



A novel CuFe-based catalyst for the oxygen reduction reaction in alkaline media

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ABSTRACT

The primary objective of this work is to develop alternative electrocatalysts to Pt-based materials for the oxygen reduction reaction (ORR) in alkaline fuel cells. We synthesized a bicore CuFe/C composite electrocatalyst by impregnation of iron and copper phthalocyanine-based complexes into a carbon support, followed by pyrolysis at 800–900 °C in an Ar atmosphere. This novel composite catalyst exhibits electrochemical performance for ORR in 0.1 M KOH similar to a commercial Pt/C (BASF Fuel Cell, 30%) catalyst at 6-fold lower CuFe loading. High resolution X-ray photoelectron spectroscopy (HR-XPS) results indicate that coordination bonding between Fe and N atoms still remains and show that a mixed Cu(I)/Cu(II) valency exists in the CuFe/C catalyst after high temperature heat treatment. The Cu(I)/Cu(II) redox mediator adjacent to Fe atoms is crucial to provide electrons to the N_xFe-O_2 adduct and maximize the overall rate of the reduction reaction. The results of this study may offer a new approach to development of efficient catalysts for oxygen reduction to water in alkaline media.

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1. Introduction

Alkaline fuel cells (AFCs) were one of the first fuel cell technologies developed and they have demonstrated efficiencies near 60% in space applications. Unfortunately, the inherent low power density and electrolyte poisoning by CO_2 [1–3] added to the relatively high cost of AFCs and led to the rapid growth of acidic analogs such as the proton exchange membrane fuel cells (PEMFCs). On the other hand, the fast kinetics of alcohol oxidation in alkaline media and development of alkaline anion exchange membranes have reinvigorated the search for non-noble metal catalysts for ORR, and revitalized the interest in anion exchange membrane fuel cells (AEMFC) [4–7]. One of the main advantages of AEMFCs over their acidic analogs [8,9] is the availability of effective and inexpensive non-platinum electrocatalysts such as MnO_2 [10,11], nickel [12,13], silver [14,15], cobalt [16,17], and iron [18,19].

The discovery of cobalt phthalocyanine cathodic catalyst by Jasinski [20] was followed by numerous studies of organometallic complexes as promising alternatives for Pt-based electrocatalysts for ORR [21–25]. Among the variety of transition metal macrocycle complex catalysts with different central metal atoms [26] and synthesis methods that have been reported in the literature [24,25],

iron- and cobalt-based materials have been identified to exhibit the best activity for ORR under various metal loadings [27–30]. Furthermore, major progress has been reported on metal complex systems reminiscent of enzymes which mimic their coordination environment [31] and proton-coupled electron-transfer process [32–34]. These cofacial porphyrins and related compounds have the basic structure of cytochrome c oxidase or related heme/copper terminal oxidases and appear to be the best molecular electrocatalysts with regard to ORR yet found [35,36].

In this paper, we report the results of the evaluation and characterization of a novel carbon-supported bicore CuFe electrocatalyst. The bulk structural and electronic properties of this material were characterized in the context of its kinetics behavior and overall electrochemical performance toward the ORR in an alkaline electrolyte.

2. Experimental

The CuFe/C catalyst was produced on a commercial scale and provided by Acta S.p.A., Italy. The catalyst was synthesized by adsorption of a mixture of iron and copper phthalocyanine-based complexes onto a carbon black support followed by a heat-treatment at 800–900 °C in an Ar atmosphere. A more detailed synthesis procedure can be found in the relevant patent [37]. The metal content of the CuFe/C composite catalyst was determined by ICP-MS (VG Elemental Plasmaquad-2 (PQ2)) to be 1.5 wt.% for Fe and 1.7 wt.% for Cu. The catalyst surface area was $751\text{ m}^2\text{ g}^{-1}$.

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