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Facile and Catalytic Synthesis of Conductive Titanium Suboxides for Enhanced Oxygen Reduction Activity and Stability in Proton Exchange Membrane Fuel Cells

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Titanium suboxides (TSO) are generally used in electrochemical devices due to excellent electronic conductivity and enhanced electrochemical stability. We synthesized TSO as a support material through catalytic reaction in the presence of Co catalysts at 800 ^{o}C in H_2 atmosphere. The Pt/TSO catalyst shows enhanced electrochemical activity and stability in oxygen reduction reaction in comparison with Pt/C.

Keywords: Titanium suboxide, Catalytic reaction, Oxygen reduction reaction, Activity, Stability

1. INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have been of considerable interest because of a variety of merits such as low operating temperatures, high energy density, and applications to automobile industries. In the PEMFCs [1-5], carbon supports are well known as the most effective electrode supports for the hydrogen oxidation and oxygen reduction reaction due to it has higher surface area, excellent electronic conductivity, and, low cost of production [6-8]. In the case of cathode reaction, however, carbon support materials exhibit corrosion of carbon resulting in serious agglomeration of catalysts during electrochemical reaction such as oxygen reduction reaction [9,10]. Furthermore, the carbon corrosion situation is most intensifying during fuel cell start up and shut down, as indicated by the following reaction [11,12]:

$C + 2H_2O \rightarrow CO_2 + 4h^+ + 4e^-$ (0.207 V *vs.* NHE)

Also, the carbon corrosion situation leads to reduce active site of catalysts for agglomeration, coalescence, and dissolution of metallic catalysts.

Accordingly, it has been suggested that the utilization of transition metal oxides as a support is an effective way to promote the electrocatalytic activity and stability for electrochemical reactions. In particular, the transition metal oxides such as TiO_2, WO_3, SnO_2, RuO_2, MoO_3, and Ta_2O_5 have been reported as alternatives to carbon supports to enhance the catalytic activity and stability for electrochemical reaction [13-18]. However, the transition metal oxide supports for electrochemical reactions have a critical problem such as low electrical conductivity in comparison with carbon materials. The poor electrical conductivity of the supporting material can reduce the electrochemical performance in PEMFCs [19-21].

Recently, it has been reported that the transition metal suboxides as a support material in fuel cells show improved electrochemical stability and electrical conductivity [22]. The typical transition metal suboxides are W_xO_{3x-1}, Mo_xO_{3x-1}, and Ti_xO_{2x-1}, (x = 2, 3, 4,.., n) [23,24]. Among them, the titanium suboxides are generally used in various applications such as sensors, photochemical devices, and electrochemical devices due to excellent electronic conductivity, enhanced chemical stability, and commercial availability [25,26]. Wills *et al.* reported that the Ti_xO_{2x-1} (x = low value) have higher conductivity in comparison with other titanium suoxides (x = high value) [27]. However, the transition metal suboxides have been expensive in production due to high reaction temperature (T > 1200 ^oC) or pressure [28,29].

Here, we easily synthesized titanium suboxides (denoted as TSO) as a support material through catalytic reaction at a relatively low temperature. The titanium suboxides were synthesized through catalytic reaction in the presence of cobalt metallic catalyst at 400, 700, and 800 ^oC for 3 h in H_2 atmosphere (Supporting Information). Also, to confirm formation mechanism of titanium suboxide, we synthesized the sample by heat treatment in the presence of the catalyst at 800 ^oC for 3 h in N_2 atmosphere. The structure properties of the NPs were characterized by field-emission transmission electron microscopy (FE-TEM) and X-ray diffraction (XRD). The electrochemical properties of the catalysts were measured and compared using a potentiostat.

