Evaluation and Enhancement of the Oxygen Reduction Reaction Activity on Hafnium Oxide Nanoparticles Assisted by L(+)-lysine

Mitsuharu Chisaka*, Noriaki Itagaki

Department of Electronics and Information Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan

ABSTRACT

Evaluation of the oxygen reduction reaction (ORR) on oxide compounds is difficult owing to the insulating nature of oxides. In this study, various amounts of L(+)-lysine were added to the precursor dispersion for the hydrothermal synthesis of hafnium oxide nanoparticles on reduced graphene oxide sheets (HfO$_x$–rGO) to coat the HfO$_x$ catalysts with layers of carbon, thereby increasing the conductivity and number of active sites. When the mass ratio of L(+)-lysine to GO, R, was above 26, carbon layers were formed and the amount monotonically increased with increasing R, as noted by cyclic voltammetry. X-ray photoelectron spectroscopy and rotating disk electrode analyses revealed that pyrolysis produced ORR-active oxygen defects, whose formation was proposed to involve carbothermal reduction. When $53 \leq R \leq 210$, HfO$_x$–rGO contained a similar amount of oxygen defects and ORR activity, as represented by an onset potential of 0.9 V versus the reversible hydrogen electrode in 0.1 mol dm^{-3} H$_2$SO$_4$. However, the number of active sites depended on R due to the amount of L(+)-lysine-derived carbon layers that increased both the number of active sites and resistivity towards oxygen diffusion.

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1. Introduction

The electrocatalytic reduction of oxygen has garnered significant attention owing to the need for cathodes in energy conversion devices for use in a variety of applications. Typical examples include Zn-air batteries in hearing aids, Al-air and Mg-air batteries in underwater propulsion devices, alkaline fuel cells (AFCs) in space craft, and polymer electrolyte fuel cells (PEFCs) in compact portable devices, stationary power systems, and vehicles. The electrolyte used in most of these energy conversion devices is alkaline media, where the oxygen reduction reaction (ORR) proceeds more smoothly than in acidic counterparts; therefore, the cathodes do not necessarily require catalysts based on platinum group metals (PGMs). PEFCs that utilize acidic polymer electrolyte membranes are of particular interest owing to the economic impact of the potential applications; however, the cathode requires excessive amounts of PGM catalysts for widespread use [1]. Therefore, extensive efforts have been made towards the development of non-PGM catalysts in acidic media [2–20].

The number of non-PGM catalysts for use in PEFC cathodes is limited owing to the corrosive conditions; the pH value is

estimated to be equal to or less than 1 [2], in addition to the high operating potential, e.g., 0.6–1.0 V versus the reversible hydrogen electrode, in vehicles. Most of the recent works on non-PGM catalysts have focused on nitrogen-doped graphitic carbon materials synthesized in the absence [3–6] and presence of iron/cobalt sources [2,7–12]. This type of catalyst has been synthesized via various routes and can show high ORR activity in acidic media when the graphitic layer is disordered by nitrogen doping to expose a large number of edges. Some of the activities are comparable to that of platinum, although the durability is often insufficient [12].

We have focused on another type of non-PGM catalyst, namely oxide compounds containing group 4/5 metals, owing to the high durability in acidic media confirmed by chemical leaching tests with inductively coupled plasma spectroscopy [13–16]. The drawback of this type of catalyst is the moderate current density, due to the electrical insulation properties. Therefore, recent works have focused on synthesizing oxide/oxynitride nanoparticles on conductive graphitic carbon materials to enlarge the specific surface area [17–20]. We recently developed a new route to synthesize hafnium oxynitride on reduced graphene oxide sheets (HfO$_x$N$_y$–rGO) to avoid the use of ammonia gas pyrolysis and to reduce the required catalyst volume by using the rGO sheets [19]. Nonetheless, the "active" surface area should be restricted to the point where the HfO$_x$N$_y$ nanoparticle catalysts contact the carbon supports. For the accurate evaluation of ORR activity on this

* Corresponding author. Tel.: +81 172 39 3559; fax: +81 172 39 3559.
  E-mail address: chisaka@hirosaki-u.ac.jp (M. Chisaka).

catalyst, coating the surface with conductive carbon layers that connect catalyst particles with supports are necessary. From this viewpoint, the decomposition of oxy-tantalum phthalocyanine was recently used to produce carbon layers that connected nano-tantalum oxide catalysts with multi-walled carbon nanotube supports [20]. However, the use of phthalocyanine-based polymers inevitably increases the cost of the catalyst and the carbon content of the resulting catalyst cannot be controlled because the molar ratio of tantalum to carbon is fixed in the oxy-tantalum phthalocyanine precursor. Therefore, an alternative metal-free carbon source is necessary.

