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Tantalum oxide-based electrocatalysts made from oxy-tantalum phthalocyanines as non-platinum cathodes for polymer electrolyte fuel cells

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ABSTRACT

The development of non-platinum-based cathodes is required in order to commercialize polymer electrolyte fuel cells. We have previously investigated group 4 and 5 transition metal oxides because they exhibit high chemical stability under cathode conditions and are less costly than platinum. In this paper, tantalum oxide-based cathodes were prepared from oxy-tantalum phthalocyanines by heat treatment under low oxygen partial pressures. We successfully obtained nano-sized tantalum oxide-based particles dispersed on multi-walled carbon nanotubes to increase the oxygen reduction reaction (ORR) current density. We investigated the factors which influence ORR activity in terms of the onset potential and ORR current density. The onset potential increased with increasing crystalline distortion of orthorhombic Ta_2O_5, which was experimentally observed as changes in the position and full width at half maximum of the Ta_2O_5 (0 0 1) peak in the X-ray diffraction patterns. In addition, the amount of the deposited carbon strongly influenced the ORR current density because it affected the surface area of the oxides and the formation of local electron conduction paths.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) offer many advantages including high power densities, high energy conversion efficiencies, and lower operating temperatures. They are therefore suitable as power sources for vehicles and residential cogeneration power systems. However, the use of Pt as a cathode electrocatalyst for PEFCs is a problem because of its high cost, limited availability, and insufficient stability. To successfully commercialize PEFCs, low-cost non-platinum cathode catalysts with high stability must be developed. Iron- and/or cobalt-complex-based catalysts such as Fe–N–C [1], carbon-based catalysts [2], and chalcogenides [3] have been investigated as non-platinum cathode catalysts under cathode conditions for PEFCs. Recently, Cheon et al. reported that the oxygen reduction reaction (ORR) activities of Fe- and Co-doped ordered mesoporous porphyrinic carbons were greater than that of platinum [4]. However, these catalysts were unstable under cathode conditions, which include a severely corrosive (e.g. acidic) environment and oxidative atmosphere.

We have focused on Group 4 and 5 transition metal oxide-based compounds because of their high chemical stabilities under cathode conditions. We have previously described the acid stability and catalytic ORR activity for a number of materials, including tantalum-doped tungsten carbide [5], tantalum oxynitride [6–8], zirconium oxide [9–11], titanium oxide [12], zirconium oxynitride [13,14], tantalum carbonitride [15], and tantalum-oxide- or zirconium-oxide-based catalysts [16–18]. In addition, we revealed that the tantalum oxide-based catalysts prepared from tantalum carbonitride by heat treatment under low oxygen partial pressure showed definite ORR activity, and identified the active sites as oxygen vacancies on the oxide [19].

Unfortunately, the tantalum carbonitride precursors in the aforementioned work had small surface areas because they were prepared via heat treatment at high temperature (around 2000 K). Therefore, the surface areas of the oxide-based catalysts prepared by heat treatment under low oxygen partial pressures remained as low as several $m^2 g^{-1}$ [16]. However, the carbon and nitrogen components of the carbonitride precursors are considered to be

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effective for creating the oxygen-vacancy active sites [19]. Thus, an investigation of new methods for the synthesis of the oxide-based catalysts, which would increase the ORR current by increasing the surface areas of the catalysts, is warranted.

In this study, we prepared tantalum oxide nanoparticles using the organometallic complex oxy-tantalum phthalocyanine (TaOPc) as a precursor. We used multiwalled carbon nanotubes (MWCNTs) as both the support and electrical conductive material to form macro electron conduction paths in the catalyst powders. In addition, we investigated the relationship between the physicochemical properties and ORR activity (such as onset potential and ORR current density) to clarify the factors which influence the ORR activity.

2. Experimental

2.1. Catalyst preparation

Oxy-tantalum phthalocyanine (TaOPc [$TaOC_{32}H_{16}N_8$], Dainichiseika Color & Chemicals Mfg. Co., Ltd) was used as the starting material. The TaOPc (0.6 g) and MWCNTs (0.256 g, diameter = 10–15 nm, length = 3 μm) as a conductive material were dry ball milled with 180 chrome steel balls (5 mm in diameter) for 3 h at 400 rpm. The powders and balls were separated by sieving and the powders were ground in a mortar to obtain the catalyst precursor (TaOPc/MWCNT). The catalyst precursor was placed in a quartz tube and heated from room temperature to 900 °C at 20 °C/min under inert N_2 atmosphere. When the temperature reached 900 °C, a reactive gas mixture consisting of 2% H_2 with either 0.5 or 0.05% O_2 was introduced and continuously supplied at 1.7×10^{-6} $m^3 \cdot s^{-1}$ for 0.5 – 15 h. During this heat treatment, the precursor was oxidized gradually to form tantalum oxide. This oxidation process under low oxygen partial pressure is denoted as LO, and the heat treatment time is termed the oxidation time. The obtained catalysts are designated in the form "$TaC_xN_yO_z$/MWCNT_oxygen partial pressure-oxidation time", as for example, $TaC_xN_yO_z$/MWCNT_0.05%O_2–10 h. $TaC_xN_yO_z$ indicates that the compound has tantalum oxide structures and contains both C and N. X-ray diffraction spectroscopy (XRD; Rigaku Ultima IV, X-ray source: CuKα) was performed to reveal the crystalline structure, peak position, and full width at half maximum (FWHM) of the catalysts. X-ray photoelectron spectroscopy (XPS; PHI Quantum-2000, X-ray source: monochromated AlKα radiation) was used to reveal the valence of the tantalum at the surface of the tantalum oxide. Transmission electron microscopy (TEM; JEOL LEM-2100F) and scanning electron microscopy (SEM; JEOL JSM-7100F) were used to observe the morphology of the catalysts.

