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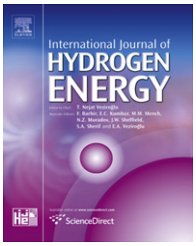

New non-platinum Ir–V–Mo electro-catalyst, catalytic activity and CO tolerance in hydrogen oxidation reaction

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ABSTRACT

Very active 40%Ir–10%V–3%Mo/C and 40%Ir–10%V–10%Mo/C (in weight) catalysts, as novel, suitable anode electrode materials in polymer electrolyte membrane fuel cells (PEMFCs), have been synthesized by an ethylene glycol (EG) reduction method. The nanostructured catalysts have been characterized by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (TEM). Ir nanoparticles, after modification with V and further with Mo, show a narrow particle size distribution centered at 2 nm, and are uniformly dispersed on Vulcan XC-72 supports. Investigation of the catalytic activity by means of linear sweep voltammetry (LSV) employing a rotating disk electrode (RDE) has revealed that 40%Ir–10%V–10%Mo/C catalyst exhibited very high electrocatalytic activity toward the hydrogen oxidation reaction (HOR). About 77% higher current density was obtained for 40%Ir–10%V–10%Mo/C compared to that of 40 wt.% commercial carbon-supported platinum catalyst (Pt/C), and 282% higher current density compared to that of the pure 40 wt.% Ir/C at 0.1 V versus RHE. The performance of a membrane electrode assembly (MEA) prepared with the 40%Ir–10%V–10%Mo/C as the anode catalyst generated a maximum power density of 598.4 mW cm^{-2} at 70 °C, which is 26.4% higher than that of commercially available Pt/C under air/H_2 testing condition. The ternary 40%Ir–10%V–10% Mo/C catalyst was also tested for 10 ppm CO tolerance, and the results showed that the 40% Ir–10%V–10%Mo/C has much better CO tolerance than commercial Pt/C catalyst. The mechanism of the ternary 40%Ir–10%V–10%Mo/C catalyst may be a bi-functional mechanism.

1. Introduction

Due to the excessive price and global scarcity of platinum (Pt), partial or complete replacement of Pt metal has been a significant focus for low temperature polymer electrolyte membrane fuel cell (PEMFC) research [1]. Some Pt-free catalysts have shown remarkable catalytic activity toward O_2 reduction [2], such as carbonized catalase [3], Co- or Fe-based catalysts [4,5], and macrocyclic [6] or pyrolyzed macrocyclic compounds [7]. Nevertheless, few efforts have been devoted toward materials that can replace Pt as the anode catalyst in PEMFCs, since the requirements for good resistance to both CO and acid are difficult to achieve for normal alloy catalysts. Most recently, tungsten carbide, WC and compounds

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containing elements such as nickel, cobalt and molybdenum have been suggested as promising candidates for replacing Pt/C catalyst toward the hydrogen oxidation reaction (HOR) for application as the PEMFC anode catalysts due to its similar behavior to Pt catalyst and similar corrosion properties [8]. Nevertheless, these materials have traditionally shown very low activity for HOR and are not practical for commercial purposes. Furthermore, CO poisoning is another major issue as hydrogen used in PEMFC is mainly from reformed gas, which will contain small amounts of CO contaminants [9]. Even small amounts of CO, as little as 1 ppm present in the fuel stream will cause poisoning of precious metal catalysts, leading to polarization losses and a great decline in the PEMFC performance [10,11]. Therefore, it is a matter of considerable interest to search for Pt-free anode catalysts with high electrocatalytic activity and CO tolerance.

This paper reports the results of an investigation on the preparation and characterization of carbon-supported iridium–vanadium–molybdenum (Ir–V–Mo) catalysts as novel, Pt-free anode materials possessing high activity for the HOR and good CO tolerance in PEMFCs. Ir is one of the most stable platinum group metals in acidic media [12] and is moreover currently only one half the price of Pt [13]. Very good performances have been reported for ethanol oxidation on Ir–Sn [14] catalyst in DEFC, formic acid oxidation on Pd–Ir [15] catalyst in DFAFC, and Ir–Se [16] and Ir_xCo_{1-x} [17] methanol tolerance for oxygen reduction and oxygen reduction on the IrO_2/Ti and IrM (M = Ru, Mo, W, V) Ox/Ti binary oxide electrodes [18]. However, there have only been limited studies on the use of Ir-based nanoparticles as the anode catalyst in hydrogen fueled PEMFCs. Recently, our group found that Ir–V/C catalysts showed good catalytic activity both for the HOR and the oxygen reduction reaction [19,20], encouraging results that have inspired us to further explore Ir-based catalysts. Both Ir and Mo show very good chemical stability particularly in acid media, which is crucial to life time of PEMFCs. Thus, the ternary Ir–V–Mo/C catalysts were prepared based on Pt-free binary Ir–V/C catalysts previously investigated by applying ethylene glycol (EG) as both the solvent and reducing agent.

