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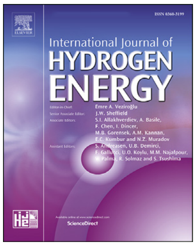

Synthesis and electrochemical analysis of novel IrO_2 nanoparticle catalysts supported on carbon nanotube for oxygen evolution reaction

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ARTICLE INFO

Article history:
Received 24 April 2018
Received in revised form
23 June 2018
Accepted 7 August 2018
Available online xxx

Keywords:
Water electrolysis
Oxygen evolution reaction
Iridium oxide
Carbon nanotube

ABSTRACT

In this paper, we report synthesis of novel nanoparticle catalyst of iridium oxide supported on carbon nanotube (IrO_2/CNT) and characterization of activity and durability for oxygen evolution reaction (OER). The IrO_2/CNT catalyst was prepared from iridium complex and COOH-CNT by hydrothermal method. The synthesized IrO_2/CNT catalysts was characterized by transmission electron microscopy, x-ray diffraction, Raman microscopy, Fourier transfer-infrared spectroscopy, x-ray photoelectron spectroscopy, thermogravimetric analysis and electrochemical methods. The average particle size of the IrO_2 particles on CNT is 1.7 nm and the loading amount of IrO_2 is 4 wt%. The XPS measurement reveals that Ir complex was completely converted to iridium oxide through hydrothermal treatment. The IrO_2/CNT catalyst showed sufficient performance for OER activity and durability in sulfuric acid solution. Our results indicate that IrO_2/CNT is one of the prospective candidate catalysts for water electrolyzer.

Introduction

Recent years, the development of sustainable societies with renewable energies has become important topic to overcome environmental issues, such as global warming and depletion of fossil fuels. In order to utilize effectively the renewable energies possessing the nature of volatile output power, such as wind-powered electricity and solar cells, conversion of the surplus energies to hydrogen via water electrolysis has attracted attention as a candidate of energy storage systems [1–4]. Polymer electrolyte water electrolyzer (PEWE), which is composed of polymer electrolyte, Pt/C cathode, and iridium oxide as anode, is one of the water electrolysis systems [5,6]. The PEWE system is one of the cleanest way to produce hydrogen, and its advantages are operation at high current density, which represents production of higher amount hydrogen per cell size, fast response to electricity fluctuation, and simple structure similar to PEFC. Thus PEWE is expected as a next generation hydrogen production system. However, in water electrolysis systems, activity, durability, and cost of catalysts are insufficient for practical application due to high over-potential and low kinetics of electrode reactions, especially, oxygen evolution reaction (OER) at the anode [5,7,8].

At the anode of the PEWE cell, oxygen and proton are produced by splitting water. Oxide of Iridium, which is one of the Pt group metals, has been used as electro-catalysts for OER because Iridium oxide shows second best activity amongst

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https://doi.org/10.1016/j.ijhydene.2018.08.034

Please cite this article in press as: Badam R, et al., Synthesis and electrochemical analysis of novel IrO_2 nanoparticle catalysts supported on carbon nanotube for oxygen evolution reaction, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.08.034

metal oxide catalysts [9–18], whereas RuO_2, most active catalysts, has poor durability [19–21]. The phenomena for water splitting, such as reaction pathway and catalytic activity, on metals or metal oxides, including IrO_2, are theoretically discussed by many research groups [21–27]. They reported that binding or adsorption free energy of oxygen species, HOO*, O*, HO*, as well as oxygen vacancy on surface are important factors for OER [25–27]. As electrode for OER or water electrolyzer, in general, iridium dioxide (IrO_2) powder catalyst without support have been used as anode [11,12,15–18], and the diameter of traditional IrO_2 powder catalysts is 5–30 nm. Therefore, a loading amount of IrO_2 is high and specific surface area, surface area per weight, is low. Mass activity, activity per weight, is an important index for precious metal catalysts and estimated by multiply specific surface area by specific activity, activity per surface area. Whereas the IrO_2 powder catalyst has high durability, mass activity of the catalyst is low due to low specific surface area. To commercialize the PEWE cell, improving mass activity and reducing the loading amount of iridium are important topics. Many researchers demonstrated improvement of catalytic activity by alloying the IrO_2 catalysts [28–38]. Other approach to improve mass activity is increment of specific surface area of OER catalysts by employing nanoparticle catalyst. In theory, specific surface area is depended on particle size of a catalyst, therefore stable and conductive materials are employed as support materials of nanoparticle catalysts to increase the surface area and suppress agglomeration of the catalyst nanoparticles. Carbon black, graphene, and conductive oxide were examined as support materials for IrO_2 catalysts [39–46]. It is well known that carbon materials have high surface area and high conductivity, and is one of the most standard support materials for electrodes. However, a carbon black is unstable at the potential region where oxygen evolution reaction takes place, and carbon supported IrO_2 catalyst was tested as cathode catalyst for hydrogen evolution reaction (HER) [39]. Nano carbon materials such as carbon nanotube (CNT) possess higher durability because of its high crystallinity, high chemical and mechanical stability [47–49]. The strategy of our research is utilization of nanocarbon as supporting materials to control the size of IrO_2 nanoparticles. The nanocarbon supports will improve specific surface area of the IrO_2 nanoparticles and increase electron conductivity of the catalysts, as used for electrodes of LiO_2 battery [50], supercapacitor [51], and direct methanol fuel cell [52].

