Full Paper Wiley Online Library ELECTROANALYSIS

DOI: 10.1002/elan.201400499

Iodine-Doped Cobalt Phthalocyanine Supported on Multiwalled Carbon Nanotubes for Electrocatalysis of Oxygen Reduction Reaction

Stephen Nyoni,[a] Philani Mashazi,[a] and Tebello Nyokong*[a]

Abstract: 4-(4,6-Diaminopyrimidin-2-ylthio) phthalocyaninatocobalt(II) (CoPyPc) was iodine doped, and its electrocatalytic properties explored. Physical characterization techniques such as UV-vis, X-ray photoelectron, electron paramagnetic resonance and infra-red spectroscopy were used. Cyclic voltammetry, electrochemical impedance spectroscopy and rotating disk electrode were used for electrochemical characterization of electrodes modified with the prepared phthalocyanine and its nanocomposites. The electrocatalytic effect of a new iodine-doped cobalt phthalocyanine derivative supported on multiwalled carbon nanotubes was then investigated towards oxygen reduction reaction. The electrocatalytic activity of the iodine-doped cobalt phthalocyanine was found to be superior in terms of current over the undoped phthalocyanine nanocomposite.

Keywords: Oxygen reduction · Electrocatalysis · Cobalt phthalocyanine derivative · Iodine-doping · Carbon nanotubes.

1 Introduction

Metallophthalocyanines, (MPcs) are well known electrocatalysts for many reactions including oxygen reduction reaction (ORR) [1–4]. MPcs may suffer from chemical destruction by H_2O_2 produced as either an intermediate product for a 4-electron system or final product for a 2-electron system during oxygen reduction. Tuning the substituents of the metallophthalocyanines can result in changes in their physicochemical properties which might lead to enhanced electrocatalytic activity towards ORR and greater stability in H_2O_2 environment. Doped nanocomposites appear to be one way that can be used to improve on ORR electrocatalysis [5–12]. Some metallophthalocyanine derivatives were found to have improved conductivity upon iodine-doping [13,14]. Apart from one study [15] using iodine doped unsubstituted cobalt phthalocyanine (CoPc), oxygen reduction using iodine doped phthalocyanines has not been explored. A careful selection of ring substituents can improve the electrocatalytic activity of phthalocyanines. Hence in this work, cobalt (II) phthalocyanine was ring substituted with 4-(4,6-pyrimidin-2-ylthio) (CoPyPc, Figure 1) [16], and further doped with iodine to promote electron transfer. The sulfur and amino substituents will result in red shifting of the Q band [17], which is known to result in facile reduction of phthalocyanines, aiding the electrocatalysis. Multi walled carbon nanotubes (MWCNTs) have been used to promote electron transfer properties of phthalocyanines [18–22], hence are employed in this work in combination with iodine doped CoPyPc. There are no reports which combine both iodine doped Pc and MWCNTs, even though the advantage of the combination is beneficial for improved electron transfer.

The individual components (CoPyPc and iodine doped CoPyPc) and when adsorbed on MWCNT were used for the modification of a glassy carbon electrode (GCE) and used for ORR for the first time.

2 Experimental

2.1 Materials

Multiwalled carbon nanotubes (MWCNT), dimethylformide (DMF), unsubstituted CoPc, hexanol, and dichlorobenzene were from Sigma Aldrich. HCl and sodium nitrite from BDH Laboratory supplies, NaOH from Minema, and potassium iodide from Merck chemicals. The synthesis of CoPyPc (Figure 1) has recently been reported [16].

2.2 Equipment

Ground state electronic absorption spectra were performed on a Shimadzu UV-2550 spectrophotometer. Transmission electron microscope (TEM) micrographs for the nanomaterials were obtained using a Zeiss Libra 120 TEM operating at 80 kV. Scanning electron microscopy (SEM) images were obtained using a TESCAN Vega TS 5136LM Electron microscope.

[a] S. Nyoni, P. Mashazi, T. Nyokong
Department of Chemistry, P. O. Box 94, Rhodes University, Grahamstown, 6140, South Africa
Tel.: +27-46-603 8260; fax: +27-46-622 5109
*e-mail: t.nyokong@ru.ac.za

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/elan.201400499.