2. EXPERIMENTAL PART

2.1. Synthesis of titanium suboxide using catalytic reaction

The titanium suboxide were prepared using TiO_2 (Degussa, P-25) as a starting material by means of heat treatment under hydrogen gas atmosphere. For absorption of Co ions as catalyst on TiO_2 nanoparticles (NPs), the TiO_2 powder (2 g) and $CoCl_6 \cdot 6H_2O$ (0.2 g, Aldrich, 98%) were dispersed into 100 ml ethanol (Samchun Chem. Co., 99.9%). The mixed solution was stirred at room temperature for 2 hr and evaporated at 65 ^oC and then the obtained powder was dried at 50 ^oC oven for 12 h. The as-prepared Co ions deposited on TiO_2 powders (0.1 g) were put into a quartz boat, and then the quartz boat was set at the quartz tube system under the flow of hydrogen gas. At first, the flow rate of N_2 gas

was kept for 30 min to get rid of O_2 inside the tube. Under H_2 flow rate of 100 ml min^{-1}, the furnace was heated at 400, 700, and 800 ^oC and then maintained for 3 h. After the heat treatment, the furnace was cooled down to room. Finally, the flow rate of N_2 gas was kept for 30 min to get rid of H_2 inside the tube at room temperature. For investigation of catalyst effect on synthesis of titanium suboxides, in the present synthesis process, we prepared the titanium suboxide NPs in the absence of Co ions using heating treatment in H_2 gas atmosphere at 800 ^oC. Also, we prepared the titanium suboxide NPs in the presence of Co ions using heating treatment in N_2 gas atmosphere at 800 ^oC.

2.2 Preparation of Pt nanoparticles deposited on titanium suboxides

To prepare supported Pt (20 wt.%) catalysts, 780 mg of titanium suboxide synthesized by heating treatment in H_2 gas atomsphere at 800 ^oC were dispersed into de-ionized water and then $H_2PtCl_6 \bullet H_2O$ (40.9 mg, Aldrich) was dissolved in the solutions with continuous stirring for 1 h. After the stirring, an excess of $NaBH_4$ (0.20 g, Aldrich) solution as a reductant was added to the mixture solution with continuous stirring at 25 ^oC for 2 h. The resulting precipitate was washed with de-ionized water several times and dried at 80 ^oC oven for over night.

2.3. Structural analysis

For the structure analysis of the catalysts, X-ray diffraction (XRD) analysis was carried out using a Rigaku X-ray diffractometer with Cu K_α (λ = 0.15418 nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 60° was explored at a scan rate of 3° min^{-1}. For all the XRD measurement, the resolution in the scans was kept at 0.02°. The morphology and size distribution of the catalysts were characterized by field-emission transmission electron microscopy (TEM) using a Tecnai G2 F30 system operating at 300 kV. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid. For measurement of the electrical conductivity, the pellets were made by conventional method. The electrical resistance of the compressed pellets was measured in current *vs.* voltage curves using potentiaostat (CH Instrument, CHI 700C) at ambient temperature. Also, the conductivity was calculated by the follow equation:

$$\sigma = \frac{1}{\rho} = \frac{l}{RA}$$

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

2.4 Electrochemical analysis

Electrochemical properties of the catalysts were measured in a three-electrode cell at 25 ^oC using a potentiostat. A Pt wire and Ag/AgCl (in saturated KCl) were used as a counter and reference electrode, respectively. The catalyst ink was prepared by mixing 2 mg metal of all catalysts, 50 μL of

Millipore water, 57.2 μL of 5 wt% Nafion® solution (Aldrich), and 195 μL of 2-propanol solution (C_3H_8O, Sigma). The catalyst ink was dropped onto a glassy carbon working electrode (area ~ 0.125664 cm^2). After drying in 50 ^oC oven, total loading of catalyst was 47.4 μg cm^{-2}. To evaluate electrocatalytic activities of the as-prepared catalysts, CVs were obtained between -0.2 to +1.0 V in Ar-saturated 0.1 M $HClO_4$ with a scan rate of 50 mV s^{-1} at 25 ^oC. The oxygen reduction current–potential curves were obtained using linear sweep voltammetry at various rotation speeds of 1600 rpm in O_2-saturated 0.1 M $HClO_4$ solution by sweeping the potential from 0.8 to 0 V at a scan rate of 5 mV s^{-1}. The accelerated stability test was performed by applying the positive potential of 1.2 V for 30 min in O_2-saturated 0.1 M $HClO_4$ at 25 ^oC.

