



Temperature dependence of oxygen reduction mechanism on a titanium oxide–based catalyst made from oxy–titanium tetra–pyrazino–porphyrazine using carbon nano–tubes as support in acidic solution



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ARTICLE INFO

Article history:

Received 1 February 2016

Received in revised form 7 May 2016

Accepted 9 May 2016

Available online 10 May 2016

Keyword:

polymer electrolyte fuel cell
non-platinum cathode
oxygen reduction reaction
titanium oxide
temperature dependence

ABSTRACT

Kinetic analysis of the oxygen reduction reaction (ORR) was performed on a titanium oxide–based cathode in 0.1 M HClO₄ based on the Damjanovic model by using a rotating ring disk electrode, as proposed by Hsueh et al. The titanium oxide–based cathode, produced from oxy–titanium tetra–pyrazino–porphyrazine via oxidation under a low partial pressure of oxygen using carbon nano–tubes as support, showed high reactivity in the four–electron reduction of O₂.

In addition, we applied Hsueh's method to the study of the temperature dependence of the ORR for the first time. The activation energies of the four–electron reduction reaction at an overpotential of –0.40 V and the two–electron reduction reaction at an overpotential of –0.50 V were calculated to be 45.6 and 45.5 kJ mol^{–1}, respectively.

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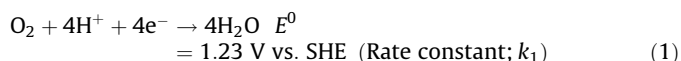
1. Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted great interest as power sources for vehicles and residential cogeneration systems. PEFCs offer many advantages including high power densities, high energy conversion efficiencies, and low operating temperatures. However, they also require large amounts of platinum for the cathode catalyst due to the slow rate of the oxygen reduction reaction (ORR). The high cost, limited supply, and low stability of platinum are obstacles to the commercialization of PEFCs. In addition, the ORR activity of Pt–based catalysts is insufficient, because an overpotential of approximately 0.2 V decreases the energy conversion efficiency of the PEFCs. Therefore, the development of highly stable, low–cost cathode catalysts is desirable.

We focused on group 4 and 5 transition metal oxide–based compounds, because of their high chemical stabilities under the operating conditions of the PEFC cathode, which include a severely

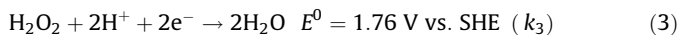
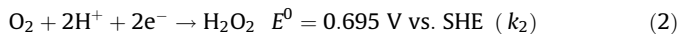
corrosive (i.e., acidic) environment and an oxidative atmosphere [1]. A basic principle of oxide–based cathodes is to use highly durable materials as cathode catalysts. In a previous study, we revealed that the active sites of group 4 and 5 metal oxide–based catalysts for the ORR are oxygen vacancies on the oxides, and that heat treatment under a low partial pressure of oxygen is useful for increasing the activity of the ORR [2–6]. Recently, we successfully prepared nano–sized titanium oxide–based cathodes using oxy–titanium tetra–pyrazino–porphyrazine (TiOTPPz) dispersed on multi–walled carbon nanotubes (MWCNTs) via heat treatment [7]. The titanium oxide–based catalysts showed higher ORR activity than other precious metal–free cathodes. However, the mechanism of the ORR on titanium oxide–based catalysts has not yet been analyzed in detail.

A representative ORR mechanism first proposed by Damjanovic et al. has two pathways, one with and another without formation of hydrogen peroxide [8].



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The rate constants k_1 and k_2 correspond to four- and two-electron reduction reactions of molecular oxygen, respectively. In addition, Hsueh et al. estimated the individual rate constants of these reactions (k_1 , k_2 , and k_3) on platinum using an analytical procedure based on rotating ring–disc electrode (RRDE) voltammetry [9]. This analytical method has been also applied to non-precious metal catalysts such as ruthenium–based catalysts [10–13], cobalt–based catalysts [14–16], iron–containing nitrogen-doped carbon catalysts [17–19], tantalum oxide–based catalysts [20], and titanium oxide–based catalysts in 0.1 M H_2SO_4 [7]. In this study, we have applied Hsueh's method to the ORR on a titanium oxide–based catalyst in 0.1 M HClO_4 instead of H_2SO_4 . HClO_4 solution is usually used for the study of the electrochemical behavior of the ORR because the perchlorate is non-adsorbable anion, similar to the solid acid (Nafion[®]).

Temperature is one of the most important parameters affecting reaction activity. PEFCs are operated at high temperature ($>80^\circ\text{C}$) to improve the activity of the ORR. Therefore, investigation of the temperature dependence of the ORR activity is necessary for applications that require high operating temperatures. Systematic research has been already reported on this topic for platinum catalysts [21]; however, the temperature dependence of oxide–based catalysts has not yet been investigated. In particular, there are few studies that have applied Hsueh's method to examine the temperature dependence of the ORR. Clarification of the temperature dependence of the ORR would improve our understanding of the characteristics of titanium oxide–based catalysts. In this study, we investigated the ORR mechanism using RRDE measurements between 20–60 °C.

