Electrocatalytic properties of manganese and cobalt polyporphine films toward oxygen reduction reaction

Dmitry V. Konev¹,²,* Olga I. Istakova¹,², Beata Dembinska³, Magdalena Skunik-Nuckowska³, Charles H. Devillers⁴, Olivier Heintz⁵, Pawel J. Kulesza³,*, Mikhail A. Vorotyntsev¹,²,⁴,⁶,*

¹ D. I. Mendeleev Russian University of Chemical Technology University, Moscow, Russia
² Institute for Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia
³ Faculty of Chemistry, University of Warsaw, Warsaw, Poland
⁴ ICMUB, UMR 6302 CNRS-Université de Bourgogne-Franche-Comté, Dijon, France
⁵ ICB, UMR 6303 CNRS-Université de Bourgogne-Franche-Comté, Dijon, France
⁶ M. V. Lomonosov Moscow State University, Moscow, Russia

ABSTRACT

Novel member of polymetalloporphines, namely manganese polynmetalloporphine of type I (pMnP-I) obtained by ion exchange from magnesium polyporphine of type I (pMgP-I) is reported for the first time and compared to its cobalt analogue (pCoP-I). Both polymer films have been obtained via two-step procedure: demetallation of the pMgP-I electrode film via its exposure to trifluoroacetic acid solution, resulting in formation of the metal-free polyporphine of type I (pH₃P-I) followed by electrochemically induced incorporation of Co or Mn ions from the acetonitril solution of cobalt and manganese perchlorates. A further oxidative transformation of pCoP-I, pMnP-I polymer films has led to the corresponding polyporphines of type II, pCoP-II and pMnP-II, possessing such unique features as condensed polymer structure with a very high density of active sites and high electronic conductivity within a very broad potential range including the one corresponding to the neutral (uncharged) state of the polymer matrix. Both polymers of type II also exhibit interesting electrocatalytic activity toward oxygen electroreduction in aqueous neutral (pH 6.7) and alkaline (pH 13) media which was evaluated under cyclic voltammetric and steady-state conditions. The results demonstrate that the efficiency (regardless of the electrolyte) of both polynmetalloporphines is comparable to bare platinum electrode. The effect of annealing of polymer-modified electrodes on their catalytic properties has also been considered.

Keywords: electropolymerization, electroactive polymers, metalloporphines, Mg(II) porphine, polymer film coated electrode, oxygen electroreduction

* Corresponding authors: dkfrvzh@gmail.com (D.V. Konev); pkulesza@chem.uw.edu.pl (P.J. Kulesza); mivo2010@yandex.com (M.A. Vorotyntsev)
Introduction

Various optical and electrochemical features as well as a high chemical and thermal stability make porphyrins promising materials for electronics, optoelectronics and photonics. These properties can be easily adapted to specific applications by introducing new metal ions in the center of the porphyrin ring or by chemical chain functionalization [1–3]. Due to the presence of active catalytic $\text{MN}_4$ centers (where $\text{M}$ is $\text{Co}^{2+}$, $\text{Mn}^{2+}$, $\text{Fe}^{2+}$, etc. and $\text{N}_4$ is a porphyrin heterocycle), porphyrin based compounds found applications in various fields of electrocatalysis, chemical and biological sensing and molecular photovoltaic devices [4–10].

Electrochemical properties of metal porphines, i.e. the simplest, unsubstituted metalloporphyrins were for a long time barely known, mainly due to the lack of the commercial availability and multi-stage low-yield laboratory syntheses. A novel, three-step methodology of a relatively high yield synthesis of magnesium porphine (MgP), proposed by Lindsey et al. [11], significantly increased the interest in porphine and porphine-based materials. Thanks to this progress, it became possible to study both the behavior of these substances in the solution [12] and the processes resulting in formation of metalloporphine-based polymer films at electrode substrates, by potentiostatic or potentiodynamic electrooxidation of porphine monomers [13]. Such immobilization of porphines on solid electrode surfaces is of especial importance, in particular in a field of electrochemical sensing and electrocatalysis. An original approach based on a combination of electrochemical and spectroscopic methods allowed us to establish the molecular structure of such polymer films with Mg as a central metal ion. It has been demonstrated that during formation of the oxidation product, namely magnesium poly-porphine of type I (pMgP-I) under a very low oxidation potential, each porphine ring forms ca. 2.1-2.2 bonds with adjacent monomer units. It implies that the polymer structure consists of chains of single meso-meso bonded monomeric porphine macrocycles, with a relatively small number of intermolecular bonds [14]. Comparative diagnostic studies of magnesium 5,15-di(p-methoxyphenyl)porphine and unsubstituted MgP polymerized under identical conditions have shown that contrary to the 5,15-substituted poly-porphine, characterized by the linear chain structure, the structure of pMgP-I can be linear but also can contain zigzag and even cruciform fragments [15].

It has also been found that further oxidation of poly-porphines of type I leads to formation of additional bonds between neighboring porphine rings, presumably in beta-beta positions. Such condensed tape structures (poly-porphine of type II, pMgP-II) possess high electronic conductivity and redox activity within a very wide (over 3 V) potential range in organic media [16]. Furthermore, as previously demonstrated [17], the efficiency of the polymerization process can be increased by introducing a proton-acceptor additive into the electropolymerization medium, such as 2,6-dimethylpyridine (lutidine) which enhances the rate of film formation by the factor of two while it is not included inside the polymer film.
As aforementioned, owing to their unique properties polyporphines containing electrocatalytically active metal sites may serve as powerful electrocatalysts and redox mediators supporting various oxidation/reduction processes. Therefore, our recent research has been focused on developing procedures of ion exchange replacement in pMgP-I polymeric coatings as a means to incorporate therein transition metal ions, with conservation of the molecular structure of the starting polymer. It has been achieved by demetalation of the pMgP-I polymer with trifluoroacetic acid of hydrochloric acid, leading to the formation of “free-base” polyporphine of type I, pH2P-I. Subsequent treatment of demetalated polymer films by saturated Zn or Co ion containing solutions in relevant temperature intervals resulted in relatively fast (within 1 h) formation of the corresponding polymetalloporphines, pZnP-I or pCoP-I [18,19]. It is noteworthy that ion-exchange procedure does not change either the initial polymer morphology or its molecular structure, as well as the polymer electroactivity is preserved within a broad potential range. In order to optimize the preparation methodology, a novel synthetic approach has been developed recently, based on electrochemical (potentiodynamic) treatment of the metal-free polyporphine coating, pH2P-I, in contact with a solution containing the corresponding metal ion [20,21]. Such a synthetic route leads to much faster film preparation, besides with the use of dilute solutions and ambient temperature.