3. RESULTS AND DISCUSSION

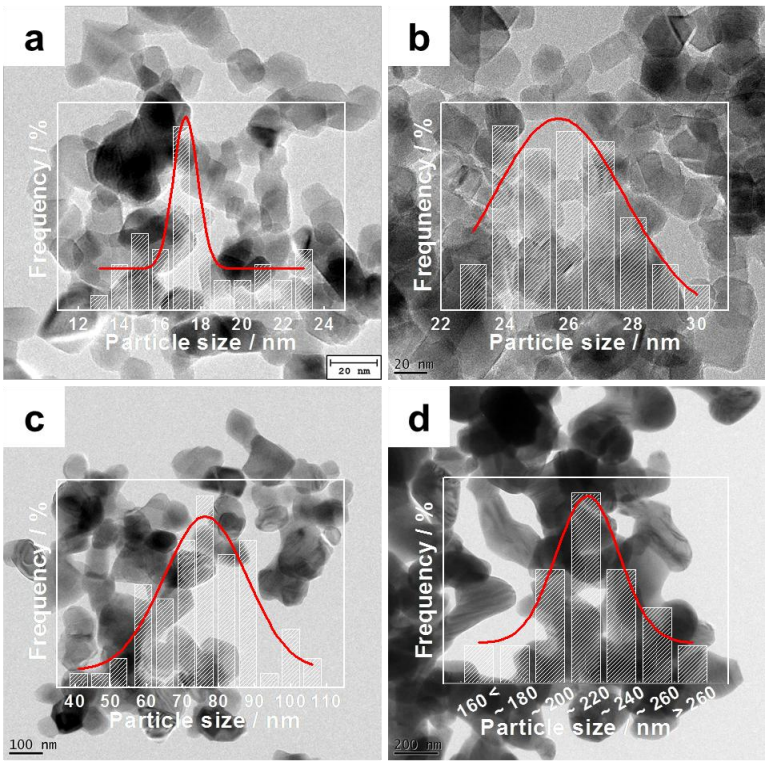

Figure 1. TEM images and size distribution of (a) fresh TiO_2 (Degussa, Co.), (b) TiO_2-400CH, (c) TiO_2-700CH, and (d) TiO_2-800CH NPs.

The structural analysis of fresh TiO_2 (Degussa, Co.) and as-synthesized titanium oxide NPs after heat treatment was carried out by FE-TEM. The fresh TiO_2 NPs exhibit fairly uniform average particle size of 17.22 ± 0.6 nm as indicated in Fig. 1(a). Fig. 1(b-d) shows FE-TEM images of as-synthesized titanium oxides through catalytic reaction using the catalysts at 400, 700, and 800 ^oC in H_2 atmosphere, respectively (denoted as TiO_2-400CH, TiO_2-700CH, and TiO_2-800CH). The average particle sizes of TiO_2-400CH, TiO_2-700CH, and TiO_2-800CH are 25.7 ± 2.1, 76 ± 12, and 221 ± 17

nm, respectively. As reaction temperature increases, the average particle size of the titanium oxide NPs increases with particle aggregation.

