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ВЛИЯНИЕ МЕТАЛЛА В СТРУКТУРЕ ПОРФИРИНА НА КИНЕТИКУ ЭЛЕКТРОПОЛИМЕРИЗАЦИИ И МОРФОЛОГИЮ ПЛЕНКОК НА ОСНОВЕ ГИДРОКСИФЕНИЛПОРФИРИНА

Продемонстрирована принципиальная возможность получения пленок из ДМСО при активированном кислородом электрохимическом окислении гидроксифенилпорфиринна и его цинкового комплекса. Изучена кинетика осаждения и морфология пленок. Показано, что происходит пассивация поверхности рабочего электрода при осаждении пленки порфиринна-лиганда; при осаждении пленки металлокомплекса поверхность не пассивируется. Поэтому электрохимический метод позволяет сформировать достаточно толстые пленки с глобулярной структурой на базе металлокомплекса, и пленки малой толщины и слоистой структуры на базе порфиринна-лиганда.

Ключевые слова: 2H-5,10,15,20-тетракис(4-гидроксифенил)порфирин, Zn-5,10,15,20-тетракис-(4-гидроксифенил)порфирин, электрополимеризация, морфология, кинетика

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METAL INFLUENCE IN PORPHYRINE STRUCTURE ON KINETIC OF ELECTRODEPOSITION AND MORPHOLOGY OF HYDROXYPHENYLPORPHYRINS BASED FILMS

The films formation via activated by oxygen electrochemical oxidation of hydroxyphenylporphyrin and its zinc complex in dimethyl sulfoxide media was demonstrated. The different kinetics of deposition and morphologies of the films were observed. During the film deposition the working electrode surface was passivated in case of porphyrin-ligand, and was not passivated in case of metal complex. As a result, the electrochemical method leads to sufficiently thick films with a globular structure based on the metal complex and films of small thickness films and layered structure based on the porphyrin-ligand.

Key words: 2H-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin, Zn-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin, electrolypolymerization, morphology, kinetics

Porphyryn based film materials are promising as an effective catalysts [1, 2], an active elements of sensor devices [3, 4], in creating of organic transistors [5, 6], LEDs [7], nonlinear optical transmitters [8] and electrochromic devices [9, 10]. Their use as component of photovoltaic cells [11-13] is commercially attractive due to the ease of manufacturing technology, low cost, light weight, high efficiency at low light levels, possibility of manufacturing the flexible elements. There are several methods for film materials fabrication [14-16]. Formation of the film materials by electrochemical deposition makes it easy to control and adjust the film deposition process, as well as getting on a solid substrate (working electrode surface) of different types of materials [17, 18]. The proposed mechanism of the polyporphyrin films formation via electrochemical method is the recombination of the radical particles obtained after the porphyrin precursors oxidation [19-21]. Polymer hydroxyphenylporphyrin films or their metal complexes have been obtained previously in different media: aqueous solutions [22], dichloromethane [23], acetonitrile [24, 25]. Though, the influence of metal in the porphyrin cage on the film formation process was not sufficiently investigated yet.

In this paper polyporphyrin films obtained by activated electrochemical deposition. Formation of polyporphyrin films was performed from solutions 2H-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (H2T(4OHPh)P) and Zn5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (ZnT(4OHPh)P) in dimethyl sulfoxide (DMSO). The formation and morphology kinetics of the films obtained on the basis of the porphyrin ligand and its metal complexes were compared. EXPERIMENTAL

Procedure of synthesis

H2T(4-OHPh)P was synthesized by the two-step method via demethylation of 2H-5,10,15,20-tetrakis(4-methoxyphenyl)porphirins [26, 27] obtained in high yield by condensation of benzaldehydes with pyrrole [28]. ZnT(4-OHPh)P was synthesized by refluxing of H2T(4-OHPh)P in methanol with Zn(OAc)2 excess for 3-4 hrs. The porphyrins were purified by preparative column chromatography on aluminum oxide (Brockmann activity III). The purified products were studied by thin-layer chromatography (silufol plates), UV-VIS spectrometry (Varian Cary 50 spectrometer) and 1H-NMR spectrometry (Bruker AVANCE-500 spectrometer) methods. The mass spectra were recorded on a Shimadzu Axima Confidence (MALDI-TOF) mass spectrometer. The products characteristics agree quite well with the reported data [29, 30]. The structures of porphyrins under study are shown in the Fig. 1.