MN₄-type macrocyclic metal complexes, in particular cobalt and iron porphyrins and phthalocyanines, are well known as oxygen reduction catalysts [22-28]. Compared to most other materials containing these complexes, polyporphines possess certain benefits such as very high density of active sites due to the absence of spacers (cross-linking groups) between monomer units, spatial matrices and side substituents. Moreover, the fact that porphine centers are situated inside the main chain results in a high degree of conjugation through which the electrons can be transferred from the electrode to the substrate and back. Our preliminary studies have shown that indeed, pCoP films of both type I and type II exhibit electrocatalytic properties towards oxygen reduction reaction in alkaline media [29]. It is noteworthy that for the Co(II) polyporphine of type II, the $E_{1/2}$ potential of the oxygen reduction reaction was very close to the value characteristic of platinum electrode. Current densities were also higher than those for the Co polyporphine of type I which has been attributed to much higher electronic conductivity of these films within a wider potential range, allowing for efficient electron transport between the active sites in the polymer film and a substrate to take place.

Manganese cations also belong to catalytically active transition metal ions. Therefore, based on existing preparative methods and our preliminary studies, electrocatalytic films of cobalt and manganese polyporphines of type II (pCoP-II and pMnP-II) have been prepared in this study with the use of electrochemically induced ion exchange. Then, their electrochemical and electrocatalytic activities in the oxygen reduction reaction have been evaluated under cyclic voltammetric and steady-state conditions (polarization plots) in aqueous (alkaline and neutral) media. These electrocatalytic properties have been
compared to that of the bare platinum electrode. Physicochemical properties of manganese polyporphine, reported for the first time, have been established using XPS and IR spectroscopies.

**Experimental**

**Materials and electrochemical equipment**

Magnesium porphine (MgP) monomer was synthesized according to Lindsey's procedure [11]. Acetonitrile (AN) of HPLC classification (Panreac) was dehydrated with molecular sieves (pore size 3Å) as drying agent. Background electrolyte, tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Fluka), was stored in an oven at 80°C for 24 hours prior to use. 2,6-dimethylpyridine (lutidine, 99%) and trifluoroacetic acid (TFAA, >99%) were purchased from Sigma Aldrich and tetraethylammonium perchlorate (TEACIO$_4$, Carlo Erba, 98%) was from Carlo Erba.

All electrochemical measurements were performed using Elins PI50PRO3 electrochemical workstation in the conventional three-electrode glass cell equipped with glassy carbon or platinum disc working electrode (geometric area of 0.0078 cm$^2$) and large surface area platinum foil counter electrode (separated from the AN solution by porous glass membrane). For experiments in acetonitrile (AN), silver Ag/Ag$^+$ (AN) electrode (10$^{-2}$ mol dm$^{-3}$ AgNO$_3$ + 0.1 mol dm$^{-3}$ TBAPF$_6$ in AN) separated by double frit filled in with background solution (0.1 mol dm$^{-3}$ TBAPF$_6$ in AN) was used as reference electrode. Its potential was 0.1 V more negative than the formal potential of the Fc/Fc$^+$ redox couple in the same solvent. For studies in aqueous electrolytes, Ag/AgCl/ sat. KCl (0.198 V vs. SHE) served as reference electrode.

**Deposition and characterization of polymetalloporphines (pMPs)**

Prior deposition and electrochemical characterization, all solutions were deaerated under vacuum and subsequently saturated with high-purity argon in the Schlenk system.

Starting films of magnesium polyporphine of type I (pMgP-I) were deposited via potentiostatic (0.35 V vs. Ag/Ag$^+$) electropolymerization of the MgP monomer from its 0.5 mmol dm$^{-3}$ solution in AN with the addition of 0.1 mol dm$^{-3}$ of TBAPF$_6$ and 1.5·10$^{-3}$ mol dm$^{-3}$ of lutidine as proton-acceptor additive, according to the previously reported procedure [13]. These conditions correspond to formation of the type I structure formed by Mg(II) containing porphine cycles which are singly bonded in meso-meso positions. Thickness of the film was controlled by the charge passed during deposition where 5 mC cm$^{-2}$ corresponds to the thickness of ca. 50 nm.

To prepare films of cobalt and manganese polyporphines of type I (pCoP-I and pMnP-I), the magnesium polyporphine (pMgP-I)-coated electrodes were at first demetalated in AN solution of
trifluoroacetic acid (1:50 v/v) according to the earlier developed procedure [18]. Incorporation of metal ions into the structure of demetalated polyporphine (pH$_2$P-I) films was achieved with the use of a recently proposed method of electrochemically induced ion exchange [18]. Briefly, for preparation of pCoP-I and pMnP-I films, metal-free polyporphine-modified electrode (pH$_2$P-I) was metalated in contact with 0.1 mol dm$^{-3}$ TBAPF$_6$ solution in AN containing 5·10$^{-4}$ mol dm$^{-3}$ metal salt: either Co(ClO$_4$)$_2$ or Mn(ClO$_4$)$_2$, by performing 30 voltammetric cycles in the potential range between -1.2 V (for Co) or -1.4 V (for Mn) and +0.4 V (starting potential of the procedure: 0 V) with scan rate of 0.1 V s$^{-1}$.