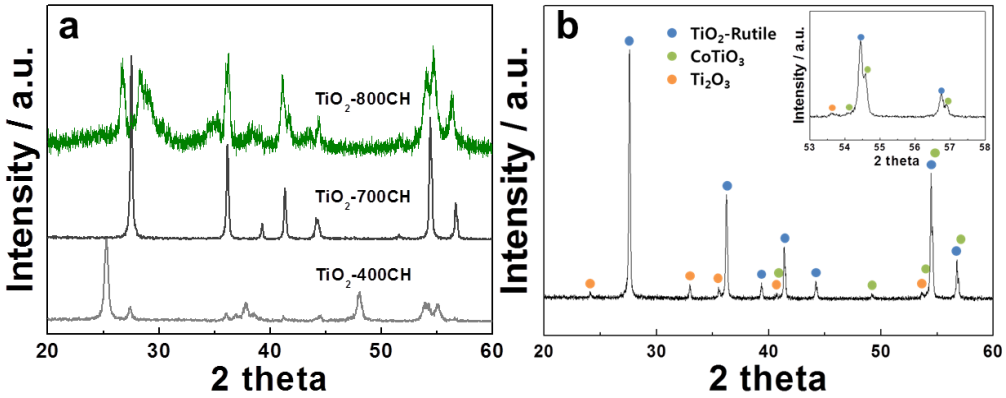

Figure 2. (a) XRD patterns of the TiO_2-400CH, TiO_2-700CH, and TiO_2-800CH. (b) XRD pattern of TiO_2-800CN [The inset indicates XRD patterns between 53° and 58°.].

Fig. 2(a) shows XRD patterns of as-synthesized titanium oxide NPs through catalytic reaction in the presence of cobalt catalysts under H_2 atmosphere. The TiO_2-400CH and TiO_2-700CH exhibit mixed anatase-rutile and homogenous rutile phase, respectively. In contrast, the TiO_2-800CH display titanium suboxide phase (Ti_8O_{15}) (JCPDS No.PDF 85-1060) without typical TiO_2 phase, i.e. anatase and rutile. Usually, the reduced titanium oxides have been synthesized at considerably high temperatures (T > 1200 ^oC) in H_2 atmosphere. Herein, it is found that the titanium suboxide can be easily synthesized by catalytic reaction at relatively low-temperature of 800 ^oC. To understand the formation mechanism of the titanium suboxide using catalytic reaction, we prepared titanium oxide through the catalytic reaction at 800 ^oC in the presence of Co catalyst under N_2 atmosphere (denoted as TiO_2-800CN). As shown in Fig. 2(b), the XRD pattern of the TiO_2-800CN consists of rutile TiO_2, $CoTiO_3$, and Ti_2O_3 phase. Among them, the formation of $CoTiO_3$ and Ti_2O_3 result from cobalt catalysts in the catalytic reaction and oxygen deficiency of TiO_2 structures, respectively.

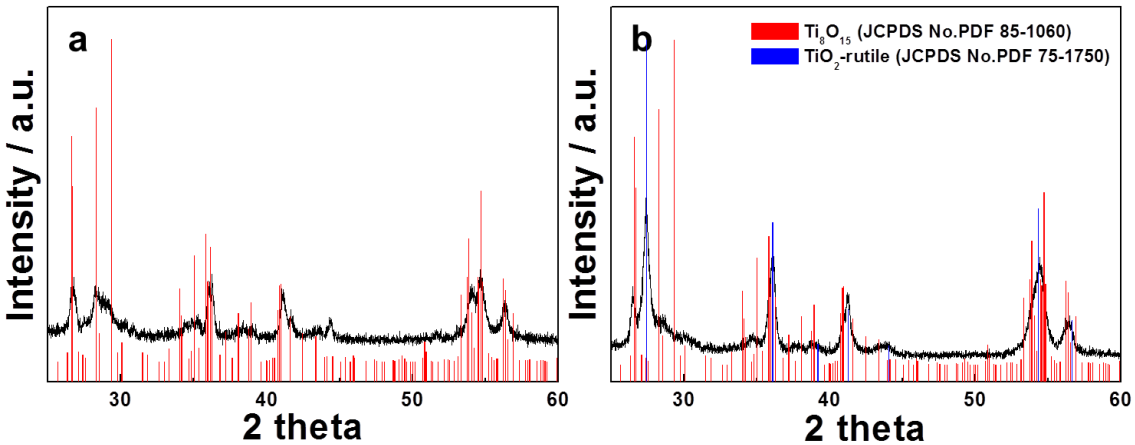

Figure 3. The XRD patterns of (a) TiO_2-800CH and (b) TiO_2-800H.