In this study, L(+)-lysine was used as a carbon source to connect nitrogen-free HfO_x catalysts with rGO sheets. L(+)-lysine was selected as Xu et al. succeeded in the hydrothermal synthesis of uniform TiO_2 nanoparticles with the average size of ca. 6 nm and these particles were connected by lysine-derived thin carbon layers. During the hydrothermal synthesis, some nitrogen atoms in L(+)-lysine were doped into the TiO_2 nanoparticles in their study [21] whereas the nitrogen atoms were removed by pyrolysis in order to generate ORR activity via the formation of oxygen defects on HfO_2 in this study. Another role of L(+)-lysine was to increase the pH of the precursor dispersion to hydrolyze the hafnium tetrachloride precursor to hafnium hydroxide, which favored the adsorption of oxygen functional groups on GO to form HfO_2 nanoparticles after pyrolysis [17]. Hafnium is not an inexpensive and abundant element: the price in 2010 is $563 per kilogram [22] and world reserves of HfO_2 is 660,000 tons, which is only one order of magnitude larger than that of PGMs [23]. However, the present study revealed that the usage could be reduced by increasing the utilization as well as activity. Besides, the developed method for evaluation and enhancement of the ORR activity should be applied to other oxide catalysts, e.g., TiO_2 and ZrO_2. The morphologies, crystal structures, and surface chemical states of the catalysts were systematically investigated using field-emission transmission electron microscopy (FE-TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), respectively. The ORR activity and selectivity of the catalysts were also evaluated by rotating disk electrode (RDE) voltammetry and rotating ring-disk electrode (RRDE) voltammetry, respectively.

2. Experimental

2.1. Synthesis of catalysts

$20\,cm^3$ of an aqueous dispersion of GO (2 mg cm^{-3}, 763705, Sigma-Aldrich, U.S.) and $120\,cm^3$ of distilled water were sonicated for 1 h. The GO dispersion was then poured into a Teflon-lined autoclave under stirring, followed by the addition of $40\,cm^3$ of ethanol, 0.3 g of $HfCl_4$ (Mitsuwa Chemicals Co., Japan), and various amounts of L(+)-lysine (Wako Pure Chemical Industries, Ltd, Japan) to set the mass ratio of $GO:HfO_2:L(+)$-lysine to 1:5:R, where R ranged from 26 to 210. The pH of the resulting dispersion measured by pH test paper was always greater than 10. Next, the autoclave was closed then set in an aluminum block which was placed on a hot stirrer; hydrothermal treatment commenced at 453 K for 12 h with continuous stirring. After the hydrothermal treatment, the autoclave was allowed to cool and stirring was stopped prior to opening the autoclave. The resulting catalyst particles were washed with distilled water until a neutral pH was obtained. The particles were then dried overnight at 380 K and placed in an alumina boat that was set in a horizontal quartz tube furnace, which was slowly evacuated and purged with N_2 gas. The catalyst samples were heated from room temperature to various temperatures, T, at a rate of 10 K min^{-1}. T was maintained for 2 h, and the sample was then cooled to room temperature at an uncontrolled rate. The flow rate of N_2 was 100 standard cubic centimeters per minute (sccm; 1 sccm = $1.67 \times 10^{-8}\,m^3\,s^{-1}$).

2.2. Characterization

The crystal structures of the catalysts were analyzed using an X-ray diffractometer (M18XHF, Mac Science Co., Japan) with Cu-Kα
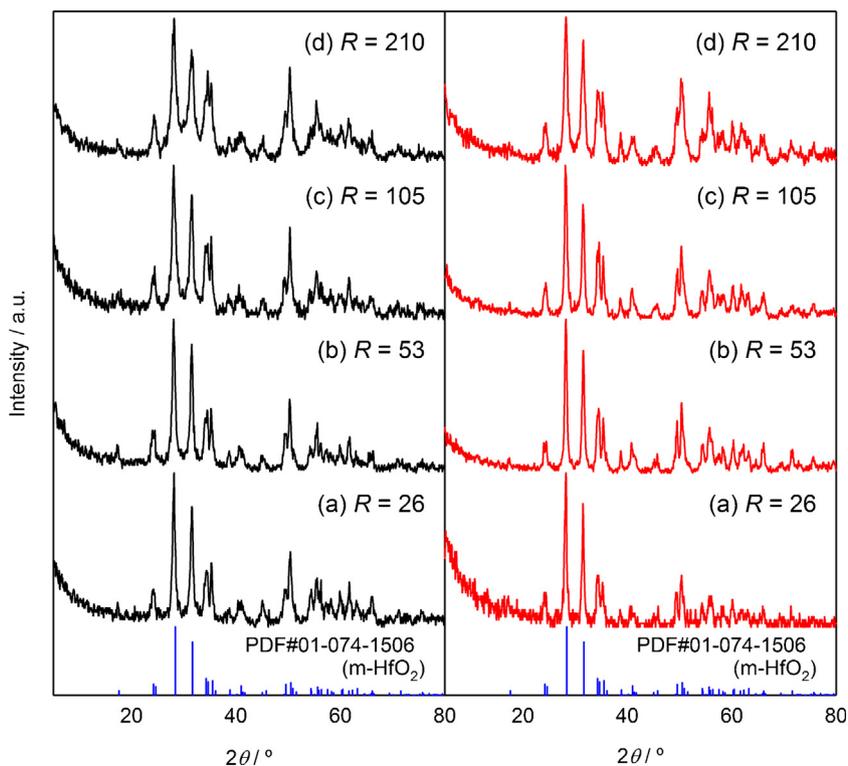
Fig. 1. X-ray diffraction patterns of HfO_x–rGO at four different R values: (a) 26, (b) 53, (c) 105, and (d) 210 before (left) and after (right) pyrolysis at T = 1273 K for 2 h under N_2.