Oxidative transformation of pCoP-I and pMnP-I into polymetalloporphines of type II with condensed structure (pCoP-II and pMnP-II) was performed under galvanostatic conditions in AN solution of 0.1 mol dm$^{-3}$ TBAPF$_6$ until the potential reached 1 V. All steps of this procedure are summarized in Scheme 1.

Fourier-transform infrared spectra under attenuated total reflectance mode (FTIR-ATR) were measured by Bruker Vertex 70v vacuum Fourier IR spectrometer equipped with diamond optical element. Various polyporphine films, pMgP-I (deposition charge: 5mC cm$^{-2}$), pH$_2$P-I and pMP-I (M = Co or Mn) were prepared on 25 µm thick platinum foil following the above procedure (Scheme 1). Then, their spectra were measured with resolution of 4 cm$^{-1}$ and averaged over 50 scans.

Samples for XPS measurements were prepared analogously. XPS spectra were recorded with the use of SIA100 device (Cameca Riber apparatus) with non-monochromatized Al Ka source (1486.6 eV).

Electrocatalytic properties

Electrocatalytic properties of cobalt and manganese polyporphines films toward oxygen reduction reaction were studied in 0.1 mol dm$^{-3}$ tetraethylammonium perchlorate (TEAClO$_4$, pH=6.7) and 0.1 mol dm$^{-3}$ NaOH (pH=13) solutions under voltammetric regime as well as under steady-state conditions: potential step of 0.05 V, potential hold time of 20-50 s, i.e. until the current reached plateau.

To illustrate the influence of the annealing treatment on the activity and stability of pCoP-II and pMnP-II coatings, the metalation of metal-free polyporphine of type I, pH$_2$P-I (corresponding to step 3 in Scheme 1) was performed via chemical method [18,19,29,30], i.e. by holding the pH$_2$P-I-modified electrode in dimethylformamide (DMF) solution of 5·10$^{-2}$ mol dm$^{-3}$ of CoCl$_2$ or Mn(OAc)$_2$ for 1 h at 130°C. Subsequent oxidative transformation of type I coatings into those of type II was performed galvanostatically, as already described. The samples were subsequently subjected to pyrolysis of the polymers by annealing at 800°C for 2 h. Glassy carbon rods (diameter: 2mm; length of immersed part: ca 3mm; geometrical surface area: ca 0.2 cm$^2$) were used as substrate. Their surface was roughened by means of abrasive paper (grain size of about 30 µm) to prevent possible peeling of the polymer layer during annealing process.
Results and discussion

Fabrication and electrochemical identity of polynitroporphines

Introduction of manganese (II) and cobalt (II) ions into the pH2P-I polyporphine film deposited on platinum electrode was conducted with the use of the electrochemically induced ion exchange [20,21]. Since electrochemical and physicochemical properties of cobalt polyporphine have already been presented in details, here only the formation of its manganese analogue is shown as a representative example. Cyclic voltammetry response in the course of the electrochemically induced ion exchange (resulting in formation of pMnP-I) achieved upon exposure of the metal-free pH2P-I polyporphine deposit to Mn(ClO4)2 containing solution is presented in Fig. 1. Almost complete disappearance of n-doping currents of pH2P-I (in the potential range below -1.25 V) [18,20,21] and some increase in the electroactivity of the film at more positive potentials (increase of capacitive-type currents) can be seen during consecutive potential cycling. There is also a small shift and broadening of weak current responses (from -0.85 to -0.67 V for the negative potential sweep and from 0.03 to 0.1 V for the positive one), the existence of which is attributed to so-called "trapped charges" [18,20,21].

In order to confirm that manganese ions have successfully been incorporated into the polymer films, FTIR-ATR spectra of 50 nm-thick coatings of polyporphines of type I, namely, initial pMgP-I, metal-free pH2P-I and pMnP-I deposited on the surface of platinum foil were recorded (Fig. 2). Three regions, A, B and C, have been distinguished to illustrate changes in the vibrational bands at ca. 1050, 1000 and 780-850 cm⁻¹, respectively. The bands appearing within regions A and C of the spectra are related to vibrations of different symmetries of external hydrogen atoms in the porphine plane and out of it, respectively. In conformity with expectations, demetallation process does not affect the vibrational bands in these regions (Figs. 2a and 2b) [18,31,32]. The most pronounced changes for demetalated polyporphine, pH2P-I, can be seen in region B: splitting of the intensive signal at ca. 1000 cm⁻¹ for pMgP-I (Fig. 2a) into three bands of lower intensities shifted towards lower wavelengths for pH2P-I (Fig. 2b). The signal is related to in-plane deformational vibrations of macrocycles with most intensive displacement of nitrogen and carbon atoms of pyrrole rings. The observed changes clearly indicate that demetallation has been accomplished, resulting in lowering the symmetry of porphine units upon replacing of Mg cation by two protons.

As can be seen in Fig. 2c, single band with the intensity comparable to pMgP-I (Fig. 2a) appears again in region B after passage of the remetallation process. It means that the porphine symmetry has been restored to its initial state, i.e. that the Mn cation has successfully been incorporated into the structure. However, the existence of a small signal at 970 cm⁻¹ (Fig. 2c), also observed for pH2P-I at the same wavelength might imply that metallation process has not been fully completed. It was established earlier for pCoP-I [21] that the degree of metallation achieved via this procedure depends on the film thickness. According to Fig. 2c the same effect is also observed for pMnP-I.
XPS spectra of various polyporphines of type I, pMP-I (M = Mg, 2H, Co or Mn, Fig. 3), deposited on platinum foil also confirm the presence of Co or Mn ions inside the coating after the electrochemically induced ion exchange in contact with solutions of the corresponding salt. This conclusion is based on both the existence of characteristic peaks of Co or Mn (Fig. 3a) and on the shape of N 1s band (395-400 eV) as shown in Fig. 3b. As seen, a single peak for pMgP-I due to 4 equivalent nitrogen atoms of deprotonated pyrrole groups is split into doublet for pH2P-I due to two non-equivalent groups (containing 2 deprotonated and 2 protonated pyrrole nitrogen atoms) at binding energies of 398 and 400 eV, respectively [33]. Incorporation of the metal ion (Co or Mn) into porphine units restores the equivalence of all 4 nitrogen atoms owing to identical bonds between the ion and each nitrogen atom.

