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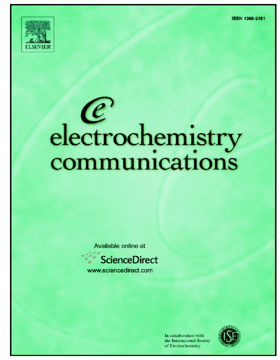

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Step-by-step synthesis of a heteroatom-doped carbon-based electrocatalyst for the oxygen reduction reaction

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Keywords

Co, Zn-ZIF, carbon-based electrocatalyst, oxygen reduction reaction, fuel cells

Abstract

A heteroatom-doped carbon-based electrocatalyst for the oxygen reduction reaction (ORR) was prepared from a hybrid zeolitic imidazolate framework (ZIF) using a step-by-step approach. A bimetallic Co,Zn-ZIF was synthesized by a microwave-assisted method and then enriched with Fe and N. The resulting ZIF was pyrolysed at 700 °C in an inert atmosphere, producing a complex morphology including an amorphous carbon matrix, cobalt nanoparticles and bamboo-like nanotubes. A range of techniques were used to characterize the initial ZIF and the resulting catalyst. The catalytic activity and stability of the carbon-based electrocatalyst towards the ORR were investigated by cyclic voltammetry and chronoamperometry using a rotating disc electrode (RDE) in an acidic medium. The highest electrocatalytic activity for the ORR was reached when an equal weight of commercial carbon black (Vulcan XC-72) was added to the composite. Analysis of Koutecky–Levich plots showed that the reaction followed a four-electron transfer mechanism. A durability test over 1000 cycles showed no signs of decreasing catalytic activity. This catalyst appears to be a promising material for application in fuel cells.

1. Introduction

Advances in clean energy technologies depend on the development of cheap and efficient materials for energy storage and conversion. The growing number of fuel-cell-powered electric vehicles is stimulating improvements in fuel cells aimed at reducing their cost and increasing their lifetime [1]. The function of an air–hydrogen fuel cell is limited by the oxygen reduction reaction (ORR), which relies on the presence of a catalyst [2]. The most efficient platinum-based catalysts are not suitable for large-scale commercial application, primarily due to their high cost, poor durability and limited natural reserves. The development of new ORR electrocatalysts is proceeding along two main pathways: (i) lowering the Pt content by forming core-shell or skeleton structures, Pt–transition metal alloys, etc. [3], or (ii) replacing Pt with other materials [4]. In the latter case, heteroatom-doped carbon materials (HDCM) produced by the pyrolysis of metal-organic frameworks (MOFs) are likely to achieve the desirable activity and stability towards ORR [5,6,7,8].

Efficient Pt-free HDCMs are frequently prepared from zeolitic imidazolate frameworks (ZIFs), resulting in a uniform distribution of heterogeneous atoms in a carbon matrix [9]. The Pt-free HDCMs can be further modified using metal ions and nitrogen atoms to form metal/nitrogen/carbon (M/N/C, M = Fe or Co) catalysts for the ORR, which are stable in alkaline or acid solutions [10,11]. It has also been reported that (Fe,Zn)/N/C and (Fe,Co)/N/C systems have been obtained from monometallic MOFs after doping with iron cations [9,12]. Wang *et al*. [13] reported the preparation of MOF-253 materials enriched with Fe and N using $FeCl_2$ and 1,10-phenanthroline in acetonitrile. The resulting porous carbon-based materials demonstrated excellent ORR activity.