Durability of Titanium-niobium Oxides Mixed with Ti_4O_7 as Non-precious- and Carbon-free Cathodes for PEFCs in H_2SO_4 at 80°C

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ABSTRACT

To develop durable cathodes, their durability in acidic media at 80°C , which is close to the operation temperature of present polymer electrolyte fuel cells, must be evaluated. We attempted to use a Ti_4O_7 rod as the substrate, and it was observed to be more suitable than a glassy carbon rod because of its higher electrochemical stability. We evaluated the durability of titanium-niobium oxides mixed with Ti_4O_7 powder ($\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$) as a non-precious- and carbon-free cathode in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . We successfully demonstrated that the $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ did not deteriorate during start-stop and load cycle tests when a Ti_4O_7 rod substrate was employed.

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1. Introduction

Platinum (Pt) and Pt-alloy-supported carbon catalysts are used as cathodes in current polymer electrolyte fuel cells (PEFCs). However, the use of Pt is a problem because of its high cost and limited availability. We therefore focused on group 4 and 5 metal-oxide-based compounds because of their low cost and high stability in acidic media. In addition, the carbon commonly used as a support is oxidized at high potential, suggesting that carbon-free cathodes could result in highly durable cathodes. We prepared non-precious- and carbon-free cathodes composed of titanium–niobium oxides ($\text{Ti}_x\text{Nb}_y\text{O}_z$) with active sites and titanium oxides with the magneli phase of Ti_4O_7 as the electrically conductive phase.¹

We revealed that titanium–niobium oxides with Ti_4O_7 ($\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$) catalysts exhibited high durabilities in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 30°C .² However, we have not yet evaluated the durabilities of these catalysts at higher temperature, 80°C , which is close to the operation temperature of current PEFCs.

Another problem for the evaluation of the durability at 80°C is that the glassy carbon (GC) rod commonly used as a substrate for the working electrode cannot be used because GC is severely oxidized at high potential in acidic media at 80°C . In this study, we attempted to apply a Ti_4O_7 rod as the substrate because of its high electrochemical stability and conductivity.¹ In addition, we evaluated the durability of the $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C .

2. Experimental

2.1 Substrates

A TiO_2 rod (Toshima Manufacturing Co., Ltd., 4.8-mm diameter) was heat-treated at 1050°C in Ar gas containing 4% H_2 for 40 h to form Ti_4O_7 (a Ti_4O_7 rod). The crystalline structure of the TiO_2 and Ti_4O_7 rods were analyzed by X-ray diffraction (XRD; Rigaku corporation, Ultima IV, X-ray source: $\text{CuK}\alpha$). A GC rod (Tokai carbon, 5.2-mm diameter) was also examined as a substrate.

To evaluate the electrochemical stabilities of the GC and Ti_4O_7 rods in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C , a start-stop cycle test³ (triangular wave, 1.0–1.5 V vs. reversible hydrogen electrode (RHE), N_2 , scan rate: 500 mV s^{-1}) was performed as a degradation test using a 3-electrode cell. An RHE and GC plate were used as the reference and counter electrode, respectively. Cyclic voltammetry (CV) was performed in N_2 from 0.05 to 1.2 V vs. RHE at a scan rate of 150 mV s^{-1} to calculate the electric charge. The ratio of the electric charge of the initial state to that during the degradation test, N_{Q} , was calculated to estimate the electrochemical surface area. The apparent specific resistances of the Ti_4O_7 rod before and after the start-stop cycle test were measured under a pressure of 1.8 MPa.

2.2 Catalysts

The catalyst and electrode preparations were performed in the same manner as described elsewhere.² We prepared $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ catalysts by dry ball-milling TiO_2 and Nb_2O_5 powder mixtures and performing a reductive heat-treatment at 1050°C in Ar gas containing 4% H_2 for 50 h.

As a pre-treatment, 300 cycles of CV were performed in an O_2 atmosphere from 0.05 to 1.2 V vs. RHE at a scan rate of 150 mV s^{-1} . Chronoamperometry (CA) was performed to evaluate the catalytic activity of the oxygen reduction reaction (ORR) in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . Each potential was maintained for 300 s, and the average current during the last 10 s based on the mass of the catalysts was used as the ORR current density (i_{ORR}).

To evaluate the durability of the catalysts, load cycle³ (rectangular wave, 0.6–1.0 V vs. RHE, O_2 , holding time: 3 s) and start-stop cycle tests were performed as degradation tests in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . During the degradation test, CA was performed to evaluate the ORR activity. The durability was evaluated based on the initial ratio of $i_{\text{ORR}@0.7\text{V}}$ to that during the degradation test, $N_{i_{\text{ORR}@0.7\text{V}}}$. In addition, we examined the particle size and surface condition of $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ before and after the degradation tests using a field-emission scanning electron microscope (FE-SEM; JEOL JSM-7001F).

Figure 1. (Color online) XRD patterns of TiO_2 and Ti_4O_7 rods.

Figure 2. (Color online) Variation of N_Q of GC and Ti_4O_7 rods during start-stop cycle test.