Results for the atomic compositions (C, N, Mg, Co, Mn) of various polyporphines, on the basis of the XPS spectra, are given in Table 1. Calculated ratios of the atomic contents for C to N and N to M show that the degree of metalation, i.e. the fraction of Co or Mn containing porphine units, is close to the complete one as a result of the electrochemically induced ion exchange procedure. The difference in conclusions on this point on the basis of the IR and XPS spectra may be explained in terms of the practically complete metalation of the external surface layer of a film (responsible for the XPS signal) while the degree of the metal ion incorporation into porphine units in the depth of the film (affecting the IR signal in Fig. 2) may be lower. This conclusion is in conformity with the earlier observation [21] that the metalation degree is lower for thicker polyporphine films.

Comparative cyclic voltammetric characteristics of the pMnP-I and pCoP-I films (deposited onto platinum electrodes) recorded in 0.1 mmol dm\(^{-3}\) TBAPF\(_6\) + AN solution are shown in Fig. 4a. It is evident that in case of pCoP-I (black curve in Fig. 4a) two sets of redox peaks, located at around -1.25 V and 0.1 V, are well pronounced. They can be ascribed to Co(I)/Co(II) and Co(II)/Co(III) transitions, respectively [19]. It is also apparent that these peaks are separated by a large potential interval of low electroactivity of the polymeric film (low capacitive-type currents) where it exists in the neutral insulating state [13,19]. In the case of pMnP-I (red curve in Fig. 4a), there is no signal in the potential range (expected on the basis of the corresponding monomeric porphyrins) corresponding to the redox transition of the central Mn atom, Mn(II)/Mn(III) [27,34] but, in comparison to pCoP-I, the electroactivity of the film is higher in the whole intermediate potential range. The absence of the characteristic peak related to the redox transition of Mn ions presumably originates from the fact that it should take place in the potential range where the polymeric matrix has a low conductivity, thus the electron transfers between the electrode and Mn centers are practically inhibited.

In our previous reports we have shown that polyporphines of type II, pMP-II (M = 2H\(^+\), Mg\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\)), are characterized by a substantially higher electrical conductivity than polyporphines of type I, pMP-I [17,18]. As apparent from Fig. 4b, where cyclic voltammetric responses of the pMP-II films
recorded in contact with background solution are presented, the range of the electroactivity (observed as increased capacitive-type currents) is broadened for both pCoP-II and pMnP-II polyporphines in comparison to those of type I (Fig. 4a). For the pCoP-II film, well-pronounced peaks originating from Co(II)/Co(III) redox transitions (at around 0.1 V) are preserved while the signals corresponding to Co(I)/Co(II) couple are less distinct, compared to the response of the pCoP-I film (black lines in Figs 4a and b). Probably the Co(I)/Co(II) signals in pCoP-II are masked by increased capacitive currents of the polymer. As further seen for pMnP-II, highly reversible peaks corresponding to the Mn(III)/Mn(II) couple (located at around -0.5 V) appear while the corresponding signals were absent for the pMnP-I film (red curves in Figs 4a and b). The observation confirms that the electrical conductivity of polyporphines of type I, pMP-I, considerably increases within a broad potential range upon their conversion into pMP-II, irrespective of the central metal ion as it has recently been proven for Mg, Zn and Co containing films [17,18] and for the first time is presented here for Mn. Fig. 4c illustrates the potential-time dependence for the pCoP-I and pMnP-I films in the course of their galvanostatic oxidative transformation into type II. Similarity of these curves as well as of the charges passed during the transformation for these films testify in favor of the identical mechanism of this process for all polyporphines which consists in formation of two beta-beta bonds between every couple of neighboring porphine units inside polymer chain. Further studies of electrocatalytic properties have been performed for the films of type II.

**Electrocatalytic activity of pMnP-II and pCoP-II toward oxygen reduction**

The electrocatalytic efficiency toward oxygen reduction of pMnP-II and pCoP-II films was examined in neutral and alkaline aqueous solutions of 0.1 mol dm$^{-3}$ TEAClO$_4$ (pH 6.7) and 0.1 mol dm$^{-3}$ NaOH (pH 13), respectively. A glassy carbon was used as a support for polyporphine films since platinum is known as a highly efficient oxygen electroreduction catalyst so that the origin of the catalytic activity would be unclear. In contrast, the oxygen reduction at bare glassy carbon is rather poorly efficient and starts at much more negative potentials. Prior to experiments in oxygen-saturated solutions, the electrochemical properties of pMnP-II and pCoP-II polymer films were first examined in deaerated aqueous electrolytes of different pH (Figs 5a,b). For pCoP-II, a pair of broad symmetrical peaks, appearing in the potential ranges from 0 to 0.4 V in neutral (black curve in Fig. 5a) and from -0.4 to 0 V in alkaline (black curve in Fig. 5b) solutions, most likely reflects redox transitions of cobalt cations. In the case of pMnP-II in neutral medium, the redox response which should be attributed to transitions of Mn cations, can be noticed as poorly developed waves at potentials below -0.1 V (red curve in Fig. 5a). On the other hand, the same couple (evident in the potential range between -0.8 and -0.3 V) is much better pronounced in alkaline media (red curve in Fig. 5b).
Figs 6 and 7 show conventional cyclic voltammograms as well as steady-state polarization curves for the oxygen electroreduction in neutral (a) and alkaline (b) solutions at pMnP-II and pCoP-II films deposited on glassy carbon electrodes (black and red curves, respectively). For comparative purposes, results of analogous experiments conducted for unmodified glassy carbon and platinum electrodes (having the same geometrical surface areas) are also shown in Figs 6 and 7 (green and blue curves, respectively). Comparison of the heights of characteristic peak currents and limiting currents with those obtained for bare platinum and glassy carbon electrodes allows to roughly predict the number of electrons participating in the electrocatalytic reaction, i.e. assigning it to 2- or 4-electron mechanism. As seen, the peak (Fig. 6) as well as the steady-state (Fig. 7) currents of the oxygen reduction for both polyporphine coated electrodes, pCoP-II and pMnP-II, are of the same amplitudes as those of bare platinum, while they are more than twice as high as the currents observed for bare glassy carbon electrode. This observation would suggest primarily the 4-electron reaction mechanism of the process (with formation of water as the main product). However, it is well established that the activity of macromolecular complexes depends on numerous factors such as central metal ion, ligand, substituents in the ring, support or the preparation methods of the modifying layer [35-39]. It has been proven for instance that, in contrast to most monomeric cobalt porphyrins (and other macrocyclic compounds), the simplest Co porphine (not polymerized) is able to reduce oxygen directly to water in acidic electrolyte (due to spontaneous dimerization of porphine units), but irreversible oxidation of the porphine ring leads to 2-electron reduction of O₂ catalyzed by the complex [35]. In other studies it was revealed that unstable monomeric Co(II) tetra-aminophthalocyanine, which participates in the 2-electron oxygen reduction, turns into stable catalyst capable of reducing oxygen to water after its polymerization [36]. Rather scare data for manganese macromolecular complexes imply the promotion of 2-electron reduction of oxygen in neutral and 4-electron reduction in basic solutions, while electropolymerized tetratolyl porphyrin drives the reaction to water in neutral media [37-39]. Here we can further go with your explanation suggesting rather 4-electron reduction mechanism, will it be ok?

