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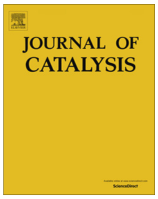

PtIr/Ti_4O_7 as a bifunctional electrocatalyst for improved oxygen reduction and oxygen evolution reactions

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ABSTRACT

A unitized regenerative fuel cell (URFC) that combines a fuel cell with a water electrolyzer is attractive as a portable power source. To enhance the efficiency of the URFC, a bifunctional oxygen catalyst for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) needs to be developed. In this study, Ti_4O_7 supported Pt-based catalysts were prepared for a bifunctional oxygen catalyst (BOC) in URFC. Ti_4O_7 support was prepared using a low-temperature process with TiO_2 and cobalt chloride hexahydrate at 950 °C under an H_2 atmosphere. The metal catalysts (60 wt%) were deposited on a Ti_4O_7 support using a borohydride reduction method. The catalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Compared to Pt/C and Pt/Ti_4O_7, PtIr/Ti_4O_7 exhibited enhanced activity and stability in ORR and OER. The improved electrocatalytic performance of PtIr alloy supported by Ti_4O_7 might be attributed to the PtIr alloy phase, the highly stable Ti_4O_7 support in an acid medium, and the interaction between catalyst and support.

1. Introduction

A unitized regenerative fuel cell (URFC) is an energy storage system that combines a fuel cell with a water electrolyzer [1–3]. Due to its simplicity and compactness compared to the regenerative fuel cell (RFC), URFC can be extensively utilized as a portable power source for drone and military applications [4]. Furthermore, URFC exhibits higher energy density (packaged: 400–1000 Wh kg^{-1} and theoretical: 3660 Wh kg^{-1}) and long-term energy storage compared to Li-ion batteries [2,5]. In the fuel cell mode of URFC, hydrogen oxidation reaction at the anode and oxidation reduction reaction (ORR) at the cathode occur with the generation of electricity and water [5–7]. On the other hand, in the water electrolyzer mode, hydrogen and oxygen are electrochemically produced at the anode and cathode, respectively, using the electrolysis of water provided at the cathode [4,8]. In particular, to enhance the efficiency of URFC, the ORR and oxygen evolution reaction (OER) at the cathode are essential [9]. In the cathode, a bifunctional oxygen catalyst (BOC) for both ORR and OER needs to have high electrocatalytic activity, stability in acid media, and electrical conductivity [10–12]. Currently, platinum (Pt) exhibits the excellent electrocatalytic activity towards the ORR in proton exchange membrane fuel cells (PEMFCs) whereas iridium (Ir) and ruthenium (Ru) have an improved OER activity compared to Pt catalyst [10,13–16]. Thus, alloy structures for the BOC combined with Pt and Ir or Ru have been proposed in order to simultaneously improve the ORR/OER performance in the URFC [17–21].

In general, carbon nanostructure materials in PEMFCs can support the catalyst and increase the utilization of the catalyst [22–25]. However, in the URFC, carbon oxidation can occur in the water electrolyzer mode as follows [10,26,27]:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-, \quad 0.207\ V\ vs.\ NHE\ at\ 25\ ^\circ C \qquad (1)$$

As the operation time increases, the oxidation and corrosion of the carbon support significantly increase and thus the catalytic activity of metal catalysts can decline due to the dissolution and sintering of the catalysts on the carbon supports [22,28–30]. Thus, the reduced Ti_nO_{2n-1} as a promising support for the BOC has been proposed due to electrochemical stability in acid media and comparable electrical conductivity to carbon [31–33]. In particular, the electrical conductivity of Ti_nO_{2n-1} structures depends on the value of n [34,35]. In particular, among the reduced structures, Ti_4O_7 (n = 4) has been known as having a Magnéli phase with excellent electrical conductivity (10^3 S cm^{-1}) and high stability in an acidic electrolyte [33,36–38]. The oxygen vacancy sites in the

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reduced titanium suboxide such as Ti_4O_7 can induce O—O bond splitting with increased electric conductivity, and thus result in enhanced electrocatalytic activity [39–42]. Yao et al. proposed improved performance of Pt nanoparticles (NPs) deposited on fiber-like nanostructured Ti_4O_7 in an acid medium compared to Pt/C catalyst [43]. In particular, Pei et al. reported that a defect in titanium oxide can act as an electrocatalytic active site for ORR [40].

In this study, Ti_4O_7 as a support for both ORR and OER was prepared using a heating process at 950 °C under an H_2 atmosphere with pure TiO_2 in the presence of a cobalt precursor. The Pt and PtIr catalysts supported by Ti_4O_7 (denoted as Pt/Ti_4O_7 and PtIr/Ti_4O_7, respectively) for the BOC were prepared using a borohydride reduction method with a Ti_4O_7 support. The structure and chemical states of the catalysts were analyzed using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), field emission transmission electron microscopy (FE-TEM), and X-ray photoelectron spectroscopy (XPS). The electrocatalytic activity and stability of the catalysts for ORR and OER were evaluated using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in an acid medium.

2. Experimental

2.1. Synthesis of Ti_4O_7 support

Ti_4O_7 as a support was prepared using a low-temperature catalytic reaction with TiO_2 and cobalt(II) chloride hexahydrate as a catalyst under an H_2 atmosphere at 950 °C. TiO_2 powder (2 g, Degussa) and 0.2 g cobalt(II) chloride hexahydrate (98%, $CoCl_2{\cdot}6H_2O$, SIGMA ALDRICH) as a catalyst were mixed in 100 ml ethanol (95%, SAMCHUN) and stirred for 2 h. The precursor powder was collected using an evaporator (EYELA SB-1000) operating at 65 °C and completely dried in a 50 °C oven overnight. The resulting sample as a support was obtained by heating the precursor powder at 950 °C for 3 h under an H_2 atmosphere. To remove the cobalt-related compounds, the heated sample was continuously stirred in 1 M HCl solution for 2 h, washed in de-ionized water and ethanol, and dried in a 50 °C oven.