Electrochemical procedure

Dimethylsulfoxide (DMSO ≥ 99.5, ALDRICH) was purified by zone melting and then stored over molecular sieves in a dry box before use. Tetrabutylammonium perchlorate (TBAP ≥ 98.0, ALDRICH) was purified by recrystallization from ethanol. 10-3 M solutions of porphyrins containing 0.02 M TBAP as the supporting electrolyte were prepared by the gravimetric method using the electronic analytical balance «Sartorius» ME215S (the mass determination
error did not exceed 3%). A potentiostat SP-150 (Bio-
Logic Science Instruments, France) was used for elec-
trochemical measurements. The experiments were
carried out in a three-electrode temperature-controlled
(25±0.5 °C) electrochemical cell in freshly prepared
solutions. The saturated calomel electrode (SCE)
inserted into the electrochemical cell through the
Luggin capillary was used as the reference electrode.
The Pt wire was used as an auxiliary electrode.

As the working electrode, we used a polishing
Pt strip (the working surface equaled 1.2 cm²) rigidly
fixed in the fluoroplastic lid. Before every measure-
ment the active surface of the working electrode was
mechanically mirror-polished, degreased with etha-
hol, etched with a chromic mixture for 20 min, care-
fully cleaned in distilled water and then in the solu-
tion under study. The working electrode was im-
mersed in the cell with the test solution where the po-
tential of the working electrode reached a steady val-
ue over 10 min. In order to degas or oxygenate solu-
tions before the electrochemical measurements, argon
or oxygen was bubbled through the capillary tube for
30 min. In earlier paper we have shown that in DMSO
media the more effective electrochemical deposition
of polyporphyrin films was obtained under activation
by oxygen [31, 32]. Therefore, in this paper the pol-
yporphyrin films deposition included cycling of the
working electrode potential in the oxygenated solu-
tions (to activate the deposition process), then cycling
in degassed solutions (to stabilize the resulting film).
The deposition process consisted of three stages. Each
stage consisted of 10 cycles in the degassed solution
and 10 cycles in an oxygenated solution. CV response
was recorded at scan rate of 0.02 V/s. The CV data
were corrected for Ohmic (iR) losses using the current
interruption technique [33].

Electrochemical impedance spectroscopy (EIS) measures-
tments during of polyporphyrin films formation were performed using Solartron SI 1260
analyzer at frequency range from 10⁴ to 10⁶ Hz with sinu-
soidal excitation voltage of 10 mV. We use two-
electrode cell for EIS study. The working and auxilia-
ry electrodes were placed at 5 mm opposite to each
other. Face of polished Pt wire diameter of 2.5 mm,
pressed in teflon sleeve was used as working elec-
trode. Platinitized platinum disc 25 mm in diameter
was used as auxiliary electrode. Electrochemical cell
was connected to the measuring device by two-
electrode four-wire scheme to avoid an effect of current-
carrying wires. Analysis of EIS data was performed us-
ing ZView2 program. Atomic force microscope (AFM)
images were obtained using the Solver-47-Pro equip-
ment and processed by a Nova RC software.

RESULTS AND DISCUSSION

Fig. 2 shows cyclic voltammograms obtained at
polyporphyrin films deposition from DMSO solutions.