The efficiency of the oxygen electroreduction was estimated based on both the peak potential of cyclic voltammetric curves (Fig. 6) and the half-wave potential of steady-state voltammograms (Fig. 7). The results for various electrode materials are summarized in Table 2. As seen, in both neutral and alkaline electrolytes the potentials values obtained for pMnP-II and pCoP-II catalytic films approach those characteristic of compact platinum which indicates the high electrocatalytic efficiency of these polynitrophenylporphines towards oxygen reduction. The most positive potentials of the process, that even slightly exceed that of compact platinum (at least under voltammetric conditions), are observed for pCoP-II (Fig. 6, Table 2).
It is noteworthy that the electrocatalytic activity of metal macrocyclic complexes presented here is practically identical in terms of the limiting current (0.3-0.4 mA cm\(^{-2}\)) compared to those for monomeric [23] or electropolymerized [27] metalloporphyrin-modified porous electrodes (containing graphene oxide frameworks or carbon nanotubes), in spite of the fact that the thickness of pMnP-II and pCoP-II was on the level of 50 nm, and thus the overall concentration of active sites per 1 cm\(^{2}\) of the surface area was very low. Moreover, the characteristic potentials for polymetalloporphines of type II are more positive than the corresponding ones (for the same metal ion) for electropolymerized porphyrins [27].

What is more, in contrast to results concerning metalloporphyrins [23] or polymerized metalloporphyrins [27], the activity of our Mn-containing macrocyclic compound is close to the activity of its Co counterpart in terms of both the limiting current and the potential (merely 0.1 V negative shift). These observations may originate from the unique structure of polymetalloporphines of type II characterized by the highest possible density of active MN\(_4\) sites and excellent electron conductivity, compared to conventional macromolecular complexes like porphyrins or phthalocyanines.

The most significant problem of MN\(_4\)-type catalytic centers with respect to oxygen reduction reaction is their poor stability. To estimate the stability of Co and Mn polyporphines, the pMP-II films were subjected to potential cycling in contact with aerated electrolyte solutions (data not shown). For both pMnP-II and pCoP-II-modified electrodes, the peak currents decrease and a slight displacement of peak potentials toward lower potential values were clearly observed after several voltammetric cycles, especially in neutral media. The phenomenon might imply a certain decrease in the number of catalytically active sites due to aggressive action of various peroxides, i.e. intermediate products of the oxygen reduction reaction. Furthermore, it should be kept in mind that the applied electrolyte, TEA\(_2\)ClO\(_4\), does not possess buffering properties, thus local pH changes may clearly occur. Even though its pH was 6.7, i.e. the content of protons in the bulk solution was very small, a progressive demetalation of polyporphine ring may proceed. Besides, due to the presence of the H\(_2\)O\(_2\) intermediate, the Fenton-type reaction (generating radical oxygen species) may take place [40]. What important, both polymetalloporphines were more stable in alkaline media, probably since the demetalation of macromolecular complexes is avoided, which is a well-known feature of catalysts based on MN\(_4\)-type centers.

Conventional treatment for the stability enhancement of the transition metals coordination compounds is the annealing (typically at 800–900°C) of the complex, previously adsorbed or polymerized on the surface of carbon support [22,41-44], leading to their pyrolysis. As a result, metal-nitrogen-carbon type catalysts are produced in which MN\(_x\) structures are present inside the carbon matrix. Fig. 8 shows comparison of voltammetric curves of oxygen electroreduction proceeding at the films of pMnP-II and pCoP-II recorded in contact with 0.1 mol dm\(^{-3}\) alkaline electrolyte before and after annealing at 800 °C.
In these experiments, a glassy carbon rod with a rough surface was used as substrate in order to prevent possible peeling of the polymer layer during annealing process. This roughness explains an increase in the capacitive contribution to the observed currents in argon-saturated solutions.

It is evident from Fig. 8a that the thermal treatment of the polyporphine, pMnP-II, with its pyrolysis and carbonization, leads to almost complete loss of its activity towards oxygen reduction, compared to the non-heated sample, which confirms previous observations that Mn (in opposite to most macrocyclic metal complexes) may lose its N₄ structure [38]. In case of pCoP-II, as expected, the stability of the voltammetric responses in the oxygenated solutions in the course of the multi-cycle procedure (at least within a short timescale) has increased. However, the comparison of the currents of oxygen electroreduction shows that the electrocatalytic effect is also weakened after annealing of pCoP-II (Fig. 8b) although to a much less extent than that for its Mn analogue. As a whole, it can be concluded that for the newly obtained coatings of polymetalloporphines, the annealing process is not an efficient route to increased efficiency of the oxygen reaction process since it leads to the significant deterioration in electrocatalytic current densities as well as to the shift of the oxygen electroreduction potential towards more negative values.