Furthermore, to confirm the effect of metallic cobalt catalyst in the catalytic reaction, we synthesized titanium oxide by prepared at 800 ^{o}C in the absence of cobalt catalyst in H_2 atmosphere (denoted as TiO_2-800H). As indicated in Fig. 3(a), the TiO_2-800H shows dominant rutile TiO_2 with titanium suboxide (Ti_8O_{15}). Thus, it is concluded that the present synthetic process for titanium suboxides using the catalytic reaction in the presence of Co catalyst under H_2 atmosphere can be a facile method for synthesis of titanium suboxides at relatively low temperature of 800 ^{o}C.

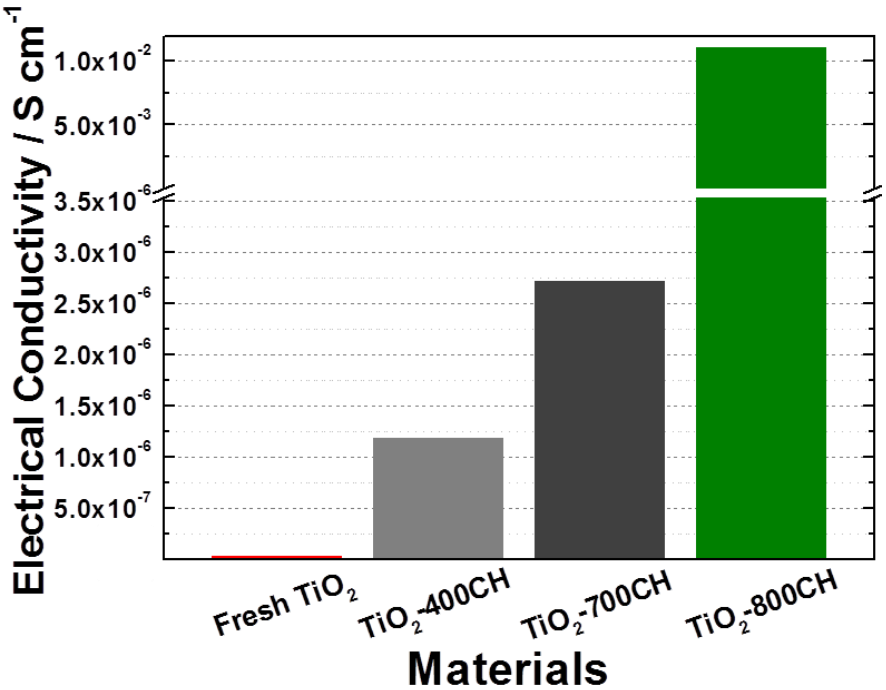

Figure 4. Electrical conductivity of the fresh TiO_2 (Degussa, Co.), TiO_2-400CH, TiO_2-700CH, and TiO_2-800CH NPs.

Fig. 4 shows electrical conductivity of the as-synthesized titanium oxide NPs through catalytic reaction in the presence of cobalt catalysts under hydrogen atmosphere. The fresh titanium dioxide used as a starting material appears extremely low electrical conductivity (2.89×10^{-8} S cm^{-1}). The electrical conductivities of the TiO_2-400CH and TiO_2-700CH are 1.18×10^{-6} and 2.76×10^{-6} S cm^{-1}, respectively. On the other hand, the TiO_2-800CH exhibits ~10^4 times higher electrical conductivity (1.10×10^{-2} S cm^{-1}) in comparison with other titanium oxides. For electrochemical analysis, we prepared Pt NPs deposited on the TiO_2-800CH (denoted as Pt/TSO) having the highest electrical conductivity and suboxide structure. To identify electrochemical properties of the catalyst, as shown in Fig. 5(a), cyclic voltammograms (CVs) were obtained in Ar-saturated 0.1 M $HClO_4$ between -0.2 and +1.0 V (*vs.* Ag/AgCl). The ORR activity of the Pt/TSO was measured using linear sweep voltammetry (LSV) in O_2-saturated $HClO_4$ solution between 0.0 and +0.8 V in comparison with typical Pt/C in Fig. 5(c and d). The Pt/TSO exhibits an improved oxygen reduction activity in comparison with the Pt/C. At 0.55 V as half-wave potential [30,31], the current density (3.07 mA cm^{-2}) of the Pt/TSO for ORR is 1.60 times higher than that of the Pt/C (1.92 mA cm^{-2}). The ORR activities of the Pt/TSO and Pt/C

before and after the accelerated stability test were measured by comparing current density of the LSVs at 0.55 V as shown in Fig. 5(c and d). The ORR accelerated stability test was performed by applying the positive potential of 1.4 V (*vs.* NHE) for 30 min in O_2-saturated 0.1 M $HClO_4$ at 25 ^oC [32-34]. In Fig. 5(c), the Pt/TSO exhibits a negligible loss in ORR activity after the accelerated stability test.