Degassed solutions CV response (Fig. 2 a, b, curve 2) shows low-intensity wide irreversible oxida-
tion peaks at the potentials more than +0.12 V for the
porphyrin ligand and +0.17 V for the metal complex
and irreversible reduction peaks with half-wave po-
tential of -1.03 for H₂T(4OHPh)₆P and -1.35 V for
ZnT(4OHPh)₆P. The irreversibility of the electro-
chemical peaks of porphyrins associated with the in-
tramolecular electron transfer following the oxidation
or reduction processes [34, 35]. The CV shape is
slightly varied from cycle to cycle for the degassed
solutions. Oxygenated solutions of porphyrins CV
response (Fig. 2 a, b, curve 3) shows intense irreversible peak of oxygen electroreduction at potentials more negative than -0.5 V. In the absence of porphyrins the electroreduction of oxygen in DMSO is quasi reversible (inset in Fig. 2a) and leads to superoxide anion radicals formation through the one-electron mechanism: \((\mathrm{O}_2^-): \mathrm{O}_2 + e \rightarrow \mathrm{O}_2^-\) [36-39]. At the porphyrins presence the electroreduction of oxygen turn to irreversibility due to an effective interaction of superoxide with porphyrins [40-43]. Additionally CV shape of oxygenated porphyrins solutions is significantly changed from cycle to cycle. The gradual change in CV curves was accompanied with the polyporphyrin film formation on the surface of the working electrode. The resulting film has a golden color and is insoluble in water, alcohol, dichloromethane.

According to AFM images the obtained polyporphyrin films have different morphology (Fig. 3). In the case of polyporphyrin (Fig. 3a) there are micro-scratches, typical for polished Pt electrode that indicates a small thickness of the film. The observed growth steps and a histogram of heights with two maximums (Fig. 3b) let us to conclude layered structure of polyporphyrin film. Unlike polyporphyrin films the structure of the particles forming the polyporphyrin films can not be discern at Solver-47 Pro resolution. ZnT(4OHPh)P surface (Fig. 3c) is formed of round globules with a lateral size of 40-100 nm. The globular structure of the film leads to a heights histogram with a single maximum (Fig. 3d). The substrate microroughnesses can not be seen on the AFM image, due to the large thickness of the films.

EIS study of polyporphyrin films formation was performed in aerated solutions for the stationary potential of the working electrode. The deposition potential had been determined by a preliminary experiment. For this purpose obtained at different potentials of the working electrode EIS data were modeled by Randles-Ershler scheme (Fig. 4) [44]. The calculated polarization resistance values reached a minimum at potential about +0.95 V for \(\mathrm{H}_2\mathrm{T}(4\text{OHPh})\mathrm{P}\) and about +0.8 V for \(\mathrm{ZnT}(4\text{OHPh})\mathrm{P}\) vs Pt quasireference electrode. These potentials were used at studying of the films formation kinetics via impedance monitoring during the process (Fig. 4) [45].

It is clear to see the difference in Nyquist plots of \(\mathrm{H}_2\mathrm{T}(4\text{OHPh})\mathrm{P}\) and \(\mathrm{ZnT}(4\text{OHPh})\mathrm{P}\) during the whole experiment. In case of \(\mathrm{H}_2\mathrm{T}(4\text{OHPh})\mathrm{P}\) the Nyquist plots generally are elements of the circle, that allows to suggest a minor contribution of diffusion limitations in the electrode process. In case of \(\mathrm{ZnT}(4\text{OHPh})\mathrm{P}\) elements of the circles come to a slop
where A – independent of frequency pre-exponential factor; n – index extent determined with the nature of the frequency dependence \((1 < n < 1)\) i – imaginary unit; \(\omega = 2\pi f\) – circular frequency. Element Q is capacitive type for \(n\) close to 1 and one is diffusion type for \(n\) close to 0.5.

\[
\text{Warburg element: } W = \frac{W_R \cdot \tanh(B_0)^p}{(B_0)^p},
\]

where \(W_R\) – diffusion mass transfer resistance; B – characteristic time of diffusion transfer; p – the dimensionless exponent which can take values from 0 to 1.

