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ScienceDirect

Ceramics International 41 (2015) 2271–2278

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Co/CeO$_2$-decorated carbon nanofibers as effective non-precious electro-catalyst for fuel cells application in alkaline medium

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Received 10 September 2014; received in revised form 24 September 2014; accepted 4 October 2014
Available online 6 November 2014

Abstract

In this study, Co/CeO$_2$ decorated carbon nanofibers are introduced as effective electro-catalyst for methanol oxidation. Poly(vinyl alcohol) was used as carbon source due to its high carbon content characteristic as compared to many others polymer precursors for CNFs synthesis. Preparation of the introduced nanofibers could be achieved by calcination of electrospun nanofibers composed of cerium (III) acetate hydrate, cobalt (II) acetate tetra hydrate and poly(vinyl alcohol) in nitrogen environment at 700 °C. The produced sintered powder was characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), field-emission scanning electron microscopy (FESEM) equipped with rapid EDX (energy dispersive analysis of X-ray). The invoked characterization techniques indicated that the obtained material is carbon nanofibers decorated by Co/CeO$_2$ nanoparticles. Investigation of the electrocatalytic activity of the introduced decorated nanofibers toward methanol oxidation indicated good performance as the corresponding current density increased with increasing methanol content in the alkaline medium. Interestingly, the introduced catalyst revealed negative onset potential (-50 mV vs. Ag/AgCl) which is a superior value among the reported non-precious electrocatalyst. Moreover, methanol oxidation takes place at relatively low applied voltage (180 mV vs. Ag/AgCl) which adds additional advantage for the introduced material. Overall, the introduced study opens new avenue for cheap and effective transition and rare earth family-based nanomaterials as non-precious catalyst for fuel cell application.

Keywords: E. Fuel cells; Non-precious catalyst; Electrospinning; decorated carbon nanofibers; Methanol electro-oxidation

1. Introduction

Because of the serious environmental condition, global warming and the possible exhaustion of the fossil fuels within decades, it will be indispensable to find ways of energy production that drop the atmospheric pollution caused by fossil fuels to a low level and yet license the economic growth of a country and a good class of life for its population. Among possible alternative sources of energy, fuel cell is a worthy technological option for resolving energy and pollution problems. Fuel cells comprise the direct conversion of chemical energy into electrical energy with minimum power losses and without intermediate steps that are required in similar diesel-powered generators by electrochemical oxidation. The first fuel cell was developed by Sir William Robert Grove in 1839 and was based on the electrochemical conversions of hydrogen and oxygen [1].

Direct methanol fuel cell (DMFC) is a significant power foundation due to its high-energy conversion efficiency, low operating temperatures and ease of handling a liquid fuel [2,3]. The use of methanol as a fuel is popular because it is a liquid which can be easily stockpiled and handled. Methanol is also easier to be supplied to the community using our existing infrastructure. In the DMFCs, methanol is directly oxidized

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http://dx.doi.org/10.1016/j.ceramint.2014.10.031
0272-8842/

to carbon dioxide and water, providing a new way to store and convey the energy [4]. The fruitful commercialization is fairly dependent on the cost, activity, and durability of the electrocatalysts [5]. Almost all pre-commercial low temperature fuel cells are worked on Pt-based electrocatalyst [6,7]. However, the high price and the imperfect presence of Pt stop it from further commercialization [8]. Additionally the developed cost is comparatively high which constrains wide applications; moreover it is well known that Pt surface can be easily adulterated by CO or HCO species which is considered as another real problem faced by most of the Pt based electrocatalyst leading to the rapid loss of catalytic activity due to intermediate product which blocks the active sites of Pt [9,10].

Nowadays, many different metal mixed oxides such as CeO_2, NiO, MoO_x, TiO_2, V_2O_5, and La_2O_3 have been employed to increase the electrocatalytic activity for methanol oxidation [11–16]; particularly, CeO_2 has received considerable attention due to its remarkable properties in improving the catalytic action and the CO patience of Pt/CeO_2 particles. Moreover, ceria (CeO_2) owns a structure-sensitive formation of oxygen vacancy (O-vacancy) on surface [17–19]. The O-vacancy helps ceria gain remarkable capabilities to catalyze CO oxidation [21,22] and to assist the adsorption of oxygenated species, such –OH [18,20].