2.2. Synthesis of Ti_4O_7 supported catalysts

To prepare Pt and PtIr catalysts, the intended salt amounts of chloroplatinic acid hydrate (99.99%, $H_2PtCl_6{\cdot}6H_2O$, SIGMA ALDRICH) and iridium(III) chloride hydrate (99.99%, $IrCl_3{\cdot}xH_2O$, SIGMA ALDRICH) were completely dissolved in 30 ml de-ionized (DI) water (18.2 MΩ cm) as follows: Pt (3.9 mM), PtIr (2.93 mM: 0.975 mM). 100 mg of Ti_4O_7 powder was well dispersed in 100 ml ethanol and 140 ml DI water with stirring and ultrasonication and the metal precursor solutions were then added to the Ti_4O_7–disperesed solution with continuous stirring. To completely reduce the metal salt to metal phase, 1.5 g sodium brohydride (99%, $NaBH_4$, SIGMA ALDRICH) as a reducing agent dissolved in 30 ml DI water was added to the metal precursor and Ti_4O_7 mixed solution with vigorous stirring at room temperature, followed by the reduction process. The resulting powders were washed with DI water, ethanol, and acetone (99.7%, SAMCHUN) and dried in a 50 °C oven overnight. For comparison, Pt catalyst with carbon as a support was prepared using the same procedure as that for the Ti_4O_7 supported catalyst.

2.3. Structural analysis

The crystal structures of the samples were analyzed using an X-ray diffractometer (XRD, Bruker, D2 Phase system) operating with K_α source (λ = 0.15406 nm) and a nickel filter. The tube voltage and current for the XRD analysis were 30 kV and 10 mA, respectively. To measure the specific surface areas of the samples, nitrogen adsorption and desorption isotherms were obtained using a Micromeritics ASAP 2020 analyzer. The electrical conductivity of the samples was determined using Eq. (2):

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} \qquad (2)$$

where σ is electrical conductivity (S cm^{-1}), ρ is specific resistance, l is thickness of pellet, R is resistance, and A is area of pellet.

The morphology of the samples was visualized using a FE-SEM (JEOL, JSM-6700F). The structure and chemical composition of the samples were characterized using a FE-TEM (Philips, Tecnai F20 system) operating at 200 kV. The chemical states of the catalysts were observed using an XPS (Thermo scientific, K-Alpha) with an Al X-ray source of 1486.8 eV.

2.4. Electrochemical analysis

The electrochemical properties of the samples were characterized using a potentiostat (AUTOLAB, PGSTAT302N) in a three-electrode cell, which consisted of Pt wire and Ag/AgCl (in 3 M KCl) as a counter and reference electrode, respectively. The inks were prepared by homogeneously mixing the samples with 5 wt % Nafion® solution (SIGMA ALDRICH) and ethanol. The working electrode was prepared by dropping the ink (2.0 μL) on a rotating disk electrode (glassy carbon) and then drying in a 50 °C oven for 10 min. Cyclic voltammograms (CVs) of the samples were obtained in Ar- and O_2-saturated 0.5 M H_2SO_4 with a scan rate of 50 mV s^{-1}. The ORR and OER performance of the catalysts was evaluated using linear sweep voltammetry with a rotating speed of 1600 rpm in O_2– and N_2-saturated 0.5 M H_2SO_4, repsectively. A stability test was carried out by sweeping between 0.8 and 1.6 V for 80 cycles in O_2-saturated 0.5 M H_2SO_4 with a scan rate of 5 mV s^{-1}. The measured potentials were converted to reversible hydrogen electrode (RHE).

3. Results and discussion

Fig. 1 shows the XRD patterns of the TiO_2 powders before and after the heating process under an H_2 atmosphere at 950 °C for 3 h. The pristine TiO_2 (Degussa) before the heating process had a mixed phase consisting of anatase and rutile phases. After the heating and washing process, the XRD patterns of the resulting sample correspond to those of Ti_4O_7 as a main Magnéli phase and Ti_5O_9 as a minor phase without cobalt-related phases. This demonstrates that the dominant Ti_4O_7 magneli phase can be obtained with a commercial TiO_2 via a heating process at a relatively low temperature of 950 °C in the presence of cobalt salt. The low-temperature reduction of TiO_2 to Ti_4O_7 might result from the catalytic role of the cobalt precursor with a proper amount under the reducing atmosphere, as suggested in our previous study [44], as the following equation: $TiO_2 + H_2 + Co(catalyst) \rightarrow Ti_4O_7 + H_2O(g) + Co$. The Ti_nO_{2n-1} structures as titanium suboxides can be typically formed using a heating process under a reducing atmosphere at a high temperature such as >1200 °C [45,46]. However, it has been reported that titanium suboxides can be obtained by heating pure TiO_2 at a relatively low temperature of <1000 °C with transition metals such as Cu, Mo, and Ni [39,47,48]. Reza et al. proposed the Ti_3O_5 structure as a support using heat treatment at 850 °C with Mo [39]. The specific surface area of the as-prepared Ti_4O_7 was determined to be 6.64 $m^2\,g^{-1}$ (Fig. S1). As shown in the FE-SEM, TEM, and HR-TEM images (Fig. 2(a)–(c), respectively), the resulting Ti_4O_7 is a blue black powder with an average particle size