygen electroreduction occur in the potential range of −0.15–0.4 V, observed current is higher as compared to the film's electrochemical response in the absence of irradiation, and this difference increases when the potential moves to the more negative region.

Photocathode irradiation by light always causes multiple electron-hole pairs at the film–solution interface [14,15]. However, this process is compensated by a reverse process — their recombination. Recombination centers can be, for instance, film structure defects or surface states. These pairs can be efficiently separated due to the presence of dissolved oxygen in the solution. Adsorption of oxygen molecules on the film surface causes a partial charge transfer from the film to oxygen, thus hindering the recombination of electron-hole pairs formed under the light.

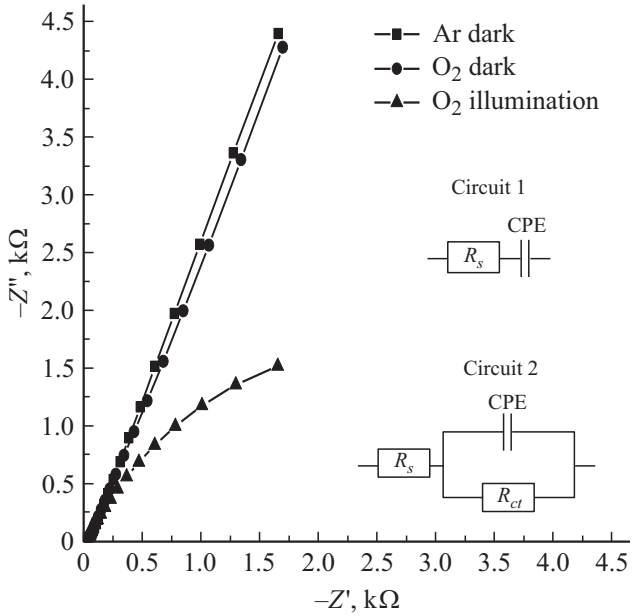


Figure 2. Nyquist plots of the electrochemical impedance spectra of the poly-Ni(CH_3O-Salen) film obtained in phosphate buffer solution (pH = 6.86) in the presence/absence of dissolved oxygen with the potential of 0 V, as well as with and without film irradiation by light. The electric equivalent diagrams for calculations of the main parameters are also given.

Electrochemical impedance spectroscopy studies have been performed to determine the limiting stage of the process of oxygen photoelectroreduction on the surface of the polymer poly-Ni(CH_3O-Salen) film.

Figure 2 shows the impedance spectra in Nyquist coordinates, obtained at 0 V (the potential of beginning of oxygen photoelectrochemical reduction). Without light irradiation, the spectra plots obtained for the oxygen-saturated and deaerated solution virtually coincide and consist of linear segments that correspond to the constant phase element, which is determined by capacitance of the double electric layer at the film–solution interface. Such systems can be described by an electric circuit comprising a solution resistance (R_s) connected in series to a constant phase element (CPE) (circuit 1). Spectra plot of the film on irradiation changes shape. A distorted semicircle appears in the plot, which shows the occurrence of a Faraday processes related to the electron transfer in the film and at the film–solution interface. Thus, a new element appears in the circuit — charge transfer resistance (R_{ct}) (circuit 2). The experimental data were approximated and the parameters of the chosen electric circuits were determined with the minimum deviation of the model spectrum and the experimental data spectrum. The calculated parameters are given in Table 1.

As seen from Table 1, when dissolved oxygen appears in the solution, photoelectrode capacitance increases due to the adsorption of oxygen molecules on the film surface

Table 1. Calculated parameters obtained from impedance hodographs

Conditions	R_s, Ω	CPE, $mF \cdot s^{a-1}$	a	R_{ct}, kΩ
Ar in darkness	32	0.378	0.87	–
O_2 in darkness	17	0.47	0.87	–
O_2 with irradiation	15	0.82	0.79	7.3

and partial charge transfer from the film to oxygen. Under illumination, the capacitance value almost doubles as compared to dark conditions. This means active generation of electron-hole pairs on the film surface and their efficient separation due to charge transfer to the adsorbed oxygen. Thereat, charge transfer resistance is rather high, which means that this stage is the limiting one in oxygen photoelectroreduction.

Band gap is an important characteristic of material's semiconductor properties. The band gap was determined using the spectrophotometry method; the film spectrum in the reduced state (0 V) is shown in Fig. 3.

Auxiliary lines were drawn to determine the wavelength at which electron transitions occur in the film and absorption starts growing in relation to the baseline. The intersection point of these lines corresponds to the wavelength of 530 nm, while the band gap value is 2.3 eV. Band gap for semiconductors is within 1–3 eV, the value obtained for the film shows that the film pertains to the semiconductor group.

