



The use of copper and cobalt phthalocyanines as electrocatalysts for the oxygen reduction reaction in acid medium



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ABSTRACT

Direct electrochemical generation of hydrogen peroxide in aqueous medium represents an attractive method for the production of the oxidizing agent. This paper describes the development of electrocatalysts comprising Printex L6 carbon black containing 0 to 10% (w/w) of copper or cobalt phthalocyanine (CuPc and CoPc, respectively) as modifier. Formation of H₂O₂ by the ORR in acidic medium was investigated by linear voltammetry using a rotating ring-disc electrode, whose glassy carbon disc contained a microporous layer of the catalyst. Incorporation of CuPc into Printex decreased the current efficiency for H₂O₂ formation [*i*(H₂O₂)%] from 75.4% for unmodified Printex to a minimum of 53.3% when 10% of the modifier was present. However, *i*(H₂O₂)% increased when CoPc was employed as modifier, and a maximum value of 92.3% was attained with Printex containing 1.0% CoPc. Moreover, a shift of +340 mV (relative to unmodified Printex) was observed in the overpotential required for the generation of H₂O₂ when 10% of CoPc was present. SECM demonstrated that, at a potential of -0.2 V, Printex with 10% CoPc produced larger amounts of H₂O₂ compared with unmodified Printex. It is concluded that the use of the CoPc modifier is promising for the electrogeneration of H₂O₂ on a large scale.

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1. Introduction

Advanced oxidation processes (AOPs) offer promising alternatives to conventional techniques for the removal of organic and inorganic contaminants from wastewater. The oxidative reactions associated with AOPs are mediated by highly reactive hydroxyl radicals (●OH) that are normally produced *in situ* with the aid of a primary oxidant such as hydrogen peroxide (H₂O₂). While H₂O₂ is a versatile oxidizing agent with application in a wide range of organic syntheses and industrial processes [1–3], its manufacture is subject to a number of important limitations. The industrial production of H₂O₂ involves the chemical reduction of O₂ gas through the autoxidation of an anthrahydroquinone in organic medium under high pressure and elevated temperature using a noble metal as catalyst. With this method it is possible to attain high concentrations of H₂O₂, but the process requires the storage and utilization, under controlled conditions, of large quantities of H₂, and the final product has to be extracted from the

organic medium in order to obtain aqueous solutions containing target levels of hydrogen peroxide [1–4].

The direct electrochemical generation of H₂O₂ in aqueous medium has received significant research attention, and a number of studies have been performed with the aim of optimizing the process [5–8]. Although the results were favorable in terms of electrogeneration, the process was limited by the low solubility of O₂ in aqueous medium, and an improvement in mass transport would be necessary to enhance process efficiency.

The majority of investigations concerning the electrogeneration of H₂O₂ have focused on the oxygen reduction reaction (ORR) to produce the peroxide *via* a 2-electron transfer mechanism [9–13]. Various electrode materials have been studied, but carbon black was found to be the most favorable for the 2-electron ORR pathway in aqueous medium and is currently considered to be the standard reference for this mechanism [9–13]. On the other hand, Pt deposited in carbon black (Pt/C) is considered as the standard reference for ORR involving 4-electron transfer [14], a pathway that is mainly associated with water production in fuel cells [16].

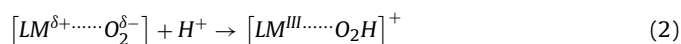
Interest has recently been directed at increasing the concentrations of H₂O₂ that can be formed by electrogeneration through the addition of organic modifiers, such as quinones and azobenzenes, to carbon black [12,15,16]. In this context, transition metal

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complexes with macrocycles, such as porphyrins [17] and phthalocyanines [18,19], are also known to promote ORR. Based on studies of the behavior of metallic macrocyclic complexes, the following redox mechanisms have been proposed [20]:



Initially, an adduct is formed by interaction between O_2 and the transition metal ion at the center of the macrocyclic complex (eq 1). The sequential addition to this adduct of protons from the electrolyte together with a 2-electron transfer gives rise to H_2O_2 (eqs 2 and 3), although the product may be reduced to water according to eq 4. The form of the interaction of O_2 with the metal ion in eq 1 is the key factor in determining the course of the ORR. Three different models, Griffiths, Bridge (*cis* and *trans*) and Pauling, have been proposed for this interaction, and for each type of mechanism there is a preferred product from the ORR. The Griffiths and Bridge models favor the formation of water by the 4-electron pathway while the Pauling model favors H_2O_2 formation by 2-electron transfer [21,22]. The type of adduct initially formed depends on the characteristics of the transition metal present, and so the same ORR product can be obtained using porphyrins, phthalocyanines or oxides of the same metal.

Electrocatalytic reduction of O_2 depends of the metal center because ORR occurs by electron transfer between O_2 molecule and metal center. Electron withdrawing or donation nature of different ring substituents of phthalocyanines or porphyrins macrocycles also contributes to this step. In the present study, microporous layers of carbon black modified with different amounts of copper and cobalt phthalocyanines were characterized by scanning electrochemical microscopy (SECM), and the effects of the modifiers on H_2O_2 generation were evaluated by linear sweep voltammetry.

