



First-row transition metal phthalocyanines as catalysts for water electrolysis: a comparative study

Natalia Chebotareva and Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

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Abstract—Modification of carbon electrodes with first row transition metal phthalocyanines results in the lowering of the potentials needed for water electrolysis in basic media, by 600 to 700 mV when compared to unmodified carbon electrodes. Nickel(II), cobalt(II) and iron(II) phthalocyanines show higher catalytic activity than zinc(II), manganese(II), copper(II) and metal free phthalocyanines.

Key words: phthalocyanine, water electrolysis, nickel, cobalt, iron, zinc, manganese, copper.

INTRODUCTION

Hydrogen and oxygen evolution by water electrolysis is a process of great technological importance since it solves the problem of conversion of electrical energy in excess into chemical energy. Research into water electrolysis has concentrated mainly on the development of catalysts that can lower the voltages involved in the process. Nickel and titanium electrodes are commonly employed for water electrolysis [1]. These electrodes, however, suffer from corrosion effects and have relatively high overpotentials for water electrolysis. Coating these electrodes with metallic oxides improves their lifetimes, but increases the overpotentials [2]. Currently, research on the fabrication of new electrodes has concentrated on lowering the overpotentials and increasing the oxidation or reduction currents of the reactions of interest, and on prolonging the lifetimes of the electrodes. Carbon electrodes modified with a variety of catalytic compounds are widely used in electrochemistry [3]. Metallophthalocyanine [MPc, $\text{Pc}(-2)$ = phthalocyanine dianion] are well known catalysts for many reactions [4, 5] and are known to lower overpotentials when employed as catalysts in electrochemical reactions [6–16]. The electrochemical reaction, involving MPc modified electrodes, that has received by far the most attention in the literature is the

electroreduction of oxygen [5]. For this reaction, maximum catalytic activity was observed for MPc complexes which exhibit oxidation at the central metal prior to phthalocyanine ring oxidation (eg FePc and CoPc). MPc complexes have also been used as sensors for the detection of sulfur-containing compounds [5, 8]. The detection of cysteine in particular has received a considerable amount of attention [5, 6, 8]. MPc complexes have been used as photocatalysts in the production of hydrogen, but very low yields have been obtained [17]. The use of MPc complexes as electrocatalysts for water electrolysis has received very little attention [5, 2]. Carbon electrodes which have been coated with MPc are convenient for oxygen evolution due to resistance of the surface to the corrosion effects that are usual for metal electrodes such as Ni, Fe and Ti, under relevant conditions. MPc modification also enhances the catalytic activity of the carbon electrodes [6, 8]. Molybdenum (MoNPc) and iron (FeNPc) naphthalocyanine modified electrodes were found to catalyse oxygen evolution from water [5, 2]. The MoNPc complex was found to show higher catalytic activity than the FeNPc complex and unmodified carbon black electrodes were found to lower the overpotential for hydrogen evolution to a larger extent than the MoNPc or FeNPc modified electrodes. It was suggested that the central Mo metal ion was reduced during the catalytic process [2]. In this communication we compare the electrocatalytic activity of the

*Author to whom correspondence should be addressed.