Conclusions

A novel representative of the polyporphine family containing Mn(II) cations as central ions (both of type I, pMnP-I, and type II, pMnP-II) have been obtained for the first time via our procedure of the electrochemically induced ion exchange. It has been demonstrated that manganese and its cobalt counterpart polyporphines of type II (pMnP-II and pCoP-II) existing as 50 nm thin films on solid electrode substrates can be considered as promising platinum-free electrocatalysts for the oxygen reduction in neutral and especially (due to a higher stability) alkaline electrolytes. The measurements conducted under cyclic voltammetric and steady-state conditions have shown that regardless of the electrolyte pH, the pCoP-II polymer is more efficient catalyst toward oxygen reduction reaction and its performance approaches to that of compact platinum. However, it is of importance to note that (contrary to literature data concerning similar porphyrin complexes) the activity of manganese-containing polyporphine of type II, pMnP-II, is quite close to the performance of its Co counterpart. The high electrocatalytic activity of both electroactive polymers should be ascribed to the unique structure of polymetalloporphines of type II, i.e. the highest possible density of active MN₄ sites and a high electron conductivity within a very broad potential range.
Acknowledgement

Financial support of the Russian Foundation for Basic Research (grant 16-03-00916 A) is acknowledged. Partial support from the European Commission through the Graphene Flagship – Core 1 project [Grant number GA-696656] is also appreciated.

References

1. Jurow M, Schuckman AE, Batteas JD, Drain CM (2010) Porphyrins as molecular electronic components of functional devices. Coord Chem Rev 254:2297-2310
2. Screen TEO, Thorne JRG, Denning RG, Bucknall DG, Anderson HL (2003) Two methods for amplifying the optical nonlinearity of a conjugated porphyrin polymer: transmetallation and self-assembly. J Mater Chem 13:2796–2808
3. Screen TEO, Lawton KB, Wilson GS, Dolney N, Ispasoiu R, Goodson III T, Martin SJ, Bradley DDC, Anderson HL (2001) Synthesis and third order nonlinear optics of a new soluble conjugated porphyrin polymer. J Chem Mater 11:312-320
4. Chou JH, Kosal ME, Nalwa HS, Rakow NA, Suslick KS (2000) In: Kadish KM, Smith KM, Guilard R (ed) Applications of Porphyrins and Metalloporphyrins to Materials Chemistry in The Porphyrin Handbook, vol. 6, ch. 41, pp. 43-131, Academic Press, New York
5. Imahori H, Kimura M, Hosomizu K, Sato T, Tae KA, Seong KK, Kim D, Nishimura Y, Yamazaki I, Araki Y, Ito O, Fukuzumi S (2004) Vectorial electron relay at ITO electrodes modified with self-assembled monolayers of ferrocene-porphyrin-fullerene triads and porphyrin-fullerene dyads for molecular photovoltaic devices. Chem Eur J 10:5111–5122
6. Canales C, Ramirez G (2015) Glassy carbon electrodes modified with supramolecular assemblies generated by π-stacking of Cobalt (II) octaethylporphyrins. A 4 electrons-dioxygen reduction reaction occurring at positive potentials. Electrochim Acta 173:636-641
7. Sun Z, Li J, Zheng H, Liu X, Ye Y, Du P (2015) Pyrolyzed cobalt porphyrin-modified carbon nanomaterial as an active catalyst for electrocatalytic water oxidation. Int J Hydrogen Energy 40:6538-6545
8. Lin S, Diercks CS, Zhang YB, Kornienko N, Nichols EM, Zhao Y Chang CJ (2015) Covalent organic frameworks comprising cobalt porphyrins for catalytic CO2 reduction in water. Science 349:1208-1213
9. Tan Y, Escorcia N, Hyslop A, Wang E (2015) Investigation of cobalt porphyrin doped polymer membrane films for the optical sensing of imidazole and its derivatives. Anal Chem Res 3:70-76
10. Chandra S, Mende C, Bahadur D, Hidebrandt A, Lang H (2014) Fabrication of a porphyrin-based electrochemical biosensor for detection of nitric oxide released by cancer cells. J Solid State Electrochem 19:169-177
11. Dogutan DK, Ptaszek M, Lindsey JS (2007) Direct Synthesis of Magnesium Porphine via 1-Formyldipyrromethane. J Org Chem 72:5008-5011
12. Devillers CH, Lucas D, Dime AKD, Rousselin Y, Mugnier Y (2010) Exploring the redox reactivity of magnesium porphine. Insight into the origins of electropolymerisation. Dalton Trans 39:2404-2411
13. Vorotyntsev MA, Konev DV, Devillers CH, Bezverkhyy I, Heintz O (2010) Magnesium(II) polyporphine: The first electron-conducting polymer with directly linked unsubstituted porphyrin units obtained by electrooxidation at a very low potential. Electrochim Acta 55:6703-6714
14. Konev DV, Istakova OI, Sereda OA, Shamraeva MA, Devillers CH, Vorotyntsev MA (2015) In situ UV-visible spectrocetrochemistry in the course of oxidative monomer electrolysis. Electrochim Acta 179:315-325
15. Konev DV, Lizgina KV, Istakova OI, Baulin VE, Kalashnikova IP, Devillers CH, Vorotyntsev MA (2016) Electropolymerization of magnesium 5, 15-di (n-methoxyphenyl) porphine. Russ J Electrochem 52:1150-1158
16. Vorotyntsev MA, Konev DV, Devillers CH, Bezverkhyy I, Heintz O (2011) Electroactive polymeric material with condensed structure on the basis of magnesium(II) polyporphine. Electrochim Acta 56:3436-3442
17. Konev DV, Devillers CH, Lizgina KV, Baulin VE, Vorotyntsev MA (2015) Electropolymerization of non-substituted Mg (II) porphine: effects of proton acceptor addition J Electroanal Chem 737:235-242
18. Konev DV, Devillers CH, Lizgina KV, Zyubina TS, Zyubin AS, Maiorova-Valkova LA, Vorotyntsev MA (2014) Synthesis of new electroactive polymers by ion-exchange replacement of Mg(II) by 2H⁺ or Zn(II) cations inside Mg(II) polyporphine film, with their subsequent electrochemical transformation to condensed-structure materials. Electrochim Acta 122:3-10
19. Rolle SD, Konev DV, Devillers CH, Lizgina KV, Lucas D, Stern C, Herbst F, Heintz O, Vorotyntsev MA (2016) Efficient synthesis of a new electroactive polymer of Co(II) porphine by in-situ replacement of Mg(II) inside Mg(II) polyporphine film. Electrochim Acta 204:276–286
20. Istakova OI, Konev DV, Devillers CH, Vorotyntsev MA, Zyubin AS, Antipov EM, Aldoshin SM (2016) Electrochemical Synthesis of cobalt polyporphine films. Dokl Phys Chem 471:181–184
21. Istakova OI, Konev DV, Zyubin AS, Devillers CH, Vorotyntsev MA (2016) Electrochemical route to Co(II) polyporphine. J Solid State Electrochem 20:3189–3197
22. Wu ZS, Chen L, Liu J, Parvez K, Liang H, Shu J, Sachdev H, Graf R, Feng X, Mullen K (2014) High-performance electrocatalysts for oxygen reduction derived from cobalt porphyrin-based conjugated mesoporous polymers. Adv Mater 26:1450-1455

