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Compressive strain as the main origin of enhanced oxygen reduction reaction activity for Pt electrocatalysts on chromium-doped titania support

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ABSTRACT

In this study, we have attempted to clarify the origin of the enhanced oxygen reduction reaction (ORR) activity of Pt on titania supports, which has been the subject of significant debate. To date, it has been claimed in several studies that the charge transfer from titania to Pt is the main origin of the enhanced ORR activity, while the theoretical adsorption model suggested that such charge transfer to Pt could lead to stronger OH adsorption and therefore a negative effect on ORR activity. We resolve this controversy by considering a lattice strain effect induced by the strong metal support interaction. EXAFS studies clearly show that a compressive strain leading to a lower *d*-band center is exerted on the Pt lattice on the titania-based supports. Hence, we strongly suggest that the main origin for the enhanced ORR activity is the compressive strain rather than the charge transfer.

1. Introduction

Because the oxygen reduction reaction (ORR) at the cathode has a significant overpotential in proton exchange membrane fuel cells (PEMFCs), it is essential to develop better electrocatalysts to enhance the ORR activity [1,2]. There have been several attempts to increase the ORR activity through, for instance, metal nanoparticle size or shape modification [3–5], metal alloying or dealloying [6–9], core–shell structure formation [10,11], or the deployment of oxide supports for the electrocatalyst to achieve a strong metal-support interaction [12] (SMSI). Among them, since the oxide supports can improve both the activity and durability through the SMSI and because their corrosion tolerance is higher than that of the conventional carbon supports, they have recently attracted intense interest from researchers in the electrocatalysis field. Most previous studies on oxide supports, however, have focused on only the durability enhancement due to their superior corrosion tolerance [13–16], while few papers have discussed the correlation between ORR activity and the SMSI. Theoretically, the correlation has been elucidated by the density functional theory (DFT) simulation performed by Linic et al. [17]. They suggested that when the electron charge transfer from a neighboring atom to Pt occurs, the chemical bond with surface hydroxyl (OH) becomes stronger, resulting in a negative effect on the ORR activity.

The conclusions of most of reports, however, conflict with this theoretical model. For example, Alonso-Vante et al. claimed that the Pt electron density was increased in the Pt/TiO_2 system based on lower observed shifts of the Pt 4*f* XPS signal, and they suggest that this density increase plays a key role in ORR activity enhancement [18]. Hwang et al. also suggested that the reason for the increased ORR activity was electron donation to Pt from an oxide such as $Ti_{0.7}Mo_{0.3}O_2$ [19] or TiO_2 [20], based on their analysis of the XANES white-line intensity. In other words, they concluded that the charge transfer is a major reason for the enhanced ORR activity. However, the theoretical model predicts that the charge transfer to Pt from the oxide supports will lead to a negative effect on the ORR activity. Hence, other factors should be considered in order to properly understand the origin of the ORR activity enhancement for Pt on titania supports. Even though both the lattice strain in Pt and the charge transfer are representative SMSI effects found in Pt on titania supports, no study investigating both effects simultaneously has been reported up to now.

Abbreviations: ORR, oxygen reduction reaction; PEMFCs, proton exchange membrane fuel cells; SMSI, strong metal-support interaction; DFT, density functional theory; XPS, X-ray photoelectron spectroscopy; XANES, X-ray absorption near edge structure; EXAFS, extended X-ray absorption fine structure; Cr-TiO_2, Cr-doped TiO_2 nanoparticles; TEM, transmission electron microscopy; XAS, X-ray absorption spectroscopy; DOS, density of states; CV, cyclic voltammetry; FWHM, full-width at half-maximum; ECSA, electrochemical surface area.

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In this study, we have investigated the lattice strain and the charge transfer simultaneously in order to resolve this controversy and to clarify the main origin of the enhanced ORR activity of Pt on titania supports. In particular, the doping of titania with Cr (Cr-TiO_2) enabled us to efficiently investigate such effects by increasing the electrical conductivity relative to that of bare titania. Pt/Cr-TiO_2 showed better ORR activity (higher specific activity at 0.9 V vs. RHE) than Pt/C. In order to identify the origin of the enhanced ORR activity, we discussed both the charge transfer based on the XPS analysis and the lattice strain based on EXAFS studies. Various high-resolution analysis techniques using a synchrotron beam revealed that, interestingly, the lattice strain effect is dominant in enhancing the ORR activity, in contrast with the previous discussion, where the charge transfer effect was considered to be the main factor involved in the increased ORR activity.

2. Experimental

2.1. Electrocatalyst synthesis

Cr-doped TiO_2 nanoparticles (Cr-TiO_2) were synthesized using a sol–gel and hydrothermal synthesis method. All the precursors were precisely measured to obtain a 5 mol% dopant ratio. Titanium isopropoxide (97%, Sigma Aldrich) and chromium nitrate (99%, Sigma Aldrich) were selected as precursors for the preparation of Cr-TiO_2 nanopowders, as reported in Kim and Han's paper [21]. Titanium isopropoxide was dispersed in acetic acid by stirring for 15 min, and then the solution was poured into an appropriate amount of distilled water with vigorous stirring for 1 h. Then, nitric acid was added to the solution, which was allowed to stand at 78 °C for 40 min, after which the temperature was continuously held for another 75 min with stirring. After this process, hydrothermal synthesis was conducted. Specifically, the solution mixed with distilled water was poured into an autoclave and the temperature was kept at 250 °C for 12 h. When the hydrothermal synthesis was finished, the solution was mixed with nitric acid and then stirred for 30 min. The prepared sample was fully filtered with distilled water then dried at 80 °C for 24 h. Then, the sample was heat-treated in the next step of the process. The sample was calcined to achieve crystallization at 500 °C for 4 h in an air atmosphere and then continuously calcined for dopant activation [22] at 300 °C for 2 h in an H_2 atmosphere. TiO_2 nanoparticles were synthesized with the same method for Cr-TiO_2 but without doping process.