Results of fitting and calculations are presented in Table. Table 1

Model characteristics of impedance at different times of deposition of \(\text{H}_2\text{T}(4\text{OHPh})\text{P}\) and \(\text{ZnT}(4\text{OHPh})\text{P}\) films on Pt electrode

<table>
<thead>
<tr>
<th>Time, min</th>
<th>(A \cdot 10^6)</th>
<th>n</th>
<th>(R_p, \Omega)</th>
<th>(W_R, \Omega)</th>
<th>B, c</th>
<th>p</th>
<th>C, (\mu F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.62</td>
<td>0.81</td>
<td>16973</td>
<td>5079</td>
<td>5.53</td>
<td>0.38</td>
<td>1.28</td>
</tr>
<tr>
<td>10</td>
<td>2.82</td>
<td>0.80</td>
<td>18474</td>
<td>7493</td>
<td>7.68</td>
<td>0.34</td>
<td>1.32</td>
</tr>
<tr>
<td>15</td>
<td>2.74</td>
<td>0.80</td>
<td>19023</td>
<td>9743</td>
<td>11.11</td>
<td>0.32</td>
<td>1.28</td>
</tr>
<tr>
<td>20</td>
<td>2.75</td>
<td>0.79</td>
<td>21005</td>
<td>7412</td>
<td>5.13</td>
<td>0.40</td>
<td>1.28</td>
</tr>
<tr>
<td>30</td>
<td>2.52</td>
<td>0.78</td>
<td>25846</td>
<td>4758</td>
<td>3.38</td>
<td>0.54</td>
<td>1.17</td>
</tr>
<tr>
<td>40</td>
<td>2.24</td>
<td>0.78</td>
<td>31732</td>
<td>2426</td>
<td>2.71</td>
<td>0.68</td>
<td>1.06</td>
</tr>
<tr>
<td>50</td>
<td>2.05</td>
<td>0.78</td>
<td>37231</td>
<td>733</td>
<td>2.18</td>
<td>0.83</td>
<td>1.00</td>
</tr>
<tr>
<td>60</td>
<td>1.92</td>
<td>0.79</td>
<td>41843</td>
<td>324</td>
<td>2.56</td>
<td>0.91</td>
<td>0.97</td>
</tr>
</tbody>
</table>

ZnT(4OHPh)P

<table>
<thead>
<tr>
<th>Time, min</th>
<th>(A \cdot 10^6)</th>
<th>n</th>
<th>(R_p, \Omega)</th>
<th>(W_R, \Omega)</th>
<th>B, c</th>
<th>p</th>
<th>C, (\mu F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.65</td>
<td>0.78</td>
<td>12244</td>
<td>63173</td>
<td>17.31</td>
<td>0.39</td>
<td>1.03</td>
</tr>
<tr>
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<td>0.80</td>
<td>13155</td>
<td>82876</td>
<td>28.97</td>
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<tr>
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<td>0.78</td>
<td>12418</td>
<td>68663</td>
<td>20.66</td>
<td>0.41</td>
<td>1.09</td>
</tr>
<tr>
<td>20</td>
<td>3.02</td>
<td>0.77</td>
<td>12039</td>
<td>67302</td>
<td>21.22</td>
<td>0.41</td>
<td>1.12</td>
</tr>
<tr>
<td>30</td>
<td>3.44</td>
<td>0.75</td>
<td>12214</td>
<td>58476</td>
<td>16.11</td>
<td>0.43</td>
<td>1.20</td>
</tr>
<tr>
<td>40</td>
<td>3.68</td>
<td>0.74</td>
<td>11821</td>
<td>56632</td>
<td>15.89</td>
<td>0.43</td>
<td>1.25</td>
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<tr>
<td>50</td>
<td>4.07</td>
<td>0.73</td>
<td>11663</td>
<td>53251</td>
<td>14.84</td>
<td>0.43</td>
<td>1.32</td>
</tr>
<tr>
<td>60</td>
<td>4.15</td>
<td>0.73</td>
<td>11128</td>
<td>51453</td>
<td>14.60</td>
<td>0.43</td>
<td>1.32</td>
</tr>
</tbody>
</table>

