



Design of a non-precious metal electrocatalyst for alkaline electrolyte oxygen reduction by using soybean biomass as the nitrogen source of electrocatalytically active center structures



Chao-Zhong Guo ^{a, b, *}, Wen-Li Liao ^c, Chang-Guo Chen ^{d, *}

^a Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Yongchuan 402160, China

^b Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Yongchuan 402160, China

^c College of Materials and Chemical Engineering, Chongqing University of Arts and Sciences, Chongqing 402160, China

^d College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

H I G H L I G H T S

- An ORR electrocatalyst was prepared by using soybean biomass as the nitrogen source of active centers.
- The nitrogen in electrocatalysts is mainly the form of pyridinic and pyrrolic N species.
- The metallic Fe can facilitate the transformation of quaternary N to planar N during pyrolysis.
- The metallic Fe facilitates the joint incorporation of planar pyridinic and pyrrolic N into the carbon matrix.
- The content of planar N species plays an important role in improvement of the ORR activity in alkaline electrolyte.

A R T I C L E I N F O

Article history:

Received 23 January 2014

Received in revised form

14 June 2014

Accepted 3 July 2014

Available online 11 July 2014

Keywords:

Oxygen reduction

Electrocatalyst

Soybean

Active site

Nitrogen source

A B S T R A C T

The development of less expensive, more active, and more stable catalyst substitute for Pt/C catalysts for oxygen reduction has recently become a hot topic. In this paper, we report a new strategy to design nitrogen-doped non-precious metal catalysts via the copyrolysis of metallic iron, soybean biomass, and carbon support at high temperatures. The results show that the nitrogen in electrocatalysts is mainly in the form of pyridinic and pyrrolic N species. The metallic Fe in the precursor can facilitate the transformation of quaternary N with a three-dimensional structure to planar pyridinic and pyrrolic N inside carbon matrix during pyrolysis, thereby improving the electrocatalytic activity of the prepared catalysts. We suggest that the planar N species may be the catalytically active center structures and may contribute to the enhancement of oxygen reduction reaction performance in an alkaline electrolyte. The prepared catalyst has superior tolerance against methanol crossover effect and outstanding stability compared with commercial Pt/C catalysts.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cell-based systems show great potential as alternative power sources for a wide range of applications because of their high efficiency, high energy density, and low emissions [1]. Direct methanol alkaline fuel cells (DMAFCs) have advantages over polymer electrolyte membrane fuel cells because of the former's less

corrosive environment and more facile kinetics for the electro-reduction of oxygen molecules. However, a serious CO₂ poisoning problem precludes the development of alkaline fuel cells (AFCs) usually when a liquid electrolyte such as potassium hydroxide (KOH) aqueous solution is used. The development of alkaline solid polymer membranes instead of an alkaline solution can potentially simplify the AFCs and greatly reduce the carbonation problem [2,3]. In addition, the oxygen reduction reaction (ORR) on the cathode of AFCs has a pivotal function in controlling their performance because of the kinetic sluggishness of ORR in a complex four-electron transfer process [4]. Pt-based catalysts for ORR such as Pt/Au composites were developed for the Apollo lunar mission as early as the 1960s, but their large-scale commercial applications

* Corresponding authors. Research Institute for New Material Technology, Chongqing University of Arts and Sciences, Yongchuan 402160, China. Tel./fax: +86 023 65111357.

E-mail addresses: guochaozhong1987@163.com (C.-Z. Guo), cgchen@cqu.edu.cn (C.-G. Chen).

have been hindered by high costs and scarcity of platinum [5]. Moreover, Pt-based catalysts are susceptible to time-dependent drift, and the high methanol crossover causes mixed potential in the cathode of fuel cells. Thus, many research efforts in the development of cathode catalysts have been focused mainly on decreasing Pt content or replacing Pt with less expensive materials [4,6].

Non-precious metal catalysts (NPMCs), especially pyrolyzed TM/N/C (TM = Fe, Co, Cu, etc.) systems, have been extensively studied as a low-cost catalyst alternative to Pt for ORR in acid or alkaline electrolytes in the past five decades [6–22]. However, none of these studies showed the necessary combination of activity and stability that could replace Pt-based catalysts in acidic fuel cells [13]. On the contrary, ORR kinetics are often more facile, and materials are more stable at alkaline environments [14]. For example, Meng et al. found that Fe/N/C catalysts exhibit enhanced activity and stability at alkaline conditions (pH = 13) compared at acidic conditions (pH = 1) [15]. Xi et al. similarly confirmed that Fe/N/C catalysts from the pyrolysis of hemin/C composites show superior ORR catalytic activity and stability in alkaline electrolyte than in acidic electrolyte [16]. These findings have significantly encouraged researchers to explore various materials that function as TM/N/C catalysts for ORR in alkaline media. Furthermore, selecting nitrogen sources to produce ORR active center structures has become a topic of interest because the nitrogen source is indispensable for TM/N/C catalyst synthesis, and an increase in the amount of nitrogen can effectively influence the amount of active sites [17]. Several nitrogen-containing precursors used in previous studies include purine and pyrimidine [10], polyaniline [18], phthalocyanine [19], amino acid [20], polypyrrole [21], and porphyrin [22]. TM/N/C catalysts with these nitrogen-rich molecules as nitrogen sources have reasonable ORR electrocatalytic activity, but their preparations are commonly carried out with complex procedures or expensive hardware. Exploring a facile method to prepare highly active and stable ORR catalysts remains a challenge.