23. Yao B, Li C, Ma J, Shi G (2015) Porphyrin-based graphene oxide frameworks with ultra-large d-spacings for the electrocatalyzation of oxygen reduction reaction. Phys Chem Chem Phys 17:19538-19545

24. Jasinski R (1965) Cobalt Phthalocyanine as a Fuel Cell Cathode. J Electrochem Soc. 112:526 – 528

25. Jasinski R (1964) A New Fuel Cell Cathode Catalyst. Nature 201:1212 – 1213

26. Zagal J, Páez M, Tanaka AA, dos Santos Jr JR, Linkous CA (1992) Electrocatalytic activity of metal phthalocyanines for oxygen reduction. J Electroanal Chem 339:13-20

27. Okunola A, Kowalewska B, Bron M, Kulesza P, Schuhmann W (2009) Electrocatalytic reduction of oxygen at electropolymerized films of metalloporphyrins deposited onto multi-walled carbon nanotubes. Electrochim Acta 54:1954–1960

28. Zagal JH, Bedioui F, Dodelet JP (2006) N4-macrocyclic metal complexes. Springer, New York

29. Konev DV, Lizgina KV, Khairullina DK, Shamraeva MA, Devillers CH, Vorotyntsev MA (2016) Preparation of cobalt polyporphine and its catalytic properties in oxygen electroreduction. Russ J Electrochem 52:869-879

30. Konev DV, Vorotyntsev MA, Devillers CH, Zybina TS, Zyubin AS, Lizgina KV, Volkov AG (2013) Synthesis of New Polyporphines by Replacing Central Ion in Magnesium Polyporphine 1. Russ J Electrochem 49:753–758

31. Zhang AL, Yoneyama M, Nakashima N, Iriyama K, Ozaki Y (1997) Molecular orientation and aggregation in Langmuir-Blodgett films of 5-(4-N-octadecylylpyridyl)-10,15,20-tri-p-tolylporphyrin studied by ultraviolet-visible and infrared spectroscopies. Langmuir 13:4422-4427

32. Ivashin NV (2010) Calculation of the structure and vibrational states for anionic forms of –Co, Ni- and Cu-porphines. J Appl Spectrosc 77:28-37

33. Wang C, Fan Q, Hu S, Ju H, Feng X, Han Y, Pan H, Zhu J, Gottfried JM (2014) Coordination reaction between tetraphenylporphyrin and nickel on a TiO2 (110) surface. Chem Commun 50:8291-8294

34. Kal S, Filatov AS, Dinolfo PH (2013) Structural, Electrochemical, and Spectroscopic Investigation of Acetate Bridged Dinuclear Tetrakis-Schiff Base Macrocycles of Mn and Zn. Inorg Chem 52:13963–13973