The data analysis shows a slight effect of diffusion on the electrode process \((WR << R_p)\) for \(\text{H}_2\text{T}(4\text{OHPh})\text{P}\). It leads to low accuracy of the calculated diffusion characteristics in the case of \(\text{H}_2\text{T}(4\text{OHPh})\text{P}\) and does not allow us to compare the diffusion behavior of \(\text{H}_2\text{T}(4\text{OHPh})\text{P}\) and \(\text{ZnT}(4\text{OHPh})\text{P}\).

Parameter \(R_p\) characterizes the rate of electron transfer at interface and it was close for both studied porphyrins for the initial time. There are no significant changes in this parameter over time for \(\text{ZnT}(4\text{OHPh})\text{P}\). Since the formation of the poly-\(\text{ZnT}(4\text{OHPh})\text{P}\) film in the experiment is confirmed, it means a high probability of charge transfer through the deposited layer and sufficient conductivity of the film forming. In contrast to poly-\(\text{ZnT}(4\text{OHPh})\text{P}\) film formation the Rp parameter increases by 2.5 times during the experiment for \(\text{H}_2\text{T}(4\text{OHPh})\text{P}\). This change in polarization resistance clearly points to the passivation of the working electrode surface as a result of the formation of the poly-\(\text{H}_2\text{T}(4\text{OHPh})\text{P}\) surface film. Apparently, the surface passivation is a reason of thinness of \(\text{H}_2\text{T}(4\text{OHPh})\text{P}\) film that could be seen at AFM (Fig. 3).

The "true capacitance" value extrapolates the interface properties to the ideal plane capacitor prop-
erties. Parameter C depends on the plate area (area of contact between the phases varied due to changing in the morphology of the surface layer) and distance between opposite charges (the distribution of charges in the interfacial layer). According to Table in the case of poly-H2T(4OHPh)P film formation “true capacitance” is close to a constant value during the 20 min, then decreases. In the case of poly- ZnT(4OHPh)P film formation “true capacitance” is constant initially, close to a constant value during the 10 min, then increases. The set of parameters changes over time indicates film formation staging for the both porphyrins. The decreasing in “true capacitance” in the case H2T(4OHPh)P may be explained by poorly conducting surface film forming which increases the distance between free charges in interfacial double layer. The capacity increasing in the case ZnT(4OHPh)P indicates an increasing in the specific electrode surface area during the film formation. Thus, in the case of poly-ZnT(4OHPh)P film growth the “true capacitance” values indicate extended surface of interfacial boundary forming. The parameter n can be interpreted in term of fractal dimension of electrode surface [47, 48]. Decreasing in n during the film deposition indicates fractal dimension increasing and formation of a more extended surface also.

CONCLUSION

We have shown the ability of obtain the electrochemically deposited poly-hydroxyphenylporphyrin films in DMSO media. On the one hand, the increasing in solvents number allows improving the variability of electrochemical method. On the other hand, DMSO solution has low toxicity that leads to safe practice of films deposition. Films were formed via activation by dissolved oxygen electrochemical oxidation of 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin and its Zn complex. The influence of metal atom in the macrocycle cage on deposition kinetics and properties of the resulting film was demonstrated. It was found in the case of H2T(4OHPh)P the electrode surface is passivated while film formation that leads to small thickness and a layered structure. At the electrochemical deposition of polymer films ZnT(4OHPh)P the surface is not passivated and it allows to obtain sufficiently thick films with a globular structure.

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