2.2. Electrode preparation

2.2.1. Stationary electrode

We used a stationary electrode system to accurately evaluate the onset potential instead of a rotating ring-disk electrode (RRDE), because the noise produced by the latter interfered with the accurate determination of the onset potential.

Catalyst powder (3 mg) was mixed in a 1:1 (mass ratio) solution of 1-propanol and distilled water (0.15 dm^3) with 0.5 wt% Nafion® solution (5 mm^3) to prepare a catalyst ink. The catalyst ink was repeatedly dropped on a polished glassy carbon rod (GC; φ = 5.2 mm) and dried at 60 °C until the oxides in the powder catalyst were supported at a loading of ca. 0.37 – 0.51 $mg \cdot cm^2$ on top of the GC.

2.2.2. Rotating ring-disk electrode (RRDE)

The RRDE consisted of a glassy carbon disk (6.0 mm in diameter) surrounded by a platinum ring with an internal diameter of 7.0 mm and an external diameter of 9.0 mm. Catalyst powder (2.45 mg) was mixed into a solution of 1-hexanol (0.10 dm^3) and 5 wt% Nafion® solution (4 mm^3) to prepare a catalyst ink. The catalyst ink (15 mm^3) was dropped on the polished disk of the RRDE and dried at 50 °C. The loading of the oxides in the powder catalyst on the RRDE was ca. 0.51–0.57 $mg \cdot cm^2$.

2.3. Electrochemical measurements

The stationary electrode measurements were performed with a 3-electrode cell and the RRDE measurements were performed with a RRDE cell. Both cells contained 0.1 mol dm^3 H_2SO_4 at 30 °C. A reversible hydrogen electrode (RHE) and a glassy carbon plate were used as the reference and counter electrodes, respectively. Slow scan voltammetry (SSV) was performed at a scan rate of 5 $mV \cdot s^{-1}$ from 0.2 to 1.2 V under O_2 and N_2 atmospheres. In the case of the RRDE measurements, the electrode rotation was set at 1600 rpm and the ring electrode was set at 1.2 V during SSV. The current density of oxygen reduction, j_{ORR}, was obtained by taking the difference between the third cycle SSV measurements in N_2 and O_2. The current density was based on the weight of the oxides: $mA \cdot g^{-1}$. For the evaluation of catalyst activity, we used the j_{ORR} at 0.8 V vs. RHE ($|j_{ORR}$@0.8 V$|$) and the potential at 5 $mA \cdot g^{-1}$ (E_{ORR}@5 $mA \cdot g^{-1}$) as the onset potential.

3. Results and discussion

During the preparation of the catalyst, we used chrome steel balls in the ball-milling step. However, there appeared to be no effect of Fe on the ORR activity because the j_{ORR} values for $TaC_xN_yO_z$/MWCNT_0.5%O_2-1 h samples prepared with either chrome steel or zirconia balls were nearly the same, as shown in Fig. S1 (Supplementary Information). Fig. 1 shows the j_{ORR} (normalized to oxide mass) versus E curves for $TaC_xN_yO_z$ (CN) made from tantalum carbonitride [19], $TaC_xN_yO_z$/MWCNT_0.5%O_2-1 h, and 0.05%O_2-10 h (We must express exactly as $TaC_xN_yO_z$/MWCNT_0.05%O_2-10 h, however, omit it 0.05%O_2-10 h when it is clear) as stationary electrodes. The total amount of supplied oxygen in the case of $TaC_xN_yO_z$/MWCNT_0.5%O_2-1 h was same as that of 0.05%O_2-10 h. The ORR currents of the $TaC_xN_yO_z$/MWCNT_0.5%O_2-1 h and 0.05%O_2-10 h started to flow at around 0.9 V. The E_{ORR}@5 $mA \cdot g^{-1}$ values of the $TaC_xN_yO_z$/MWCNT_0.5%O_2-1 h and 0.05%O_2-10 h materials were 0.894 and 0.875 V vs. RHE, and the $|j_{ORR}$@0.8 V$|$ values were ca. 463 and 310 $mA \cdot g^{-1}$, respectively. The $TaC_xN_yO_z$/MWCNT(CN) exhibited ca. 9 $mA \cdot g^{-1}$ at 0.8 V as a maximum value. Thus, the $|j_{ORR}$@0.8 V$|$ values for the

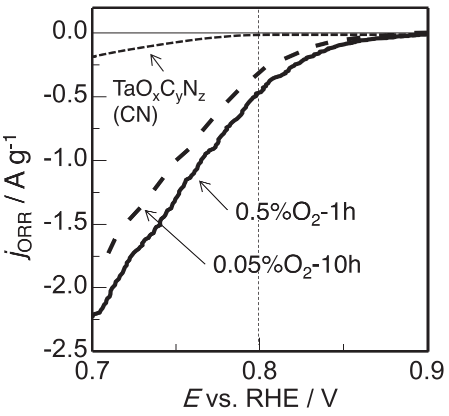

Fig. 1. j_{ORR} (normalized to oxide mass) – E curves for the $TaC_xN_yO_z$(CN) samples made from tantalum carbonitride, $TaC_xN_yO_z$/MWCNT_0.5%O_2-1 h, and $TaC_xN_yO_z$/MWCNT_0.05%O_2-10 h as stationary electrodes.

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