According to definition of IUPAC, rare earth elements contain a set of 17 chemical elements in the periodic table, definitely the 15 lanthanides along with scandium and yttrium. Among the rare earth family, cerium (Ce) is the most abundant element. Cerium is more rich in the Earth's crust (66.5 ppm) than that of copper (60 ppm) or tin (2.3 ppm) [21,22]. With a high abundance, cerium oxide (CeO_2) is a technologically important material due to its wide applications as a promoter in three-way catalysts (TWCs) for the elimination of toxic auto-exhaust gases [23,24], oxygen sensors [25,26], oxygen permeation membrane systems [27,28], low-temperature water-gas shift (WGS) reaction [29,30], glass-polishing materials [31,32], electro chromic thin-film application [33–35] and fuel cells [36–39]. Although, many researchers ignored cobalt to be utilized as the main electrocatalyst in the fuel cell applications, recent reports have proved that this metal does have good electrocatalytic performance if it could be activated by a proper co-catalyst [40].

Nanofibrous morphology has gained much importance in the recent years due to the intensified awareness of the prospective applications in many fields including defense, engineering, medicine, chemical synthesis, and textile. Electrospinning is the extensively used technique for nanofibers fabrication because of their effortlessness, high yield, effectiveness and low-cost aspects [41–44]. It is notable revealing that nanofibrous catalysts have a discrete plus point especially when consumed in the electron transfer-based processes due to their large axial ratio as compared to nanoparticles [45,46]. Currently, carbon nanofibers (CNFs) are widely used in many fields such as lithium-ion rechargeable batteries (LIBs), hydrogen energy, electrochemical capacitors (EDLCs) and fuel cells [47–51].

Agglomeration tendency is the main dilemma faced while utilizing the nanoparticulate catalysts. Therefore, the combination of CeO_2 and Co nanoparticles decorating carbon nanofibers could smash the agglomeration, enhance the surface area of the active materials and develop active support; consequently the final product will possess interesting performance for electro-oxidation of methanol.

The core goal of this study is to present a new non-precious catalyst with good electrocatalytic activity. In this study, Co/CeO_2-decorated carbon nanofibers are introduced as a novel non-precious catalyst for methanol electrooxidation. The introduced nanofibers have been synthesized by calcination of electrospun nanofibers composed of cobalt acetate, cerium acetate, and poly(vinyl alcohol) (PVA) in nitrogen atmosphere at 700 °C. The obtained nanofibers revealed good performance as electro-catalyst for methanol oxidation.

2. Experimental

2.1. Procedure

2.1.1. Materials

Cerium (III) acetate hydrate (CeAc, 99.9%) and cobalt (II) acetate tetra hydrate (CoAc, 98%) were bought from Sigma-Aldrich Corporation, St. Louis, MO, USA and Junsei chemicals Corporation Ltd. Japan, respectively. Poly(Vinyl alcohol) (PVA) with a molecular weight of 65,000 g/mol was obtained from Sigma-Aldrich Corporation, St. Louis, MO, USA, distilled water was used as a solvent.

2.1.2. Preparation of Co/CeO_2CNFs

CoAc and CeAc aqueous solutions were firstly prepared by dissolving 0.9 g of CoAc and 0.1 g CeAc in 3 ml of distilled water with 5 h stirring at room temperature and then mixed with 15 g PVA aqueous solution (10 wt%). Finally the mixture was stirred at 50 °C for 6 h to get a see-through, clear and consistent mixture. The achieved sol–gel was electrospun at high voltage of 22 kV using DC power supply at room temperature with 65% relative humidity. The distance between needle tip (positive electrode) and rotating cylinder (negative electrode) was kept constant at 22 cm. The ready nanofibers (NFs) mats were normally dried at room temperature for 12 h and then under vacuum for 24 h at 70 °C and lastly calcined at 700 °C for 6 h in nitrogen atmosphere with a heating rate of 2.0 °C/min.

2.2. Electrode preparation and electrochemical measurement

2.2.1. Preparation of working electrode

Preparation of the working electrode was carried out by mixing 2 mg of the electro-catalyst, 20 μL of Nafion solution (5 wt%) and 400 μL of isopropanol. The slurry was sonicated for 30 min at room temperature. The ultrasonically dispersed nanocatalyst (15 μL) was spread by micro-pipette on to the active area of the glassy carbon electrode which was then subjected to drying process at 80 °C for 20 min. The glassy carbon working electrode with 3 mm of diameter and $0.0706\ cm^2$ of apparent electrode area was polished with diamond suspension to a mirror finish before being used.