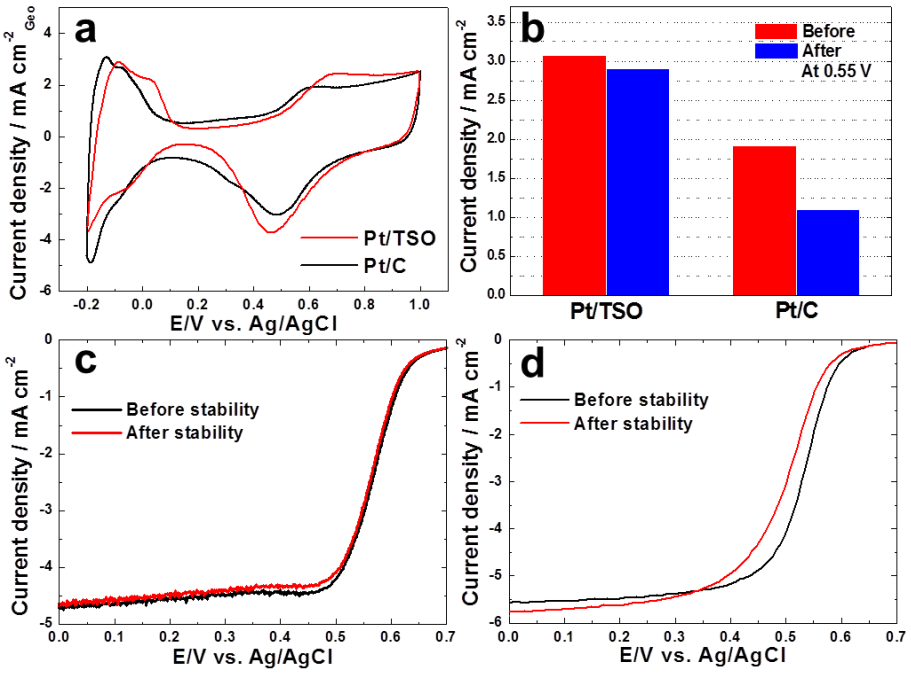

Figure 5. (a) CVs of Pt/TSO and Pt/C in Ar-saturated 0.1 M $HClO_4$. (b) Comparison of ORR current density at 0.55 V of Pt/TSO and Pt/C before and after the accelerated stability test in Figure 4c and d. ORR polarization curves of (c) Pt/TSO and (d) Pt/C before and after the accelerated stability test in O_2–saturated 0.1 M $HClO_4$.

In contrast, the Pt/C exhibits a considerable loss in ORR activity between +0.4 and +0.6 V, representing an activation polarization loss of the catalysts as indicated in Fig. 6(d). Furthermore, based on the geometric area of the glassy carbon electrode, the current density of the Pt/TSO at 0.55 V after the accelerated stability test is slight loss of 5.21 % whereas the Pt/C exhibits serious loss of 42.7% as indicated in Fig. 5(b). Krishnan *et al.* reported that the titanium suboxides as corrosion-resistant supports exhibit improved stability in oxygen reduction reaction [35]. Thus, we can demonstrate that the Pt/TSO displays enhanced electrocatalytic properties due to highly improved electrical conductivity and stability.

4. CONCLUSIONS

In summary, we synthesized electrical conductive titanium suboxides as a support material through catalytic reaction process in the presence of catalysts at relatively low-temperature. The as-

synthesized titanium suboxide support exhibited highly improved electrical conductivity. For the oxygen reduction reaction, the Pt/TSO showed much improved electrochemical activity and stability.

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