2. Experimental

2.1. Preparation of catalyst

Oxy–titanium tetra–pyrazino–porphyrazine (TiOTPPz, $[\text{TiOC}_{24}\text{H}_8\text{N}_{16}]$, Orient Chemical Industries Co., Ltd.) was used as a starting material. TiOTPPz (0.39 g) and MWCNTs (0.26 g, diameter = 15 nm, length = 3 μm , used as the conductive material) were mixed in a mortar. The mixture was placed in a dry ball mill with 180 zirconia balls (diameter = 5 mm) and milled for 3 h at 560 rpm. The powder and balls were separated by sieving, and the powder was ground in a mortar to obtain the catalyst precursor. The precursor (50 mg) was placed in a quartz tube and heated to 900 °C at 20 °C min^{-1} under an Ar atmosphere. When the temperature reached 900 °C, Ar containing 2% H_2 and 0.05% O_2 was introduced and continuously supplied at $1.7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ for 3 h. During the heat treatment, the precursor was gradually oxidized to form titanium oxide due to the supplied O_2 . Amorphous carbon derived from the tetra–pyrazino–porphyrazine of the precursor covered the oxide particles. The amorphous carbon gradually oxidized to create a local reductive atmosphere near the oxide surface, promoting the formation of oxygen vacancies. The remaining amorphous carbon stayed on the surface of the oxides, and the CNT support participated in local and macro electron conduction paths.

The catalyst used in this study was designated “ $\text{TiC}_x\text{N}_y\text{O}_z/\text{CNT}$ ”, indicating that the compound contained titanium oxide structures as well as both C and N. The titanium oxide content in the catalyst was 11–13 mass%.

2.2. Preparation of electrode

The RRDE consisted of a glassy carbon disk (diameter = 6.0 mm) surrounded by a platinum ring with an internal diameter of 7.0 mm and an external diameter of 9.0 mm. The catalyst powder (2.45 mg) was mixed with 1–hexanol (80 mm^3) and 5 wt% Nafion[®] solution (4 mm^3) to prepare a catalyst ink. The definite diffusion limiting current must be observed for the application of Hsueh's method. We tried to evaluate the minimum loading of the catalyst to observe the definite diffusion limiting current as shown in Fig.S1. In case of the loading of 1.3 mg cm^{-2} the definite diffusion limiting current was observed. Therefore, the catalyst ink (12 mm^3) was dropped onto the polished disk of the RRDE and dried at 50 °C for 90 min to adjust the catalyst loading to 1.3 mg cm^{-2} .

2.3. Electrochemical measurements

The RRDE cell was fitted with a water jacket to control the temperature of the electrolyte. The RRDE measurements were performed with an RRDE cell containing 0.1 mol dm^{-3} HClO_4 at 20, 30, 40, 50, and 60 °C. A reversible hydrogen electrode (RHE) and a glassy carbon plate were used as the reference and counter electrodes, respectively. Prior to electrochemical measurements, cyclic voltammetry was performed as a pre-treatment at a scan rate of 150 mV s^{-1} in the potential range 0.05 to 1.2 V under an atmosphere of O_2 . Then, the electrolyte solution was replaced with a fresh batch to limit impurities produced during the pre-treatment. In order to obtain the ORR polarization curves, cyclic voltammetry was performed at a scan rate of 5 mV s^{-1} from 0–1.2 V under atmospheres of O_2 and N_2 . The electrode rotation rate was set to 400–2500 rpm, and the voltage of the ring electrode was set to 1.2 V. The disk current (I_D) was obtained by measuring the difference between the currents of the negative scan in N_2 and O_2 . Rate of hydrogen peroxide generation, $X_{\text{H}_2\text{O}_2}$, was calculated from the disc and ring (I_R) currents in the usual way [22]. Collection efficiency was experimentally determined to be 0.33 by using 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 0.1 M KNO_3 solution. The individual rate constants of the ORR (k_1 , k_2 , and k_3) were calculated based on the Damjanovic model [9].

The rate constants k_1 , k_2 , and k_3 are calculated from the intercepts and slopes of the plot of I_D/I_R vs. $\omega^{-1/2}$ and from the slopes of the plot of $I_{DL}/(I_{DL} - I_D)$ vs. $\omega^{-1/2}$ at different disk potentials, where, I_{DL} and ω are the limiting disk current and rotation rate, respectively. These rate constants are given by the expressions:

$$k_1 = S_2 Z_1 (I_1 N - 1) / (I_1 N + 1) \quad (4)$$

$$k_2 = 2S_2 Z_1 / (I_1 N + 1) \quad (5)$$

$$k_3 = NS_1 Z_2 / (I_1 N + 1) \quad (6)$$

where,

$$Z_1 = 0.62 D_{\text{O}_2}^{2/3} \nu^{-1/6} \quad (7)$$

$$Z_2 = 0.62 D_{\text{H}_2\text{O}_2}^{2/3} \nu^{-1/6} \quad (8)$$

and N is the collection efficiency (0.33), S_1 and I_1 are the slope and the intercept of the I_D/I_R vs. $\omega^{-1/2}$ plot, S_2 is the slope of the $I_{DL}/(I_{DL} - I_D)$ vs. $\omega^{-1/2}$ plot, D_{O_2} is the diffusion coefficient of the molecular O_2 , $D_{\text{H}_2\text{O}_2}$ is the diffusion coefficient of the molecular H_2O_2 and ν is the kinematic viscosity.

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