2. Experimental

2.1. Preparation and characterization of electrocatalysts

Copper phthalocyanine (CuPc; Sigma-Aldrich; product #702854) and cobalt phthalocyanine (CoPc; Sigma-Aldrich; product #307696) were employed as modifiers supported on Printex L6 (Evonik) carbon black (described hereafter as Printex). The electrocatalysts were prepared by adding 1.0 g of Printex containing various proportions (0.0, 0.5, 1.0, 3.0, 5.0 or 10.0% w/w) of modifier to isopropyl alcohol (10 mL; J.T. Baker) and stirring for 1 h at room temperature [2]. The resulting mixture was heated in an oven at 60 °C for 2 h and then at 100 °C for 1 h to ensure complete removal of the alcohol. Powders containing CuPc or CoPc on Printex were characterized by X-ray fluorescence (XRF) using a PANalytical MiniPal 4 PW 4024 spectrometer with Rh X-ray tube and Ag filter (Ominian 1; 30 kV).

2.2. Preparation and characterization of microporous layers

Electrochemical experiments were performed using microporous layers deposited on the surface of the glassy carbon (GC) disc of a rotating ring-disc electrode (RRDE) as described previously [2,23]. A sample (3.0 mg) of electrocatalyst containing 0 to 10% w/w of CuPc or CoPc supported on Printex was suspended in 3.0 mL of Milli-Q ultrapure water ($18 \Omega \cdot \text{cm}^{-1}$) and maintained in an ultrasonic bath for 10 min. A 20 μL aliquot of the resulting suspension was deposited on the surface of the GC disc and subjected to

a steady stream of N_2 in order to evaporate the water completely, thereby forming a microporous layer. Nafion® perfluorinated resin solution (5% by weight in aqueous alcohol; Sigma-Aldrich; product #274704) was diluted 1/100 in Milli-Q water and a 20 μL aliquot was deposited on the microporous layer and subsequently dried under a steady stream of N_2 . Printex without modifier was used as the standard reference for ORR involving 2-electron transfer (with preferential formation of H_2O_2) and Pt deposited on carbon black (Pt/C; E-TEK) was employed as standard reference for the 4-electron pathway (with preferential formation of water).

2.3. RRDE experiments

Linear sweep voltammetry was performed in a conventional three-compartment electrochemical cell using an Autolab (Metrohm Pensalab) PGSTAT 302 N potentiostat/galvanostat. The working electrode was a Pine Research Instrumentation model E7R9-VC/Pt RRDE ($N=0.37$), comprising a GC disc and Pt ring (polarized at +1.0 V vs SCE), the rotation of which was controlled using a Pine model AFMSRCE rotation controller. Platinum foil (2.0 cm^2) was employed as the counter electrode and the reference was a saturated calomel electrode (SCE). The aqueous supporting electrolyte (150 mL) contained 0.1 mol L^{-1} K_2SO_4 and 0.1 mol L^{-1} H_2SO_4 , and was bubbled with O_2 for at least 40 min prior to experimentation.

2.4. SECM experiments

SECM experiments were performed as described previously [23] using a Sensolytics modular high resolution SECM system equipped with a Pt microdisc (10 μm radius; $RG=10$) as tip. Substrate utilized was a GC disc (1.0 mm radius), onto which microporous layers of Printex with and without modifier had been deposited, while the counter electrode was a Pt wire with an Ag/AgCl as the reference electrode. The aqueous supporting electrolyte (1.0 mL) contained 0.1 mol L^{-1} K_2SO_4 and 0.1 mol L^{-1} H_2SO_4 , and was bubbled with O_2 for at least 40 min prior to experimentation.

3. Results and discussion

3.1. XRF characterization of the electrocatalysts

Powdered electrocatalysts containing different amounts of modifier were characterized by XRF in order to verify the incorporation of CuPc or CoPc into Printex. In the XRF spectra, peaks associated with the $K\alpha$ and $K\beta$ emission lines, respectively, of Cu at 8.04 and 8.90 keV (Fig. 1a), and of Co at 6.92 and 7.64 keV (Fig. 1b) were clearly visible. The inserts in Figs. 1a and b show that the intensities of the $K\alpha$ and $K\beta$ emission lines increased as the percentage of modifier used in the preparation of the electrocatalyst increased. Correlations between the peak areas of the $K\alpha$ emission lines of the metals and the quantity of respective modifier employed in the preparation of the electrocatalyst were good (Fig. 1c) with regression coefficients of 0.9978 for Cu and 0.9982 for Co. Thus, it may be concluded that the method of preparation of the electrocatalyst was efficient.

3.2. RRDE analyses

Linear sweep voltammetry in the potential range +0.4 to -0.8 V vs SCE was performed using a RRDE with electrode rotation of 100, 400, 900, 1600 or 2500 rpm. Voltammograms obtained at 900 rpm were found to be representative for all electrocatalysts studied, hence, for comparison purposes, the plots depicted in Fig. 2 relate only to measurements recorded at this rotational velocity. The linear voltammograms measured at the disc electrode (lower panel in each figure) containing the microporous

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