ORIGINAL PAPER

Proton conduction properties of nano-titania modified by sulfuric acid impregnation

Takaaki Sakai · Seok-Jun Kim · Satoshi Kajitani ·
Jun-ichi Hamagami · Hiroyuki Oda · Maki Matsuka ·
Tatsumi Ishihara · Hiroshige Matsumoto

Abstract The proton conduction properties of sulfuric acid-modified nano-titania prepared by impregnation method were investigated. The proton conductivity of sulfuric acid-modified nano-titania was almost the same as that of hydrous sulfated nano-titania investigated in our previous work when the amount of adsorbed sulfate groups was almost the same. The highest conductivity was obtained at an adsorbed sulfate group amount of 0.42 mmol/g, not 0.97 mmol/g. This result indicates that the enhancement of conductivity with increasing amount of adsorbed sulfate groups is limited. This might be attributable to insufficient water molecule adsorption on the Ti^{4+} site coordinated with a bidentate sulfate group due to the prevention by excess sulfuric acid.

Keywords Nano-oxide · Proton conductor · Acid-modified titania · Surface conduction

Introduction

Nowadays, the establishment of a sustainable society is strongly desired to decrease environmental load. A promising approach to realize a sustainable society is to use hydrogen as a medium for energy storage and transfer. Hydrogen is produced by water electrolysis using renewable energy such as solar power and wind power, and the hydrogen thus produced is converted into electricity by fuel cells. In this manner, hydrogen can be used as an energy medium with less emission of pollutants compared with the existing economy that utilizes fossil fuels.

Currently, solid oxide fuel cells for large-scale power generation and polymer electrolyte fuel cells (PEFCs) for small-scale power generation are expected to be used in the economy. For PEFCs, Nafion, which has high proton conductivity at low temperatures, is used as electrolyte. However,

T. Sakai (✉) · H. Matsumoto (✉)
Environmental Technology Research Division, INAMORI
Frontier Research Center, Kyushu University,
744 Motooka,
Nishi-ku, Fukuoka 819-0395, Japan
e-mail: sakai@ifrc.kyushu-u.ac.jp
e-mail: matsumoto@ifrc.kyushu-u.ac.jp

S.-J. Kim · T. Ishihara
Department of Automotive Science, Graduate School of Integrated
Frontier Sciences, Kyushu University,
744 Motooka,
Nishi-ku, Fukuoka 819-0395, Japan

S. Kajitani · M. Matsuka · T. Ishihara
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University,
744 Motooka,
Nishi-ku, Fukuoka 819-0395, Japan

J.-i. Hamagami
Department of Materials Science and Engineering, Kurume
National College of Technology,
1-1-1 Komorino,
Kurume, Fukuoka 830-8555, Japan

H. Oda
Interdisciplinary Graduate School of Engineering Sciences,
Kyushu University,
6-1 Kasuga-kouen,
Kasuga, Fukuoka 816-8580, Japan

M. Matsuka
International Education Center, Faculty of Engineering,
Kyushu University,
744 Motooka,
Nishi-ku, Fukuoka 819-0395, Japan

Nafion has several problems such as low stability at high temperatures, high production cost, and crossover of reactant gases during fuel cell operation [1]. Thus, at present, the development of an alternative protonic conductor as a replacement for Nafion is highly desirable.

We have also investigated a novel proton conductor. A conceptual diagram of this proton conductor is shown in Fig. 1. Nafion consists of a polytetrafluoroethylene (PTFE) backbone and a perfluorinated ether side-chain terminating with sulfonic acid groups. Replacement of an oxide for the PTFE base is advantageous in terms of thermal stability and material costs. This type of proton conductor can be realized in *acid-modified oxides*. In addition to our group, Kanamura et al. have reported sulfuric acid-modified porous silica [2], and Miyayama et al. have reported sulfuric acid-modified zirconia [3]. Several groups have also investigated phosphoric acid-modified oxides [4–10].

