Electrochimica Acta 153 (2015) 433–438

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The Electrochemical Transformation of the Zeolitic Imidazolate Framework ZIF-67 in Aqueous Electrolytes

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ARTICLE INFO

Article history:
Received 27 October 2014
Received in revised form 24 November 2014
Accepted 25 November 2014
Available online 27 November 2014

Keywords:
Metal-Organic Framework
electrochemistry
cobalt oxide
water oxidation
catalysis

ABSTRACT

Metal-Organic Frameworks (MOFs) can serve as precursors to a range of useful materials including porous catalysts and supercapacitors. The electrochemical properties of the ZIF-67 framework were investigated in aqueous electrolytes under neutral and basic pH conditions in the presence of different anions. The redox transformations resulted in both crystalline powders and thin films deposited on the working electrodes. In the latter case, catalytic oxidation of water was observed during the electrochemical measurements due to the formation of Co_3O_4 films. ZIF-67 was found to be susceptible to ligand substitution of 2-methylimidazolate by hydroxide and phosphate anions in the electrolytes.

1. Introduction

Zeolitic Imidazolate Frameworks (ZIFs) may be classified as one subset of a vast array of highly-porous, three-dimensional coordination solids known as Metal-Organic Frameworks (MOFs). These multidimensional materials incorporate metal ions or clusters connected by bridging ligands to yield infinite, highly ordered 2- and 3-dimensional arrays [1]. A plethora of structures can be accessed by varying the nature of the metal ions and the ligands [2]. ZIFs possess zeolite-type topologies and are composed of tetrahedral metal centres (Zn^{2+}, Co^{2+} and Cd^{2+}) connected by imidazolate-based ligands [3]. These frameworks are typically characterised by high internal surface areas [4] and thermal stabilities [5]; as a result, they have been shown to exhibit exceptional gas storage properties [6]. Due to the accessibility of the metal centres to guest molecules within the pores, the catalytic activity of ZIFs such as ZIF-9, $[Co(BIm)_2]$ (BIm = benzimidazolate), for a variety of reactions has received particular attention [7,8].

In recent years, considerable interest has focused on post-synthetic transformations of frameworks to further expand the repertoire of structures, and to modulate the physicochemical properties [9]. These methods include post-synthetic modification (PSM) of the ligand [10] and metal clusters [11], post-synthetic ligand [12] and metal [13] exchange, as well as controlled decomposition of MOF structures [14]. The properties of the resulting materials can be finely tuned by selecting the appropriate MOF and the transformation conditions. A continuing challenge in this regard is gaining an understanding of the underlying mechanisms governing the transformations.

The synthesis of inorganic compounds such as metal oxides and amorphous carbons from metal-organic frameworks has been achieved under thermolysis conditions. The resultant materials have been shown to possess a high electrochemical capacity [15] owing to the porous nature of MOF precursors and their catalytic activity [16]. Unfortunately, this approach often suffers from the very high energy input required for the thermolysis reaction to proceed. Recent work by Marken et al. has demonstrated that the reaction of MOFs in hydroxide solution generates porous metal oxides and hydroxides [17,18]. For example, the framework [Fe(OH)(BDC)·DMF] (BDC = 1,4-benzenedicarboxylate) was converted to hematite (α-Fe_2O_3) upon treatment with aqueous 0.1 M NaOH solution.

The work reported herein investigates the electrochemical properties of a widely studied cobalt-based ZIF, $[Co(2\text{-MeIm})_2]$ or ZIF-67 (where 2-MeIm = 2-methylimidazolate), and the potential exploitation of the catalytic activity of the products formed from its transformation. A particular emphasis of the work is gaining an understanding of the electrochemical behaviour of ZIF-67 in aqueous electrolytes including (a) basic 0.1 M OH^- electrolyte (abbreviated as **OH^-**), and two neutral electrolytes, namely (b) the buffer 0.1 M

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http://dx.doi.org/10.1016/j.electacta.2014.11.150
0013-4686/

SO_4^{2-} + 0.1 M PO_4^{3-} (**SO_4^{2-}/PO_4^{3-}**), and (c) 0.1 M SO_4^{2-} (**SO_4^{2-}**). A range of techniques were employed to characterise the products of the resulting transformations including powder X-ray diffraction (PXRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). These experiments provided an insight into the interaction between ZIF-67 and anions present in electrolyte. The potential catalytic activity of the materials formed from the transformation of ZIF-67 has been probed in view of the propensity for cobalt oxide-based systems to catalyse the water oxidation reaction [19–23].

2. Experimental

2.1. Synthesis

All reagents and solvents were purchased from commercial sources and used without further purification. $Co(NO_3)_2{\cdot}6H_2O$ was obtained from Alfa Aesar, 2-methylimidazole (2-MeIm) from Sigma Aldrich and $CDCl_3$ from Cambridge Isotope Laboratories Inc. ZIF-67 was synthesised using a modification of the procedure reported previously [24]. In a typical synthesis, $Co(NO_3)_2{\cdot}6H_2O$ (3.0 g, 10 mmol) and 2-MeIm (2.0 g, 24 mmol) were each dissolved in 100 mL of MeCN. The solution containing $Co(NO_3)_2 \cdot 6H_2O$ was added dropwise to that of 2-MeIm resulting in the formation of a purple suspension. The mixture was stirred at room temperature for 24 h. A purple powder was isolated by centrifugation and washed with MeCN (3 × 30 mL). Typical yields were in the range from 15 to 25% based on the Co precursor.