Recently, CNTs have been used as a substrate of electrocatalyst, for example cathode catalysts for oxygen reduction reaction of polymer electrolyte fuel cell, empirically and theoretically [52–59]. The Pt nanoparticles deposited CNT catalysts showed high activity and durability for oxygen reduction reaction, because CNT has high chemical stability and conductivity [53–55]. However, it is difficult to deposit high loading amount of size controlled-catalysts on a CNT substrate due to lower number of defect sites where catalyst particles nucleate. For water electrolysis, CNT has not been employed as a substrate materials because it is difficult to modify CNT with highly dispersed IrO_2 nanoparticles. In addition, stability of the CNT support and catalyst particles on CNT is not clarified under a reaction potential where oxygen evolution is performed. The clarification of degradation mechanism is also important topic for development of the catalysts for OER.

In this study, we have prepared novel nanoparticle catalysts of IrO_2 supported on multi-walled carbon nanotube (MWCNT) by hydrothermal method. The MWCNT substrate is modified with carboxyl groups as nucleation site for IrO_2 deposition and the oxidized MWCNT is reduced during hydrothermal reaction. The IrO_2/CNT catalyst is characterized as a novel anode catalyst for water electrolysis and performance of OER activity is evaluated.

Materials and methods

Synthesis of the catalyst

The IrO_2/CNT catalyst was synthesized by hydrothermal method. Commercial MWCNT (MTR Ltd.) with diameter of 10–20 nm was used as substrate for IrO_2. Firstly, CNT was functionalized with COOH functional group to improve the nucleation sites and to enhance metal oxide-substrate interaction [60]. For this CNT was ultra-sonicated in 3:1 (vol/vol) mixture of concentrated sulfuric acid and nitric acid solution at room temperature for 90 min. Then, required amount of H_2IrCl_6 nH_2O complex (Wako Pure chemical Industries, Ltd.) and oxidized CNT (CNT-COOH) were dispersed in 9:1 (vol/vol) ethanol/water mixture solution. The mixture was heated at 80 °C for 6 h with constant stirring and then hydrothermally treated at 150 °C in a hydrothermal autoclave for 4 h [61]. The resulting material was filtered and washed with 9:1 (vol/vol) ethanol/water mixture solution. Further, the sample was dried up in vacuum oven at 120 °C for 4 h. Commercial IrO_2 powder catalyst was purchased from Alfa Aesar and commercial Ir metal powder was purchased from Sigma-Aldrich Co. All commercial catalysts were used for measurements as received.

Characterization of catalyst

The crystal structure of the synthesized IrO_2/CNT catalyst was characterized by X-ray diffraction (XRD, Ultima4, Rigaku Co.) with Cu Kα radiation (0.15405 nm). The morphology and distribution of IrO_2 nanoparticles deposited on the CNT supports were analyzed by transmission electron microscopy (TEM, JEM-2100, JEOL), operated at 120 kV. The loading amount of IrO_2 on CNT was estimated by scanning electron microscopy (SEM, SU3500, Hitachi High Technologies Co.) with an energy dispersive X-ray spectrometry (EDX, EMAX Evolution X-Max, Horiba). X-ray photoelectron spectroscopy (XPS, PHI5000 Versa Probe II, ULVAC-PHI) with Al Kα radiation (1486.6 eV) was utilized for the analysis of surface elementals and their electron states. The structure of the support CNT was investigated by a Raman microscope (lnVia Raman Microscope, Renishaw plc.) using a 532 nm excitation laser. A 1800-line mm^{-1} grating, a Peltier-cooled CCD camera, and 50 × magnification objective were utilized for Raman microscopy. The infrared spectroscopic measurements were conducted by a fourier transfer infrared (FTIR) spectrometer (FT/IR6200, JASCO Co.) equipped with an MCT detector. The spectral resolution was set at 2 cm^{-1}. All the measurements

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