35. Shi Ch, Steiger B, Yuasa M, Anson FC (1997) Electroreduction of O2 to H2O at Unusually Positive Potentials Catalyzed by the Simplest of the Cobalt Porphyrins. Inorg Chem 36:4294-4295
36. Tse YH, Janda P, Lam H, Zhang J, Pietro WJ, Lever ABP (1997) Monomeric and Polymeric Tetra-aminophthalocyanatocobalt(II) Modified Electrodes: Electrocatalytic Reduction of Oxygen. J Porphyrins and Phthalocyanines 1:3-16
37. Vasudevan P, Santosh, Mann N, Tyagi S (1990) Transition metal complexes of porphyrins and phthalocyanines as electrocatalysts for dioxygen reduction. Transition Met Chem 15:81-90
38. Masa J, Ozoemena K, Schuhmann W, Zagal JH (2012) Oxygen reduction reaction using N4-metallomacrocyclic catalysts: fundamentals on rational catalyst design. J Porphyrins and Phthalocyanines 16:761-784
39. Okunola AO, Nagaiah TC, Chen X, Eckhard K, Schuhmann W, Bron M (2009) Visualization of local electrocatalytic activity of metalloporphyrins towards oxygen reduction by means of redox competition scanning electrochemical microscopy (RC-SECM). Electrochim Acta 54:4971-4978
40. Goellner V, Armel V, Zitolo A, Fonda E, Jaouen F (2015) Degradation by Hydrogen Peroxide of Metal-Nitrogen-Carbon Catalysts for Oxygen Reduction. J Electrochem Soc 162:H403-H414
41. Masa J, Zhao A, Xia W, Muhler M, Schuhmann W (2013) Metal-free catalysts for oxygen reduction in alkaline electrolytes: Influence of the presence of Co, Fe, Mn and Ni inclusions. Electrochim Acta 128:271-278
42. LeFèvre M, Proietti E, Jaouen F, Dodelet JP (2009) Iron-Based Catalysts with Improved Oxygen Reduction Activity in Polymer Electrolyte Fuel Cells. Science 324:71-74
43. Chung HT, Cullen DA, Higgins D, Sneed BT, Holby EF, More KL, Zelenay P (2017) Direct atomic-level insight into the active sites of a high-performance PGM-free ORR catalyst. Science 357:479-484
44. Schilling T, Okunola A., Masa J, Schuhmann W, Bron M (2010) Carbon nanotubes modified with electrodeposited metal porphyrins and phenanthrolines for electrocatalytic applications. Electrochim Acta 55:7597-7602
Fig. 1. Cyclic voltammetric responses of platinum electrode modified with pH$_2$P-I (deposition charge of initial pMgP-I was 5 mC cm$^{-2}$ which corresponds to the thickness of ca. 50 nm) in the course of electrochemically induced ion exchange in contact with $5 \times 10^{-4}$ mol dm$^{-3}$ Mn(ClO$_4$)$_2$ containing AN solution. Potential sweep rate: 0.1 V s$^{-1}$. 
Fig. 2. FTIR ATR spectra of polyporphines of type I: (a) pMgP-I, (b) pH₂P-I, (c) pMnP-I deposited on platinum foil.
Fig. 3. Fragments of XPS spectra of pMP-I films deposited on Pt foil. Deposition charge of initial pMgP-I was 5 mC cm$^{-2}$ which corresponds to the thickness of ca. 50 nm. (a): bands M 2p (M = Mn or Co), (b): band N 1s.
Fig. 4. Comparative cyclic voltammetric responses of Pt electrode coated with pMPs films (M = Mn or Co) of type I (deposition charge of pMgP-I: 5 mC cm\(^{-2}\)) (a) and type II (b) in 0.1 mol dm\(^{-3}\) TBAPF\(_6\) + AN solution. Scan rate: 0.1 V s\(^{-1}\). (c) Typical potential-time dependence in the course of the galvanostatic transformation of pCoP-I and pMnP-I in 0.1 mol dm\(^{-3}\) TBAPF\(_6\) + AN solution. Applied anodic current density: 0.057 mA cm\(^{-2}\) for both films.
Fig. 5. Cyclic voltammetric curves of pMnP-II and pCoP-II coated glassy carbon electrodes (deposition charge of pMgP-I: 5 mC cm\(^{-2}\)) in deaerated aqueous solutions of 0.1 mol dm\(^{-3}\) TEACIO\(_4\) (a) and 0.1 mol dm\(^{-3}\) NaOH (b). Scan rate: 0.1 V s\(^{-1}\).
Fig. 6. Cyclic voltammograms (first cycle) of pMnP-II and pCoP-II films (deposition charge of pMgP-I: 5 mC cm$^{-2}$) on glassy carbon electrodes in oxygen-saturated aqueous electrolytes: (a) 0.1 mol dm$^{-3}$ TEAClO$_4$; (b) 0.1 mol dm$^{-3}$ NaOH. Electrochemical responses of bare platinum and glassy carbon electrodes of the same surface area are shown for comparison. Potential sweep rate: 0.1 V s$^{-1}$. Temperature: 25°C.
Fig. 7. Steady-state voltammograms of pMnP-II and pCoP-II films (deposition charge of pMgP-I: 5 mC cm\(^{-2}\)) on glassy carbon electrodes in oxygen-saturated aqueous electrolytes of (a) 0.1 mol dm\(^{-3}\) TEACIO\(_4\) and (b) 0.1 mol dm\(^{-3}\) NaOH. Steady-state responses of bare platinum and glassy carbon electrodes of the same surface area are included for comparison. Temperature: 25°C. These measurements were performed
by means of a set of 50 mV potential steps where the potential value was kept constant for 30 s after the step while the "steady-state current" was determined as the average current during the last 2 s before the next potential step.
Fig. 8. Voltammetric curves of oxygen reduction (10th scan) at roughened glassy carbon electrodes covered with films of pMnP-II (a) and pCoP-II (b) recorded at 25 °C in alkaline electrolyte, before and after annealing treatment. Scan rate: 0.1 V s⁻¹.
Scheme 1. Four-step procedure leading to formation of polyporphines of type II (pCoP-II and pMnP-II)

Tables

Table 1. Relative content of metal ions (M=Mg, Mn) in pMPs films derived from XPS measurements.

|                     | at %, XPS | C/N | N/M |
|---------------------|-----------|-----|-----|
| C_{20}H_{12}N_{4}M(calculated) | -         | -   | 5.0 | 4.0 |
| pMnP-I              | 85.1      | 11.6| 3.3 | 7.3 | 3.5 |
| pCoP-I              | 85.0      | 11.7| 3.2 | 7.2 | 3.6 |
| pCoP-II             | 84.3      | 13.4| 2.3 | 6.3 | 5.8 |
| pMnP-I              | 84.8      | 12.7| 2.5 | 6.7 | 5.1 |
| pMnP-II             | 83.5      | 13.5| 3.1 | 6.2 | 4.4 |

Table 2. Maximum peak potentials ($E_p$) and half-wave potentials ($E_{1/2}$) values of oxygen reduction derived from Figs. 6 and 7.

|                     | $E_p/E_{1/2}$, V |
|---------------------|------------------|
| Electrolyte         | GC               | Pt              | pMnP-II       | pCoP-II       |
| TEAClO_4            | -0.70/-0.52      | -0.25/-0.02     | -0.20/-0.13   | -0.12/-0.05   |
| NaOH                | -0.42/-0.33      | -0.23/-0.1      | -0.29/-0.23   | -0.17/-0.14   |