The Mott–Schottky plot at different frequencies was obtained for more detailed study of the film–solution interface and to determine the flat-band potential and charge carrier density. It is known that polymer films become *p*-doped [16–18] in the presence of molecular oxygen. As a result of electron transition through the phase boundary,

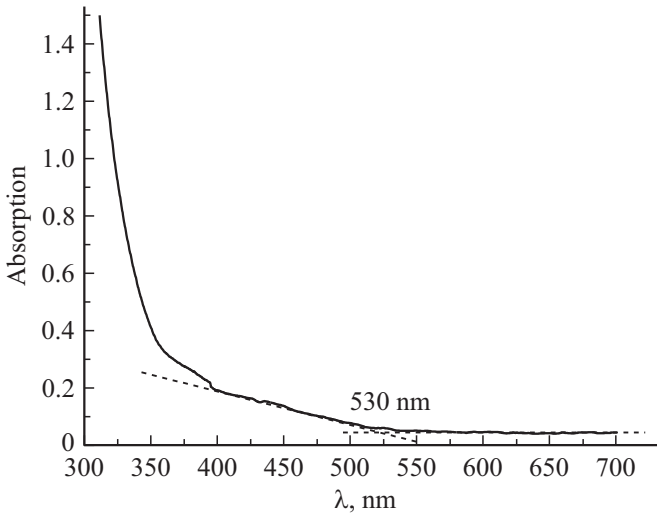


Figure 3. Spectrum of poly-Ni(CH_3O-Salen) film on an ITO-electrode, recorded in acetonitrile solution 0.1 M of Et_4NBF_4 with the potential of 0 V (reduced form).

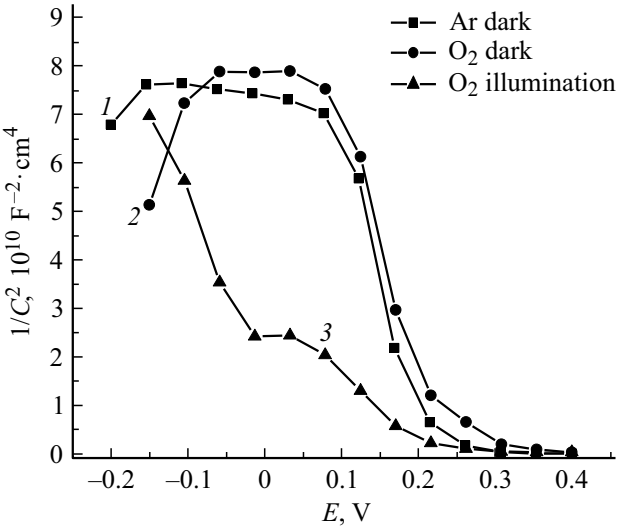


Figure 4. Mott–Schottky plots for the photoelectrode of poly-Ni(CH_3O-Salen) obtained: *1* — without oxygen and illumination, *2* — in the presence of oxygen and without illumination, *3* — in the presence of oxygen and with illumination. The measurements have been done at the 10 kHz frequency.

the film surface becomes positively charged, this charge is concentrated not only on the film surface, but forms a certain charged region near the semiconductor surface — the so-called space-charge region. A Schottky barrier forms at the film–electrolyte boundary, a depletion region forms in the film (a space-charge region) and there is bending of the energy bands at the interphase boundary of the semiconductor with the electrolyte solution [15,19,20]. Dependence of capacitance of the space-charge region in the film on potential is described by the Mott–Schottky law:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\varepsilon\varepsilon_0 A^2 eN}\right)(V - V_{FB}), \qquad (1)$$

where C_{sc} is capacitance of the space-charge region, e is the electron charge, V is the value of applied potential, ε is the dielectric constant for electrode material (film) ($\varepsilon = 2.4$ [21]), N is the density of charge carriers, k is the Boltzmann's constant, ε_0 is the permittivity of vacuum, T is the absolute temperature value, V_{FB} is the flat-band potential, A is the electrode surface area.

The slope for the linear part of the Mott-Schottky graph, $2/\varepsilon\varepsilon_0 A^2 eN$,can be used to find the charge carrier concentration N; value of the flat-band potential is determined by linear extrapolation onto the potential axis.

Figure 4 shows the Mott–Schottky plots for the photoelectrode of poly-Ni(CH_3O-Salen) in the presence and absence of oxygen, as well as with and without illumination.