3. Results and Discussion

First, we evaluated the applicability of Ti_4O_7 and GC rods as substrates. Figure 1 presents the XRD patterns of the TiO_2 and Ti_4O_7 rods. The TiO_2 and Ti_4O_7 rods consisted of tetragonal TiO_2 rutile and triclinic Ti_4O_7 , respectively, indicating that the surface of the TiO_2 rod was reduced to Ti_4O_7 . Even though the bulk of the Ti_4O_7 rod was not likely reduced to Ti_4O_7 , the surface detected by XRD was completely reduced to Ti_4O_7 . The specific resistance of the as-prepared Ti_4O_7 rod was $0.14 \Omega \text{ cm}$, which is sufficiently small for a substrate.

Figure 2 shows the variation of N_Q of the GC and Ti_4O_7 rods during the start-stop cycle test. N_Q of the GC rod significantly increased up to 2500 cycles and reached approximately 30 times the initial value at 20000 cycles, implying that the GC surface roughened up to 2500 cycles because of the oxidation. The GC rod could not be used as a substrate for the start-stop cycle test in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C because of its poor electrochemical stability. However, N_Q of the Ti_4O_7 rod hardly changed up to 20000 cycles. In addition, the specific resistance of the Ti_4O_7 rod after 20000 cycles was almost the same as the initial value, $0.16 \Omega \text{ cm}$, indicating that the surface of Ti_4O_7 was stable and that the electrical conductivity did not decrease. Therefore, Ti_4O_7 rods can be used as substrates for high-potential degradation tests in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C .

Figure 3 shows the initial activities of $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ using GC and Ti_4O_7 rods as substrates. Even for the GC rod, the ORR activity of $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ could be evaluated because the initial surface of GC was not yet roughened. The same potential-ORR current curve was obtained, indicating that the Ti_4O_7 rod could be used as a

Figure 3. (Color online) Initial activities of $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7 / \text{Ti}_4\text{O}_7$ and $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7 / \text{GC}$ rods.

Figure 4. (Color online) Variation of $N_{i\text{ORR}@0.7\text{V}}$ of $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7 / \text{Ti}_4\text{O}_7$ rod during start-stop and load cycle tests.

substrate instead of GC. In addition, a notable point was the high onset potential for the ORR, above 1.1 V vs. RHE. Although the ORR current was very small because of the large particle size (approximately $10 \mu\text{m}$), the high onset potential suggests the high quality of the active sites. Therefore, $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ has great potential as a non-precious- and carbon-free cathode.

We performed the start-stop and load cycle tests using the Ti_4O_7 rod as the substrate. Figure 4 shows the variation of $N_{i\text{ORR}@0.7\text{V}}$ of the $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ on the Ti_4O_7 rod during start-stop and load cycle tests. In both tests, the values of $N_{i\text{ORR}@0.7\text{V}}$ slightly changed during the initial potential cycling up to 2500 cycles. However, these values remained constant at 1 from 5000 to 20000 cycles. In addition, Fig. 5 presents FE-SEM images of the $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ before (a) and after the start-stop cycle test (b) and load cycle test (c). The particle size and surface condition of the $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ were almost unchanged before and after both degradation tests, indicating that the $\text{Ti}_x\text{Nb}_y\text{O}_z + \text{Ti}_4\text{O}_7$ exhibited superior stability for both the start-stop and load cycle tests in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . Therefore, we successfully demonstrated that the active sites on the titanium-niobium oxides were highly stable in both low- and high-potential regions at 80°C . In other words, non-precious- and carbon-free cathodes based on group 4 and 5 metal oxides exhibit high durability, as we expected.

4. Conclusion

We attempted to apply a Ti_4O_7 rod instead of a GC rod as the substrate for degradation tests in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . The Ti_4O_7 rod was observed to be more suitable as a substrate than GC because of its higher electrochemical stability.

Figure 5. FE-SEM images of $\text{Ti}_x\text{Nb}_y\text{O}_z+\text{Ti}_4\text{O}_7$ before (a) and after start-stop cycle test (b) and load cycle test (c).

We evaluated the durability of the $\text{Ti}_x\text{Nb}_y\text{O}_z+\text{Ti}_4\text{O}_7$ as a non-precious- and carbon-free cathode using the Ti_4O_7 rod as the substrate in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . We successfully demonstrated that the $\text{Ti}_x\text{Nb}_y\text{O}_z+\text{Ti}_4\text{O}_7/\text{Ti}_4\text{O}_7$ did not deteriorate during start-stop and load cycle tests in $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 80°C . Therefore, the oxide-based electrocatalysts exhibit great potential as highly durable non-precious- and carbon-free cathodes.

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References

1. F. C. Walsh and R. G. A. Wills, *Electrochim. Acta*, **55**, 6342 (2010).
2. A. Ishihara, M. Hamazaki, H. Imai, M. Matsumoto, Y. Kohno, K. Matsuzawa, S. Mitsuhashi, and K. Ota, *Electrochim. Acta*, to be submitted.
3. Fuel Cell Commercialization Conference of Japan (FCCJ), Proposals of the development targets, research and development challenges and evaluation methods concerning PEFCs, http://www.fccj.jp/pdf/23_01_kt.pdf.