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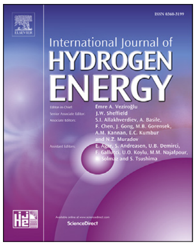

Pt–Co@NCNTs cathode catalyst using ZIF-67 for proton exchange membrane fuel cell

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ARTICLE INFO

Article history:
Received 6 January 2017
Received in revised form
5 June 2017
Accepted 9 June 2017
Available online xxx

Note: Presented at the International Symposium on Sustainable Hydrogen, Algiers, Algeria held during October 05–06, 2016.

Keywords:
ZIF-67
Nitrogen doped carbon nanotube
ORR electrocatalyst
Membrane-electrodes assembly
PEM fuel cell

ABSTRACT

Zeolitic Imidazolate Frameworks (ZIF) is one of the potential candidates as highly conducting networks with large surface area with a possibility to be used as catalyst support for low temperature fuel cells. In the present study, highly active state-of-the-art Pt–Co@NCNTs (Nitrogen Doped Carbon Nanotube) catalyst was synthesized by pyrolyzing ZIF-67 along with Pt precursor under flowing Ar–H_2 atmosphere. The multi-walled NCNTs were densely grown on the surface of ZIF particles after pyrolysis. The high resolution TEM examination was employed to examine the nature of the Pt–Co particles as well as multi-walled NCNTs. Rotating disk electrode study was used for measuring oxygen reduction reaction performance for Pt–Co@NCNTs in 0.1 M $HClO_4$ and compared with commercial Pt/C catalyst. Fuel cell performance with Pt–Co@NCNT and commercial Pt/C catalysts was evaluated at 70 °C using Nafion-212 electrolyte using H_2 and O_2 gases (100% RH) and the observed peak power density of 630 and 560 mW cm^{-2}, respectively.

Introduction

Proton exchange membrane fuel cell (PEMFC) is the most promising energy conversion technology for stationary as well as automotive applications due to its advantages such as lower operating temperature and higher power density as compared to other types of fuel cells. However, for large-scale commercialization of PEMFCs, it should overcome several challenges including reducing the cost, maximizing the utilization of platinum catalyst as well as improving the performance and durability of the membrane electrode assembly. Oxygen reduction reaction (ORR) is the most critical one due to the potentially lower exchange current density value in the

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http://dx.doi.org/10.1016/j.ijhydene.2017.06.084

Please cite this article in press as: Shi X, et al., Pt–Co@NCNTs cathode catalyst using ZIF-67 for proton exchange membrane fuel cell, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.06.084

PEMFC [1–3]. In order to improve the ORR kinetics, noble metals based alloys with Fe, Co or Ni have been reported in the literature [4–7]. In particular, Pt–Co alloy was reported to show minimum CO poisoning (weakest interaction with CO), which is beneficial for PEMFC application with reformed fuel [8]. In this context, it is important to develop highly efficient and durable electrocatalysts for ORR [9]. Recently, metal-organic frameworks (MOFs) have emerged as a novel class of porous crystalline materials both as template and precursor to produce nanoporous carbons for gas storage [10], catalyst support [11], and electrode materials for lithium batteries [12], sensors [13] and supercapacitors [14]. Zeolitic imidazolate frameworks (ZIFs), a sub-class of the MOFs are excellent materials for the synthesis of nanocarbon electrocatalysts with abundant carbon and nitrogen [15,16]. MOF-derived nanocomposites reported as poor ion and electron transport materials due to poor graphitic degree and microporous structures [17–21]. Xiao and coworkers have synthesized nitrogen doped carbon nanotubes (NCNTs) using ion exchange resin sphere under N_2 atmosphere at relatively lower temperature [22]. The use of ZIFs as a precursor for the synthesis of Pt nano-particle on the *N*-doped carbon nano-structures has rarely been reported as ORR electrocatalyst [23–25].

In the present study, Pt–Co@NCNTs nanocatalyst was synthesized and characterized by using X-ray diffraction, field emission scanning electron microscope and transmission electron microscope to ascertain the composition and nature of the catalyst particle morphology and distribution. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments were conducted in 0.1 M $HClO_4$ using rotating disk electrodes (RDE) with the Pt–Co@NCNTs thin films towards ORR performance and durability, respectively. Membrane electrode assembly (MEA) fabricated with Pt–Co@NCNTs cathode nanoelectrocatalyst (Pt loading of 0.12 mg cm^2) showed a peak power density of ~ 630 mW cm^{-2} at 70 °C with H_2 and O_2 gases at 100% RH under ambient operating pressure.