Linear parts of the Mott-Schottky plots are observed in the potential range of 0.1−0.2 V. Within the framework of the Mott–Schottky theory, this means that, depending on voltage applied to the interphase boundary, its semiconductor properties are changed. Transition from one conductivity type to another takes place (from *n* to *p* or vice versa). The type of charge carriers in the film (*p*- or *n*-type) can be determined according to dependency type. In this case, the negative slope of the Mott–Schottky curves corresponds to the *p*-type conductivity, i.e. the major charge carriers are holes (hole-type conductivity). This correlates with the voltammetry data, where a transition region from the oxidized to reduced film state is observed in the potential range of 0.1−0.2 V.

A value of the flat-band potential is obtained by extrapolating the linear parts of the curves onto the potential axis. At all conditions (presence or absence of oxygen/illumination), the value of the flat-band potential is about 0.2 V (Table 2). Thickness of the space-charge region at the flat-band potential is zero. At the more positive potentials electrode capacitance is not longer dependent on the applied potential, and the film is in the doped (oxidized) state.

Also, electrode capacitance in the absence of oxygen and illumination is no longer dependent on the potential in the range of −0.2−0.1 V (curve *1*, Fig. 4). This corresponds to the fully reduced state of the film, conductivity type changes and the major charge carriers are electron but not holes (electron conductivity).

Generally, the Mott-Schottky plot of the film in oxygenated solution (curve *2*, Fig. 4) is identical to the plot obtained in the solution with no oxygen (curve *1*, Fig. 4). However, with oxygen in the system, it is adsorbed on the film's active centers. It is particularly noticeable in the potential region below −0.1 V, where slope inversion is observed. In this case, electron concentration in the surface layer is higher than hole concentration, that can be due to oxygen adsorption on the film and partial transfer of the negative charge between the film and oxygen molecules.

When the photoelectrode is illuminated in oxygen atmosphere, a second linear region with negative slope appears on the Mott–Schottky plot in the potential range −0.15−0 V (curve *3*, Fig. 4). This linear region cannot be interpreted as a change of band bending in the semiconductor. Since a double layer is formed by a space charge in the semiconductor and ions in the solution, the full interfacial potential difference consist of a potential difference in the space-charge region in the semiconductor and a potential difference in the Helmholtz layer. A significant potential difference in the Helmholtz layer occurs in the region of negative potential values (below 0 V); this change is much more than in the space-charge region. This phenomenon is called Fermi level pinning [22–24]. The reason of Fermi level pinning is the electrochemical reaction of oxygen electroreduction. The composition of the oxidation-reduction system in the solution changes, i.e. the semiconductor electrode's Fermi level is changed not electrically but due to a change of the electrochemical potential of the solution. Moreover, the film surface may have surface states whose charge varies in the considered potential region, that may also cause Fermi level pinning. The Mott–Schottky plot

Table 2. Results of Mott–Schottky analysis

Conditions	Density of charge carriers, cm^{-3}	Potential of flat bands V_{fb}, V	Doping degree of the film in the range 0.1–0.2 V, %
Ar in darkness	$7.8 \cdot 10^{19}$	0.20	2.8
O_2 in darkness	$1.1 \cdot 10^{20}$	0.25	3.9
O_2 with irradiation	$3.7 \cdot 10^{20}$	0.21	13.3

is still a straight line, but its slope is no longer equal to $2/\varepsilon\varepsilon_0 eN$, and it cannot be used for further calculations.

The slope of the Mott–Schottky plot can be used to calculate the charge carrier density

$$N_D = \frac{2}{e\varepsilon\varepsilon_0\alpha}, \quad (2)$$

where α is the slope of the linear region of the Mott–Schottky plot.

The obtained values are given in Table 2.

The slope of data shows that the charge carrier density in the film increases when oxygen presents in the solution. About 30% of charge carriers are generated due to oxygen adsorption and partial charge transfer from the film to oxygen. Density of charge carriers in the film in case of illumination in oxygen-containing solution increases by more than 3 times compared to the identical conditions without illumination. This additional charge was generated in the film due to illumination and complete charge transfer from the film to oxygen. The reduced oxygen molecule is desorbed from the film surface and diffuses into the solution. The film doping level was about a few of percent without illumination and increased to 13.3% under illumination.

4. Conclusion

The band gap value of the poly-Ni(CH_3O-Salen) film was 2.3 eV, indicating that the material is a semiconductor. The Mott–Schottky analysis has been performed to estimate the film's semiconductor properties; it has been showed that the polymer film is a semiconductor material with a fairly narrow band gap, a high density of charge carriers and the *p*-type conductivity. The limiting stage of the oxygen photoelectroreduction has been established. It has been showed that the limiting stage of the reaction is the charge transfer from the film to molecular oxygen. Thus, the polymer poly-Ni(CH_3O-Salen) film can be considered a promising material for harvesting and conversion of solar energy, as well as for creation of photocatalytic systems.

