

Abstract

This work reports on the cobalt pyridinoporphyrazinate (CoTmtppa) as a platinum-group metal-free catalyst for hydrogen evolution and oxidation reactions with the possibility of use in hydrogen energy and hydrogen potentiometric sensing. A different interaction of CoTmtppa with various electrode substrates, highly oriented pyrolytic graphite (HOPG) and annealed gold (Au(111)), affects its electrocatalytic behaviour in hydrogen reactions. The formation of a hydride-type complex with the bonding of hydrogen atoms to cobalt centre is supposed to be the rate-determining step. In the case of hydrogen evolution, the maximum catalytic activity of mediator was reached at pH = 11,0, when the HOPG/CoTmtppa showed overpotential decrease by 300 mV and an almost 60-fold increase of current densities compared to HOPG. The electrocatalytic activity of Au(111)/CoTmtppa resulted in a further decrease of overpotential by 175 mV in comparison with HOPG/Co(I)Tmtppa. The electrochemical oxidation of hydrogen was found to depend on hydrogen source which was electrochemically generated on-site or molecular hydrogen supplied from an external source. In the case of electrochemically generated hydrogen, the maximum activity of HOPG/CoTmtppa was reached at pH = 2.1 and an additional it was observed 50 % increase in current density at the Au(111)/CoTmtppa compared to HOPG/CoTmtppa at pH = 4.3. The HOPG/CoTmtppa did not exhibit measurable activity for the oxidation of hydrogen from an external source, apparently due to the slow kinetics of hydride complex formation. In contrast, at the Au(111)/CoTmtppa proceeded well with the current density 0.055 mA cm^{-2} at potential -0.25 V vs. SCE and pH = 4.3. Unlike cyclic voltammetry, the potentiometric measurement showed a significant response to hydrogen about 150 mV at the HOPG/CoTmtppa in solution (pH = 4.3) alternately saturated with argon and hydrogen ($0.78 \text{ mmol dm}^{-3}$) within time interval 90 s. At Au(111)/CoTmtppa the potential response of 25 mV was reached within 190 s. The different behaviour of Au(111)CoTmtppa can be attributed to the formation of gold sub-oxides, partial diffusion of hydrogen to the bulk of the electrode and the synergy of CoTmtppa and Au(111) catalytic activities.