Experimental

Synthesis of ZIF-67 particles

ZIF-67 samples were synthesized as described in the published literature [3]. In a typical synthesis, 1.97 g of 2-methylimidazole (2-MIM) was dissolved in a mixed solution of 20 ml of methanol and 20 ml of ethanol. 1.746 g of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in another mixed solution of 20 ml of methanol and 20 ml of ethanol. The above two solutions were then mixed under continuous stirring for few minutes and held for 20 h at room temperature. The purple precipitate was collected by centrifuging the solution, washed in ethanol several times and dried at 80 °C overnight. The flowchart in Fig. 1 provides the process steps sequentially.

Synthesis of Pt–Co@NCNTs

The ZIF-67 particles were mixed thoroughly in $H_2PtCl_6 \cdot 6H_2O$ solution (5 wt % in DI water) and the resultant slurry was dried at 80 °C for about 2 h. The dried powder was heated at 350 °C for 1.5 h then raised to 700 °C at a ramp rate of 2 °C per minute and pyrolyzed for 3.5 h under flowing Ar–H_2 (90:10% volume ratio) atmosphere (see Fig. 1). After the as-prepared black powder product was cooled down to room temperature naturally, it was treated in 0.5 M H_2SO_4 solution for 6 h. The resultant catalyst product was collected by centrifugation, repeatedly washed with DI water and then dried at 80 °C under vacuum for about 2 h. The Pt loading on the NCNTs is 10 wt % based on the initial composition. Co@NCNTs was also synthesized by following the same process conditions without the Pt precursor for comparison purposes.

Catalyst characterization

The morphology and structure of the ZIF-67 and Pt–Co@NCNTs were characterized by Field Emission Scanning Electron Microscopy (HITACHI S-4700 FESEM) and Transmission Electron Microscopy (TEM, Philips CM200, 200 kV). Powder X-ray diffraction (XRD) were recorded using SIEMENS D5000 X-ray Diffractometer with Cu Kα radiation (Cu Kα, $\lambda = 0.154$ nm, 40 kV and 30 mA).

Thin film rotating disk electrode and electrochemical evaluation

Catalyst ink was prepared by dispersing 7.6 mg of Pt–Co@NCNTs (10 wt %) or Co@NCNTs or commercial Pt/C (46.8 wt %; Tanaka TKK, Japan) in 7.6 ml of DI water (Resistivity 18.2 MΩ cm), 2.4 ml of isopropyl alcohol and 40 μl of 5 wt % Nafion dispersion (LQ-1005-1000, Ion Power Inc.) and sonicated in cold-water bath for 20 min [26]. Thin catalyst film was deposited by dropping a required volume of the catalyst ink onto the polished glassy carbon disk (4 mm diameter, AFE3T040GC, Pine Instruments) to obtain Pt loading of 45 and 15 μg cm^{-2} in commercial Pt/C and Pt–Co@NCNTs nanocatalysts, respectively. For comparison purpose, a thin film electrode with non-platinized Co@NCNTs (~290 μg cm^{-2}) was also prepared. Uniform and well-adhered catalyst films were obtained by rotational air drying at room temperature for 15 min, for all the three different catalysts [26].

RDE experiments were carried out in 0.1 M $HClO_4$ (Sigma-Aldrich) with N_2 as well as O_2 saturation [27]. LSV experiments were conducted in the potential range of 0.7 to −0.3 V vs SCE (1 to 0 V vs RHE) at 20 mV s^{-1} rate with Pt coil as counter electrode and SCE as reference electrode using a PAR Bistat at various rpm, at room temperature. In order to evaluate the performance stability/durability of the catalyst films, CV was conducted for the disk electrodes between 1 and 0.6 V vs RHE with a sweep rate of 50 mV s^{-1} at 400 rpm for 50 cycles in 0.1 M O_2 saturated $HClO_4$ solution [26].

Electrode fabrication and fuel cell performance evaluation

Catalyst coated membranes

For PEMFC single cell tests, MEAs with an active area of 5.0 cm^2 were fabricated as described below. Commercial Pt/C (Tanaka TKK, Japan) and the Pt–Co@NCNTs were used as anode and cathode catalysts, respectively. The cathode catalyst ink was prepared by mixing 200 mg Pt–Co@NCNTs or commercial Pt/C nanocatalysts in 2.6 ml of 5 wt % Nafion dispersion (LQ-1005-

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