We recently formed NPMCs for ORR at alkaline conditions by carbonizing blood proteins from animals [23–25]. Blood proteins are notably more inexpensive and abundant as opposed to Pt. Subsequently, we also developed another method for the formation of Fe/N/C catalysts from the precursors of transition metals, carbon black, and egg-white protein [26]. However, no systematic study on the carbonization behavior and functionalization of various bio-proteins has been conducted until now.

Soybeans are one of the most important crops grown in the United States [27]. They are abundantly and cheaply obtained; more than 250 million tons of soybeans are produced every year around the world, and they are sold for only ~550 U.S. dollars per ton. The content of soy proteins in soybean is commonly between 38% and 42%. In this study, we developed a novel method to prepare an inexpensive and active Fe/N/C catalyst (Fe/C–SOYB) by using nitrogen-rich soybean biomass as the specific nitrogen source for the active center structures. Fe/C–SOYB was carefully analyzed, and its ORR catalytic activity was evaluated in detail. Our results indicate that Fe/C–SOYB with high percentages of pyridinic and pyrrolic N substantially enhances the ORR electrocatalytic performance, thereby suggesting that this catalyst has a key function in the electrocatalysis of ORR at alkaline conditions.

2. Experimental

2.1. Materials and chemicals

Soybean (SOYB) was supplied by the Food Testing Center of Chongqing Bureau of Quality and Technology Supervision, China. Vulcan XC-72R commercial carbon black (V-CB, $\Phi = 30$ nm) was

purchased from Cabot® and pretreated in 4.5 mol l⁻¹ HNO₃ solution at 80 °C for 12 h. The commercial Pt/C (20 wt.% Pt) catalyst was obtained from De Nora Elettrodi Co. Ltd., China. All other chemicals were of analytical grade and were obtained from Chongqing Chemical Reagent Co., China.

2.2. Catalyst preparation

First, 0.25 g of pretreated V-CB particles was dispersed well in FeCl₃ solution (5.0 wt.% Fe), and the suspension was then magnetically stirred for 2 h and evaporated to about three-fourths of the liquid volume on a heating plate. Subsequently, it was completely dried overnight in an oven at 100 °C. The obtained mixture was heat-treated in a tube furnace at 900 °C for 1 h in N₂ atmosphere to produce the Fe/C sample. SOYB was ball-milled with the yielded Fe/C particles (mass ratio of 2:1) for 0.5 h. The produced precursor was further treated in flowing N₂ at 900 °C for 2 h. The yielded sample is hereafter called Fe/C–SOYB.

To remove excess metal elements deposited on the support, Fe/C–SOYB was chemically treated with 0.5 mol l⁻¹ H₂SO₄ solution at 90 °C for 12 h. The sample obtained after acid-leaching is hereafter named Fe/C–SOYB-A. For the control sample, V-CB particles were first heat-treated at 900 °C for 1 h in N₂ atmosphere and then ball-milled with SOYB to form a precursor that does not contain transition metals. This precursor was further heat-treated at 900 °C for 2 h to obtain the C–SOYB sample.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out using an X-ray diffractometer by Shimadzu XRD-6000 (Japan) with Cu K α 1 radiation ($\lambda = 1.54178$ Å) at 4° min⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Scientific ESCALAB 220 iXL spectrometer with an Al K α ($h\nu = 1486.69$ eV) X-ray source. The total nitrogen content was determined using a Vario EL CUBE elemental analysis system (Germany). The morphology of the prepared samples was characterized via high-resolution scanning electron microscopy (SEM) (Ultra 55, Germany). Inductively coupled plasma-mass spectroscopy (ICP-MS) with an SCIEX ELAN DRCE ICP-MS system (PerkinElmer) was used to analyze the bulk composition of the prepared catalysts.

2.4. Electrochemical measurements

All electrochemical experiments were conducted using a CHI 600A electrochemical workstation (CH instruments, USA) at room temperature. A Pt wire and a Hg/HgO/1 mol l⁻¹ KOH were used as the counter and reference electrodes, respectively. A rotation disk electrode (RDE) with a glass carbon (GC) electrode (5 mm in diameter, LKXZ-1, Tianjing Lanlike Electrochemical Instruments, China) was used as the working electrode. The modified-GC working electrode was fabricated by coating it with catalyst ink. Typically, 10 μ l of catalyst ink that is well dispersed in 0.5 wt.% Nafion/isopropanol solution was dropped onto the GC disk surface and then dried at room temperature. About 100 μ g of the catalysts, except Pt/C (29 μ g), was loaded on the disk electrode. All the electrode potentials in this work are quoted versus a reversible hydrogen electrode (RHE).

All ORR activity measurements and methanol-tolerance tests were performed over a potential range of 1.15 V–0.15 V at a scan rate of 5 mV s⁻¹ in O₂- or N₂-saturated 0.1 mol l⁻¹ KOH solution via cyclic voltammetry (CV) or linear sweep voltammetry. The onset potentials (the potential at which a current density of –100 μ A cm⁻² is recorded) were taken from the ORR polarization curves. The stabilities of Fe/C–SOYB and 20% commercial Pt/C were

Download English Version:

<https://daneshyari.com/en/article/7735956>

Download Persian Version:

<https://daneshyari.com/article/7735956>

[Daneshyari.com](https://daneshyari.com)