Chloroplatinic acid hexahydrate (99.95%, Sigma Aldrich) was used as a precursor for the supported Pt samples. Pt nanoparticles were deposited on the surface of the support using sodium borohydride. First, the proper amount of Pt precursor was dissolved in distilled water. Then, the support material was dispersed in distilled water for 20 min using ultrasound and then vigorously mixed with the Pt precursor solution for 15 min. Next, the mixture of the Pt metal salt and support was reduced by the addition of the sodium borohydride solution. The precipitate was filtered and washed with distilled water then dried in oven at 80 °C for 24 h. For comparison, a Pt/C (Premetek, 20 wt% on Vulcan XC-72) electrocatalyst was also used.

2.2. Catalyst characterization

The amount of Pt was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Ultima 2 CHR, KBSI PN317), and the existence of the TiO_2 phase was confirmed by an X-ray diffraction (XRD, Philips PANalytical) test in which Cu Kα radiation ($\lambda = 1.5406$ Å) was used. The morphology of the powders was observed using transmission electron microscopy (TEM, JEOL JEM-2011) in the KBSI Busan Center. The electrocatalyst nanopowders were dispersed in ethanol by sonication for the TEM specimen preparation. XPS (ESCALAB 250 Busan Center, KBSI) was used to observe the oxidation of Pt and to confirm the existence of the dopant. All XPS energy data were calibrated with the C 1*s* peak (284.6 eV). X-ray absorption spectroscopy (XAS) Pt L_3-edge data were recorded in the transmission mode at the Pohang accelerator laboratory (PAL) using the 7D XAFS beam line. The source of the beam was a bending magnet (1.4557 Tesla), and the monochromator was an Si (1 1 1) double crystal with an energy resolution ($\Delta\lambda/\lambda$) of 2×10^{-5} at 10 keV. The background absorption spectra were removed using the IFEFFIT software [23]. The *k*-space range was set to 3–13 $Å^{-1}$, and the EXAFS data were obtained by performing a Fourier transform on the *r*-space, which was set to 1.5–3 Å. All XAS spectra were calibrated with Pt foil. Calculations of the charge transfer and the electron density of states (DOS) were conducted using the CASTEP code. CASTEP is a DFT-based pseudopotential total-energy code. The occupied states of the electrons were calculated using the Perdew-Wang 1991 (PW91) functional based on the generalized gradient approximation (GGA) [24]. A plane-wave cutoff of 300 eV was used to ensure convergence in the geometry optimization and DOS calculation. A grid of $3 \times 3 \times 3$ *k*-points generated by the Monkhorst–Pack scheme was used in the calculations [25]. The structure of the unit cell lattice was optimized, and the charge transfer and DOS of Pt/Cr-TiO_2 system were calculated. The UV–visible absorption spectra of samples were measured with an UV spectrophotometer (650 UV–VIS, Ocean Optics). The carrier density, mobility and electric conductivity were measured with a Hall effect measurement system (HMS 5000, Ecopia) using the Van der Pauw method with sample powders pressed into pellets at a pressure of 10 tons [26]. Cyclic voltammetry (CV) and ORR polarization test were carried out to examine the electrochemical reaction occurring on the surface of the electrocatalyst. All electrochemical tests were carried out at room temperature and ambient pressure. All the samples were mixed with acetylene black carbon at a 5:2 mass ratio to improve the electrical conductivity within the thin electrodes using a slightly modified version of the procedure reported in Gasteiger and Shao's paper [27]. A three-electrode electrochemical cell on a potentiostat (Biologic VSP) was used. Well-dispersed electrocatalysts were deposited on a glassy carbon electrode that was used as a working electrode (5 mm in diameter). A platinum rod and an Ag/AgCl electrode were used as the counter and reference electrode, respectively. The proper amounts of distilled water, isopropanol, and Nafion solution were mixed with the electrocatalysts and dropped onto the working electrode surface to enhance the bond between the working electrode surface and the electrocatalyst.

3. Results and discussion

3.1. Morphology and structure

TEM micrographs for Pt/C and Pt/Cr-TiO_2 are given in Fig. 1. The Cr-TiO_2 nanoparticles are quite homogeneous, with sizes of about 10–15 nm. The supported Pt nanoparticles are also well-dispersed, with sizes of about 3–5 nm for the sample. In the Pt/C, the particle size is slightly smaller (about 2–4 nm) than in Pt/Cr-TiO_2. The XRD patterns of Pt/C, Pt/TiO_2, and Pt/Cr-TiO_2 are shown in Fig. 2. In these XRD patterns, the strongest diffraction peak is the (1 0 1) peak of the anatase phase at 25? Along with a few other (1 0 3), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) peaks for the same phase. All peaks correspond well with the standard spectrum (JCPDS card No. 85-0439). For TiO_2 and Cr-TiO_2, only the anatase single phase