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

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ABSTRACT

Novel member of polymetalloporphines, namely manganese polymetalloporphine 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: demetalation of the pMgP-I electrode film via its exposure to trifluoroacetic acid solution, resulting in formation of the metal-free polyporphine of type I (pH₂P-I) followed by electrochemically induced incorporation of Co or Mn ions from the acetonitrile 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 polymetalloporphines is comparable to bare platinum electrode. The effect of annealing of polymermodified electrodes on their catalytic properties has also been considered.

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

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