2.2. Characterisation techniques

Structural characterisation was carried out using powder X-ray diffraction (PXRD). Data were collected on a PANalytical X'Pert PRO MPD diffractometer with Cu-Kα (1.5406 Å) radiation. The application software was X'Pert Data Collector v2.2f, and the instrument control software was XPERT-PRO v1.9E. PXRD data was collected over the 5–50° 2θ range with a 0.02° step size and 2°/min scan rate. Powders were mounted onto reflective discs with a Si(510) surface which were placed into a Bragg-Brentano reflection transmission spinner attachment. Le Bail refinement of the ZIF-67 powder pattern was performed with the *Rietica for Windows 2.1* software [25]. A histogram profile function with pseudo-Voigt peak shape [26] and Finger, Cox and Jephcoat asymmetry function [27] was used. Raman spectra were collected using an inVia Renishaw Raman Spectrometer with 514 nm laser excitation (Argon ion). The thermogravimetric analysis of samples was carried out on a TA Instruments Hi-Res TGA 2950 Thermogravimetric analyser. Powdered samples were dried in air prior to mounting on the instrument balance. The sample was maintained under a dry N_2 atmosphere during data collection. ^{1}H NMR spectra were collected using Bruker Avance III 200 spectrometers. Vis-NIR diffuse reflectance spectroscopy was used to analyse powdered samples. Spectra were collected on a CARY 5E UV-Vis-NIR spectrophotometer with a Harrick Omni Diff Probe attachment using Varian WinUV software. The data was recorded from 5000 to 25000 cm^{-1} with a scan rate of 6000 cm^{-1}/min. Samples were supported on a high density filter paper which was also used to provide the background reference. Samples were sent to the Chemical Microanalysis Facility at the Department of Chemistry & Biomolecular Sciences, Macquarie University for CHN analyses. XPS spectroscopy of powdered materials was measured at the Mark Wainwright Analytical Centre, University of New South Wales.

2.3. Electrochemistry

Cyclic voltammograms were measured using a BASi Epsilon Electrochemical Analyser. Powdered samples were mechanically immobilised onto a glassy carbon disk working electrode (Ø1 mm, BASi) by pressing the electrode against the powder to form a mechanically immobilised layer on its surface. All the electrochemical measurements for the deposited thin films were measured using a VMP2 Princeton Applied Research multi-channel potentiostat, with a Ni mesh working electrode. All the data is reported versus Ag/AgCl which was used as a single junction reference electrode, while a high surface area coiled platinum wire was used as a counter electrode which was separated by a glass frit. The measurements were performed in three aqueous electrolytes prepared from deionised water: (a) 0.1 M NaOH (pH = 12.9), denoted **OH^-**, (b) 0.1 M Na_2SO_4 + 0.0615 M Na_2HPO_4 + 0.0385 M NaH_2PO_4 (0.1 M PO_4^{3-}) (pH = 6.86), denoted **SO_4^{2-}/PO_4^{3-}**, and (c) 0.1 M Na_2SO_4 (pH = 6.35), denoted **SO_4^{2-}**.

3. Results and discussion

3.1. Electrochemistry of ZIF-67

Solid state cyclic voltammetry (CV) on ZIF-67 (Fig. 1(i)) revealed that the material undergoes an oxidation process in the region between 0.60 and 0.70 V in **OH^-** and **SO_4^{2-}** electrolytes. This process was shifted anodically to 0.90 V in the presence of the phosphate buffer. A second oxidation process was observed in the region 1.0–1.2 V and was accompanied by an increase in current, which was most pronounced in **OH^-** electrolyte. This redox behaviour was attributed to the oxidation of the Co^{II} centres in ZIF-67 to Co^{III}, which is accompanied by a significant chemical transformation of the framework as suggested by the absence of redox waves on the reverse scan. The observed current increase which accompanies the second process is attributed to the electrocatalytic activity of the generated Co^{III} species (*vide infra*).

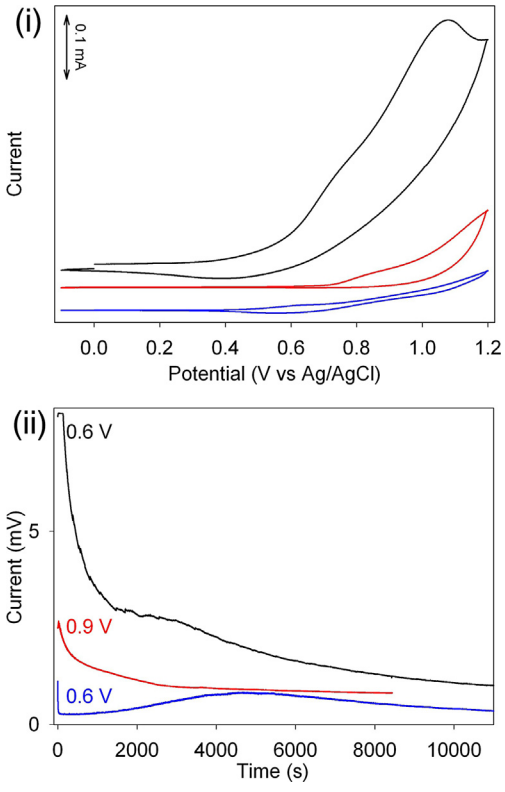

Fig. 1. i) Cyclic voltammograms (CVs) of ZIF-67 at 100 mV/s; ii) controlled potential electrolysis of ZIF-67 at the specified potentials. The electrochemical measurements were performed in **OH^-** (black), **SO_4^{2-}/PO_4^{3-}** (red) and **SO_4^{2-}** (blue) aqueous electrolytes.