



Enhanced performance for proton conducting fuel cells at low temperature

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ABSTRACT

A platinum-cobalt-iron ternary alloy is deposited on a TiO₂-coated multi-walled carbon nanotube support (PtCoFe/MWCNT–TiO₂) using a two-step hydrothermal method and evaluated as an anode catalyst for direct methanol fuel cells. Catalysts with different weight ratios of Pt:Co:Fe (3:1:1, 1:1:1 and 1:3:3) on MWCNT–TiO₂ are prepared and examined. The Pt₃Co₁Fe₁/MWCNT–TiO₂ catalyst shows higher catalytic activity and stability compared to the 1:1:1 and 1:3:3 catalysts for the methanol oxidation reaction in acidic media. Cyclic voltammetry analysis shows a maximum mass activity for Pt₃Co₁Fe₁/MWCNT–TiO₂ of 4.17 A mg⁻¹_{Pt} (vs. Ag/AgCl) with a low onset potential in 0.4 M H₂SO₄ and 0.3 M CH₃OH solution. A single fuel cell based on Pt₃Co₁Fe₁/MWCNT–TiO₂ anode catalyst exhibits a maximum power density of 117.94 mW cm⁻² at 50 °C in 1.3 M CH₃OH, which is significantly higher than that of the Pt₁Co₁Fe₁/MWCNT–TiO₂, Pt₁Co₃Fe₃/MWCNT–TiO₂, and Pt/MWCNT catalysts.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical devices due to their relatively high efficiency at low temperatures, high energy density, lack of polluting emissions, convenient refueling of methanol for long-term operation, and relatively quick start-up and shut-down processes [1–3]. Also, methanol can be comfortably stored and transported than hydrogen fuel. The performance of a DMFC is determined primarily by the efficiency of the catalyst in the anode where the methanol oxidation reaction (MOR) the predominant fuel cell reaction occurs. Platinum-based catalysts are widely used in DMFC anodes as they are highly active for methanol oxidation [4,5], readily adsorbing and decomposing methanol on the surface [6]. Unfortunately, pure Pt catalysts are expensive due to the scarcity of the metal and suffer from slow reaction kinetics. Furthermore, low efficiency in methanol conversion, aggregation, migration of the Pt from the anode to the flow channels, and a short lifetime due to poisoning by strongly adsorbed intermediate species, such as CHO and, CO [2,3]. On the

contrary, Pt with other metals or alloying may give rise to the multitudinous active sites for MOR that can be beneficial for methanol adsorption, which can easily donate OH species during the desorption process [7].

Numerous efforts are devoted to enhancing the catalytic performance and durability of Pt-based catalysts for the MOR. To this end, binary Pt–Cu, Pt–Co, Pt–Cr, Pt–Ni, Pt–Fe and ternary Pt–Ru–Co, Pt–Ru–Pb, Pt–Co–Cr, Pt–Co–Ni, Pt–Fe–Sn nanocomposites catalysts are employed, where Pt is combined with less expensive metals [8–11]. Theoretically, the addition of Cu, Ni, Fe, and Co to Pt results in a Pt *e_d* (*e_d* = d-band energy center) downshift that leads to decreased CO adsorption [10,12]. However, a significant challenge in the application of binary or ternary Pt alloys catalysts in acidic media is the leaching of transition metals from the alloys, resulting in instability, decreased oxygen reduction activity, and quick demise of the fuel cell [13]. Therefore, developing more durable anode catalysts for DMFCs remains a challenge.

The catalyst support material is critical as it can significantly enhance the surface area of the catalyst particles. Multi-wall carbon nanotubes (MWCNTs) widely used as support material for catalysts [14,15]. However, particle aggregation, de-adhesion of the nanoparticles from the support, and carbon corrosion are primary concerns when using MWCNTs [16]. Therefore, transition-metal oxides (e.g., MnO₂, TiO₂, SnO₂, CeO₂, RuO₂, WO₃, Fe₃O₄) have been used as

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DMFCs catalyst support materials to resist carbon corrosion and increase the catalytic activity and durability [17,18]. TiO₂ is extensively used in the acidic environment due to its unique advantages, including high structural stability, non-toxicity, favorable mass transfer, low cost, abundance, excellent corrosion resistance (towards CO and its intermediates), and better electrochemical performance [12,19]. Therefore, carbon-oxide nanocomposites are formed by coating carbon materials with metal oxides. Carbon-oxide nanocomposite support materials can reduce carbon corrosion and also provide strong metal-support interaction. Furthermore, the metal-support interaction increases the electronic properties and stability of the catalytic center (via a ligand effect), lowering the activation energy for CO_{ad} surface mobility, resulting in more facile diffusion of CO_{ad} from Pt sites [20,21]. Also, the agglomeration of Pt-based alloy nanoparticles can be avoided; the uniform dispersion of the catalyst particles can increase the active surface area.

In this study, we report a composite MOR catalyst, consisting of ternary PtCoFe alloy nanoparticles on TiO₂-modified MWCNT support. The MWCNTs provides a good backbone for supporting the TiO₂ nanoparticle coating and avoiding agglomeration during electrochemical reactions. To the best of our knowledge, such a combination of PtCoFe/MWCNT-TiO₂ electrocatalyst for DMFC anodes has not yet been reported.

2. Experimental section

2.1. Synthesis of MWCNT-TiO₂ supports

The MWCNT-TiO₂ support material was prepared using a hydrothermal process. Briefly, 10.0 ml of titanium isopropoxide (Sigma-Aldrich) and 130.0 mg of MWCNT (EM Power, South Korea) were added to 90 ml of an ethanol and water solution. This mixture was sonicated for 30 min and then stirred for 7 h. The mixture was then transferred to a Teflon vessel and heated to 160 °C for 36 h. The obtained product was centrifuged and washed several times using water and ethanol and then dried in an oven at 70 °C for 12 h.