Funding

This research has been carried out under the state assignment (topic number 0034-2019-0003) (chemical and electrochemical synthesis), with support by the Russian Foundation for Basic Research, grant number 18-03-00864 (photocatalytic research), Russian Foundation for Basic Research, grant number 19-29-08026 (electrochemical research).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] W. Cao, J. Xue. Energy Environ. Sci. **7**, *7*, 2123 (2014).
[2] G. Li, R. Zhu, Y. Yang. Nature Photonics **6**, *3*, 153 (2012).
[3] Z.I. Zhurayeva. Universum: Tech. Sciences **10**, *55*, 7 (2018).
[4] M. Skompska. Synth. Met. **160**, *1–2*, 1 (2010).
[5] G. Yu, A.J. Heeger. J. Appl. Phys. **78**, *7*, 4510 (1995).
[6] C. Nicolet, D. Deribew, C. Renaud, G. Fleury, C. Brochon, E. Cloutet, L. Vignau, G. Wantz, H. Cramail, M. Geoghegan, G. Hadziioannou. J. Phys. Chem. B **115**, *44*, 12717 (2011).
[7] P.A. Troshin, R.N. Lyubovskaya, V.F. Razumov. Nanotech. Russ. **3**, *5–6*, 242 (2008).
[8] E.A. Smirnova, M.A. Besedina, M.P. Karushev, V.V. Vasilyev, A.M. Timonov. Russian Journal of Physical Chemistry **90**, *5*, 808 (2016).
[9] T.V. Semenistaya, A.V. Shchukarev, G.A. Shagisultanova. Russian Journal of Applied Chemistry **76**, *2*, 225 (2003).
[10] T.V. Semenistaya, G.A. Shagisultanova. Russian Journal of Inorganic Chemistry **48**, *4*, 602 (2003).
[11] A.S. Konev, M.Y. Kayumov, M.P. Karushev, Y.V. Novoselova, D.A. Lukyanov, E.V. Alekseeva, O.V. Levin. ChemElectroChem **5**, *21*, 3138 (2018).
[12] P. Pfeiffer, E. Breith, E. Lübbe, T. Tsumaki. Justus Liebig's Ann. Der Chemie **503**, *1*, 84 (1933).
[13] V.D. Mihailetchi, H.X. Xie, B. de Boer, L.J.A. Koster, P.W.M. Blom. Adv. Funct. Mater. **16**, *5*, 699 (2006).
[14] A. Iwan, F. Caballero-Briones, M. Filapek, B. Boharewicz, I. Tazbir, A. Hreniak, J. Guerrero-Contreras. Solar Energy **146**, 230 (2017).
[15] O. Semenikhin, E. Ovsyannikova, M. Ehrenburg, N. Alpatova, V. Kazarinov. J. Electroanal. Chem. **494**, *1*, 1 (2000).
[16] C.F. Pereira, A. Olean-Oliveira, D.N. David-Parra, M.F.S. Teixeira. Talanta **190**, 119 (2018).
[17] M.S.A. Abdou, F.P. Orfino, Y. Son, S. Holdcroft. J. Am. Chem. Soc. **119**, *19*, 4518 (1997).
[18] S. Hoshino, M. Yoshida, S. Uemura, T. Kodzasa, N. Takada, T. Kamata, K. Yase. J. Appl. Phys. **95**, *9*, 5088 (2004).
[19] O.A. Semenikhin, E.V. Ovsyannikova, N.M. Alpatova, Z.A. Rotenberg. J. Electroanal. Chem. **408**, *1–2*, 67 (1996).

[20] O.A. Semenikhin, M.M.D. Hossain, M.S. Workentin. J. Phys. Chem. B **110**, *41*, 20189 (2006).
[21] V.T. Avanesyan, M.Yu. Puchkov. Physics of the Solid State **49**, *11*, 2088 (2007).
[22] V.N. Brudnyi, S.N. Grinyaev, N.G. Kolin. Phys. B Condens. Matter **348**, *1–4*, 213 (2004).
[23] G.M. Carroll, A.M. Schimpf, E.Y. Tsui, D.R. Gamelin. J. Am. Chem. Soc. **137**, *34*, 11163 (2015).
[24] H.Y. Mao, F. Bussolotti, D.-C. Qi, R. Wang, S. Kera, N. Ueno, A.T.S. Wee, W. Chen. Org. Electron. **12**, *3*, 534 (2011).