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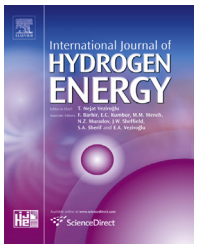

High-performance doped carbon electrocatalyst derived from soybean biomass and promoted by zinc chloride

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ABSTRACT

A high-performance doped carbon catalyst with a BET surface area of up to 949 $m^2\ g^{-1}$ has been prepared by pyrolyzing soybean biomass with $ZnCl_2$ as an activator, followed by acid leaching with H_2SO_4 and graphitization. For the cathodic reduction of oxygen, the catalyst exhibits excellent activity in an alkaline medium. Its onset potential and half-wave potential for the oxygen reduction reaction reach −0.02 V and −0.12 V (vs. Ag/AgCl) in 0.1 M KOH, almost comparable to those of commercial 20 wt% Pt/C catalyst. It is found that the addition of zinc chloride can significantly enhance the catalyst's surface area and activity. We suggest that the high performance of this type of catalyst is mainly contributed from its high active center density resulted from the high surface area of the catalyst, which is caused by the activation of zinc chloride.

Introduction

The oxygen reduction reaction (ORR) on the cathode of proton exchange membrane fuel cells (PEMFCs) is a key issue in the large-scale commercialization of these types of fuel cells, because a much more Pt catalyst is required for the cathodic ORR process than for the faster hydrogen oxidation reaction at the anode. Pt and its alloys remain the most efficient ORR catalysts, but the scarcity and consequent high cost of Pt hamper the further development of fuel cell technologies based on these materials [1,2]. Thus, developing inexpensive non-Pt cathodic catalysts with both high performance and durability is regarded as a feasible way to reduce the cost of PEMFCs.

Nitrogen-doped carbon has been recognized as a promising type of cathode catalyst for PEMFCs since Gong et al. [3] reported the high ORR activity of nitrogen-doped carbon nanotubes in 2009. Investigating doped carbon catalysts for the ORR is now becoming one of the hottest topics in the fuel cell

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field. Many types of doped carbon catalysts have been developed and reported, some of which exhibited good ORR performance in both alkaline and acid media [4–17]. However, up to now, only one literature for the doped carbon catalyst derived from biomass can be searched, Wang et al. reported a doped carbon catalyst, synthesized by pyrolyzing the hybrid of ferric chloride and egg white, and this catalyst demonstrated certain oxygen reduction reaction (ORR) activity [18]. No literature regarding the preparation of doped carbon catalyst from botanic biomass for the application of ORR catalyst of fuel cells can be searched.

Generally, biomass materials offer a wide range of variety and structural diversity. In addition, some types are rich in nonmetal elements (e.g., sulfur, nitrogen, and phosphorus) and metal elements (e.g., Fe, Co). All of these nonmetal and metal elements have been reported to be beneficial in the formation of ORR active centers and could therefore significantly promote the performance of doped carbon catalysts [3–6,19–21]. It is therefore reasonable to believe that a class of high-performance doped carbon catalysts could be prepared using some types of biomass materials as precursors.

Based on the above recognition, we chose soybean, a biomass material rich in N, S, P, and a small amount of Fe, as the precursor for our attempts to prepare a novel type of doped carbon catalyst through pyrolysis. As expected, the catalyst exhibited activity towards the ORR. We also attempted to enhance the performance by adding $ZnCl_2$ to the precursor as an activator and achieved an amazing improvement. The enhanced soybean biomass-derived catalyst exhibited excellent ORR performance in an alkaline medium, comparable to that of commercial (Johnson Matthey) Pt/C catalysts.

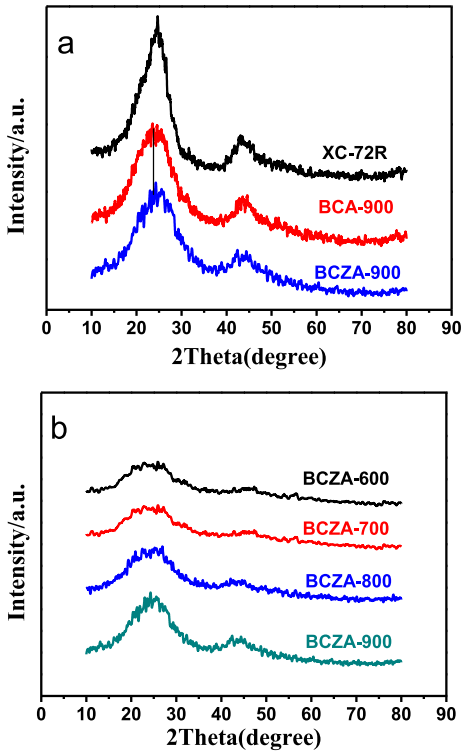

Fig. 1 – XRD patterns of (a) samples BCA-900 and BCZA-900-1/2, compared with XC-72R, and (b) BCZA samples pyrolyzed at various temperatures (soybean/$ZnCl_2$ = 1/2).

Experimental

Catalyst preparation

The doped carbon catalysts were prepared as follows. Firstly, the soybeans (purchased from a local supermarket) were washed, dried, and ground into a fine powder. Next, the powder was impregnated with $ZnCl_2$ solution, followed by vacuum drying at 70 °C, yielding a $ZnCl_2$ loading of ca. 30 wt%. Then the impregnated powder was put in a tubular furnace at 900 °C with Ar flow for pyrolysis. Finally, the sample was further leached with 0.5 M H_2SO_4 at 80 °C for 12 h, followed by calcining at 900 °C for further graphitization. We denoted the catalysts prepared by the above procedures as BCZA-900-*m*/*n*, where 900 indicates the pyrolysis temperature and *m*/*n* indicates the mass ratio of soybean to $ZnCl_2$.

We also prepared other samples for comparison and denoted them thus: the sample derived from just biomass soybean powder is BC, while the samples derived from soybean and with $ZnCl_2$ as the activator are BCZ; suffixes are used to indicate the pyrolysis temperature and the mass ratio of soybean to $ZnCl_2$.

Physical characterization

XRD measurement was conducted on a TD-3500 powder diffract meter (Tongda, China) operated at 30 kV and 20 mA, using Cu-Kα radiation sources. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD X-ray photoelectron spectrometer (Kratos, England) employing a monochromated Al-Kα X-ray source ($h\nu$ = 1486.6 eV). SEM images were recorded on a JSM-6380LA microscope (JEOL, Japan) operated at 20 kV. BET surface areas and pore sizes were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption on a Tristar II 3020 gas adsorption analyzer (Micromeritics, USA), with samples previously evacuated at 120 °C for 12 h. Elemental analysis was performed on a Vario Micro set-up (Elementar Analysensysteme GmbH, Germany) to determine the sulfur, carbon, nitrogen, and hydrogen contents of the samples. EPMA-1720 (Shimadzu, Japan) and ICP-AES (Leema PROFILE, America) was used to analyze the contents of trace metal elements.

Electrochemical measurements

Electrochemical evaluation was carried out at room temperature on an electrochemical workstation (Ivium, Netherlands) in a three-electrode configuration, filled with oxygen-saturated 0.1 M KOH solution and scanning from 0.2 to −0.8 V at a scan rate of 10 mV s^{-1}. A rotating disk electrode with a glassy carbon disk was used as the working electrode. The counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl (3 M KCl) electrode. The catalyst ink was prepared by ultrasonically dispersing 5 mg catalyst powder in 1 mL Nafion/ethanol (0.25 wt% Nafion) for 0.5 h; 20 μL of this