The fabricated carbon supported nanoparticles were extensively characterized by powder X-ray diffraction (XRD) and high resolution transmission electron microscopy (TEM). Furthermore, their catalytic activities toward HOR were screened using half-cell linear sweep voltammetry. *In-situ* cyclic voltammetry (CV), and performance evaluation using a membrane electrode assembly (MEA) was also conducted to evaluate practical Ir–V–Mo/C performance as an anode catalyst. The contaminate tolerance of these materials was also investigated by exposure to CO during MEA operation.

2. Experimental

2.1. Materials and catalyst synthesis

Carbon-supported Ir–V and Ir–V–Mo nanoparticle catalysts (40%Ir–10%V–3%Mo/C (Ir–V–Mo/C3) and 40%Ir–10%V–10% Mo/C (Ir–V–Mo/C10)) were prepared via the modified EG method using Iridium chloride hydrate [$IrCl_3 \cdot 6H_2O$], NH_4VO_3 and hexaammonium heptamolybdate tetrahydrate [$H_{24}N_6O_{24}Mo_7 \cdot 4H_2O$] mixed with Vulcan XC-72 carbon black (Cabot Corporation) in EG. Specifically, 200 mg Vulcan XC-72 carbon, 12 mL 25 mg/ml $IrCl_3 \cdot 6H_2O$, 0.09 g NH_4VO_3 and 0.022 g or 0.074 g $H_{24}N_6O_{24}Mo_7 \cdot 4H_2O$ were added to 50 ml ethylene glycol. This mixture was ultrasonicated and stirred for 4 h. 2 M NaOH solution was added into this mixed solution to adjust the pH to 12, and the mixture was stirred and refluxed at a temperature of 120 °C for 3 h. The pH of mixture was finally adjusted to 3 by 5 M HCl and cooled to room temperature. In order to ensure complete reduction of the metals, the final catalyst powders were further heat-treated at 200 °C in a tube furnace under a mixture of N_2 and H_2 gas for 2 h with a flow rate of 600 mL min^{-1} for N_2 and 70 mL min^{-1} for H_2, respectively.

2.2. Physical characterization

The crystalline phase XRD patterns were collected on a PHILIPS PW 3040/60 powder diffractometer using CuKα radiation. The working voltage was 40 kV, and the current was 40 mA. The intensity data were collected at 25 °C in a 2θ range of 10–100° with a scan rate of 1.20° min^{-1}. The microstructural parameters of the samples were determined using JADE5 software. The morphology of catalyst particles was observed using transmission electron microscopy (TEM) analyses, with a JEM 2010 EX microscope, equipped with an energy dispersive X-ray spectrometer (EDX) to determine bulk atomic concentrations, operating at 200 kV. The quantity of Ir–V–Mo/C materials has been determined with inductively coupled plasma mass spectrometry (ICP-MS).

2.3. Electrochemical characterization

One milligram of catalyst powder was suspended in 500 uL of methanol/Nafion solution (50:1 wt.%) to prepare the catalyst ink. Then 5 uL of ink was transferred to a clean glassy carbon (GC) disk electrode (6 mm diameter) twice. The overall loading of the mixed catalyst was 2.8×10^{-5} g cm^{-2}, for the apparent electrode area of the GC disk (0.283 cm^2). Catalyst materials were tested for the electrochemical HOR activity in a glass cell consisting of a three-electrode system in 0.5 M H_2SO_4 at 25 °C, which was saturated by pure nitrogen in order to expel oxygen in the solution. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire was used as the counter electrode. All potentials in this work were referred to reversible hydrogen electrode (RHE). The measurement was carried out using a rotating disk electrode (RDE) by linear sweep voltammetry (LSV) at a rotation speed of 300 rpm and scan rate of 5 mV s^{-1} [21].

2.4. Non-platinum 50 cm^2 MEA fabrication

Each MEA was fabricated by the following strategies: (i) The cathode ink was prepared by mixing 40 wt.% Pt/C (JM) with a solution of 5% Nafion® ionomer and isopropanol, then sonicated for 4 h. The resulting catalyst ink was directly sprayed onto one side of a membrane (Dupont, N212) at 100 °C to form a catalyst layer giving a metal loading of 0.4 mg_{Pt} cm^{-2}. The ratio of Pt/C catalyst to Nafion® polymer was 3:1 (in