

PREPARATION OF POLYPORPHINE FILMS CONTAINING TRANSITION METAL IONS BY ELECTROCHEMICAL METHOD

Olga Istakova^{a,b}, Dmitry Konev^{a,b}, Charles Devillers^c, and Mikhail Vorotyntsev^{a,b,c,d}

^a Institute for Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Russia

^b D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow,
Russia

^c Institute de Chimie Moléculaire de l'Université de Bourgogne, 21078 Dijon, France

^d M. V. Lomonosov Moscow State University, 119991 Moscow, Russia

Recent synthesis of Mg(II) porphine (MgP) based polymer films [1, 2] has paved the route towards other representatives of this new electroactive polymer family, via the replacement of coordinated Mg(II) ions. Such transition-metal containing polyporphine materials might be prospective as catalysts of various processes, in particular for the oxygen reduction, owing to the presence of MeN₄ active centers. Polyporphines may be obtained in the "type II" form composed of polymer chains having a condensed structure owing to three single bonds between neighboring monomer units. Treatment of the free base polyporphine with a metal ion salt, had allowed us to prepare for the first time polyporphines of cobalt and zinc [2]. However, this method suffers from potential contamination of the polymer by salt hydrolysis products, as well as from poor adhesion and poor stability of the electroactive layer, extended duration of the procedure and high temperature (requiring a sufficiently high thermal stability of the polymer).

The goal of this work has been to develop an original alternative method of the metalation of polyporphine films, via replacing the thermal treatment by electrochemical polarization of the film in solution of the corresponding metal salt (salt of cobalt (II), manganese (II) or iron (II) in this study). First, films of magnesium(II) polyporphine of type I, pMgP, have been prepared. Then, they were demetalated by ion exchange of Mg(II) by protons from CF₃COOH solution, according to the method described in Ref. [2]. Subsequent metalation step has been performed via electrochemical treatment in acetonitrile solution of corresponding metal (II) perchlorate. Resulting films were characterized by means of electrochemical and spectral techniques.

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[1] M.A. Vorotyntsev, D.V. Konev, C.H. Devillers et al, *Electrochim. Acta* 55 (2010) 6703-6714.

[2] D.V. Konev, C.H. Devillers, K.V. Lizgina et al, *Electrochim. Acta* 122 (2014) 3-10.