2.2. Catalyst synthesis

PtCoFe alloy supported on MWCNT-TiO₂ were prepared using a hydrothermal process. Briefly, 40 mg of the MWCNT-TiO₂ support material was added to 30 ml of ethylene glycol, sonicated for 10 min, and then stirred for 6 h. Next, different weight ratios of the metal precursors, 3:1:1, 1:1:1, and 1:3:3 of H₂PtCl₆·6H₂O, Co(N-O₃)₂·6H₂O, and FeCl₂, respectively (Sigma-Aldrich), were added to the MWCNT-TiO₂ mixture in a concentration of 60 wt% of the total composite. A 0.1 M KOH (Sigma-Aldrich) solution was added to maintain the pH between (9 and 10). We put dropwise 160 μl NH₂NH₂·H₂O, and the mixture was vigorously stirred for 20 min. The resulting solution was then transferred into a Teflon vessel and heated at 170 °C for 5 h. After the hydrothermal treatment, the composite was centrifuged and washed several times using ultra-pure water and ethanol and dried at 70 °C overnight.

2.3. Physicochemical characterization and electrochemical analysis

The phase structure and crystallite size of the prepared catalysts were examined by X-ray diffractometry (XRD; Rigaku D/MAX-2200) using CuKα radiation (λ = 0.15406 nm). The surface morphology was studied using high-resolution transmission electron microscopy (HRTEM; Technai G2 F30) and scanning electron microscopy (SEM, Hitachi S-4200). The surface chemical bonding and oxidation state of the samples were examined by X-ray photoelectron microscopy (XPS) using K-alpha X-ray (Thermo

Scientific Inc, U.K). Inductively coupled plasma mass spectroscopy (ICP-MS Agilent, 7900) was used to evaluate the real element content of the catalysts.

The electrochemical measurements were performed using a Biologic-science system with a standard three-electrode electrochemical cell. We used an Ag/AgCl electrode as the reference electrode, platinum gauze as the counter electrode and a glassy carbon electrode (GCE; 3 mm internal diameter and area of 0.07 cm²) coated with the composite catalysts of interest as the working electrode. Before testing, the glassy carbon was polished with fine alumina slurries to achieve a mirror finish, washed with ethanol and water to completely remove the alumina slurry, and dried in an oven (60 °C) for 5 min. A homogeneous catalyst ink was prepared by dispersing 3 mg of the prepared power catalyst in a solution of 30 μL of Nafion 117 solution (5 wt%) and 300 μL of isopropanol and sonicated for 15 min. Next, ~3 μL of the homogeneous catalyst ink was drop-cast onto the surface of the polished glassy carbon electrode and dried (60 °C). The catalyst loading on the electrode surface was around 6.9 μg, and the solution (0.4 M H₂SO₄ and 0.3 M CH₃OH) temperature was ~24 °C and the electrochemical test was carried out at room temperature. Furthermore, a commercial Pt/C (30% Pt on Vulcan XC-72) was also examined to compare with our prepared catalysts. Cyclic voltammetry (CV) tests were performed using a CHI 150 electrochemical workstation (China) over a potential range of -0.2 to +0.8 V vs. Ag/AgCl at a scan rate of 10 mV s⁻¹ in a high purity nitrogen atmosphere (99.999%; Daesung Industrial Gases Co., Ltd.). For the CO anti-poisoning results of the catalysts, the CO stripping experiment was accomplished in 0.4 M H₂SO₄ solution, as mentioned elsewhere [9].

2.4. Membrane electrode assembly and fuel cell testing

Membrane electrode assemblies (MEAs) for single cell proton exchange membrane (PEM) fuel cells with an active area of 5 cm² were prepared using a Nafion 117 (DuPont) membrane and carbon paper coated with the catalyst ink. The catalyst ink for the anode was prepared by dispersing 100 mg of the catalyst powder in 1.2 ml of isopropanol and 0.8 ml of 5 wt% Nafion solution, followed by sonication for 20 min and stirring for 2 h. The prepared catalyst ink was repeatedly hand-brushed onto the carbon paper. About 6 mg cm⁻² of the catalyst ink was loaded onto the carbon paper. A commercial Pt/C (40 wt% Pt, ~0.3 mg cm⁻² loading) paper was applied to the cathode. An anode-membrane-cathode sandwich structure was prepared by hot-pressing at 110 °C and applying pressure 1.37 × 10⁴ Pa for 1 min. The MEA was later placed between two graphite plates having serpentine flow model. The polarization peaks were obtained using a fuel cell test station (VSP potentiostat-galvanostat, Biologic-Science Instruments, France) at 50 °C. The anode side was fed with 1.3 M CH₃OH (flow rate of 5 mL min⁻¹) and cathode side with humidified air (flow rate of 200 mL min⁻¹).

3. Results and discussion

3.1. Structure and morphology

The structure and crystalline phases of the prepared catalysts as determined by XRD are shown in Fig. 1 (and Fig. S1). Pt₃Co₁Fe₁/MWCNT-TiO₂ catalyst show typical face-centered cubic (fcc) structure with three major diffraction peaks of (111), (200), and (220), which is located at 40.2°, 48.6°, and 68.8°, respectively. The diffraction peak at 25.4° corresponded to those of MWCNT and anatase TiO₂ overlapping peaks, as previously reported [13]. XRD peaks associated with the pure Fe, Co, and Fe-Co oxides were not observed. The corresponding diffraction peaks position of Pt₃Co₁Fe₁/MWCNT-TiO₂ slightly shifted towards the higher

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