We have already reported the proton conduction properties of sulfuric acid-modified nano-titania synthesized by hydrolysis of titanyl sulfate; its conductivity reached as high as 0.1 S cm^{-1} at 50 °C under a relative humidity of 80% [11]. However, in the case of hydrolysis of titanyl sulfate, control of the amount of sulfate groups adsorbed on nano-titania is difficult. Therefore, it is necessary to investigate an alternative method, which can be used to control the amount of adsorbed acid groups, for the synthesis of acid-modified nano-titania.

In this study, we report the synthesis of sulfuric acid-modified nano-titania by the sulfuric acid impregnation method. Nano-titania samples with various amounts of adsorbed sulfate groups were synthesized by changing the concentration of sulfuric acid for impregnation, and their proton conduction properties and proton conduction mechanism were investigated.

Experimental

Sample preparation

Nano-titania powder was synthesized by sol–gel method. A white precipitate was obtained by adding 21.5 g of titanium isopropoxide (95.0%, Wako Pure Chemical Industries, Co., Ltd.) to 50 g of isopropanol (99.9%, Wako Pure Chemical Industries, Co., Ltd.) and then adding 2.74 g of water dropwise into the solution under continuous stirring. After 1 h of continuous stirring, the resultant white precipitate was separated by centrifugation at 4,000 rpm for 10 min, washed by ultrasonic cleaning with 100 g of distilled water for 10 min, and separated by centrifugation again in order to remove isopropanol completely. This washing procedure was performed three times, and then the white precipitate was dried at 85 °C overnight. After that, the dried precipitate was ground with mortar and pestle and calcined at 400 °C for 5 h in air. The structure and crystallite size of the nano-titania powders were determined by X-ray diffractometry (Rint 2500HLR+, Rigaku) and transmission electron microscopy (TEM) analysis (EM-002B, TOPCON Corp.).

The nano-titania powders were impregnated with sulfuric acid and evaporated to dryness in order to adsorb sulfate groups on the surface of the nano-titania. In this case, the concentration of sulfuric acid was adjusted such that the nano-titania powders were obtained with an appropriate amount of sulfate groups. The amount of sulfate groups in the sample was estimated by using acid–base titration method; titration was performed by dispersing the sample powder into water and adding sodium hydrate (NaOH) solution, with phenolphthalein solution as an indicator. The state of the sulfate groups adsorbed on the nano-titania was observed using diffuse reflectance Fourier transform infrared spectroscopy (FT-IR) spectroscopy (FT/IR-610, JASCO Corporation).

Conductivity measurements

Conductivity was measured by a four-terminal AC impedance method at 30–350 °C under a humidified ambient oxygen atmosphere. The conditions of the measurement were almost the same as those in our previous work [11]. The sample powder obtained was shaped into a bar at 300 MPa with a cold isostatic press. Silver paste, which is conductive without baking, was printed on the bar sample as the electrode. The
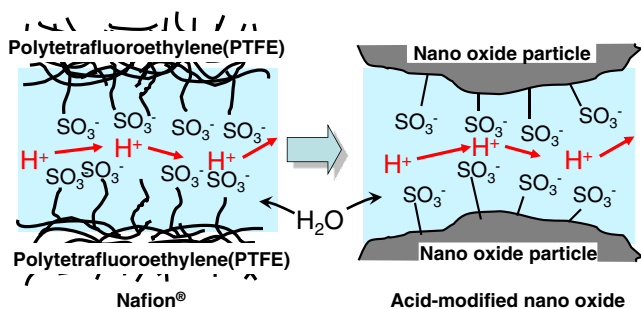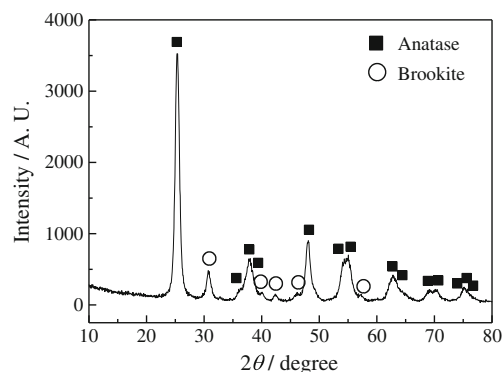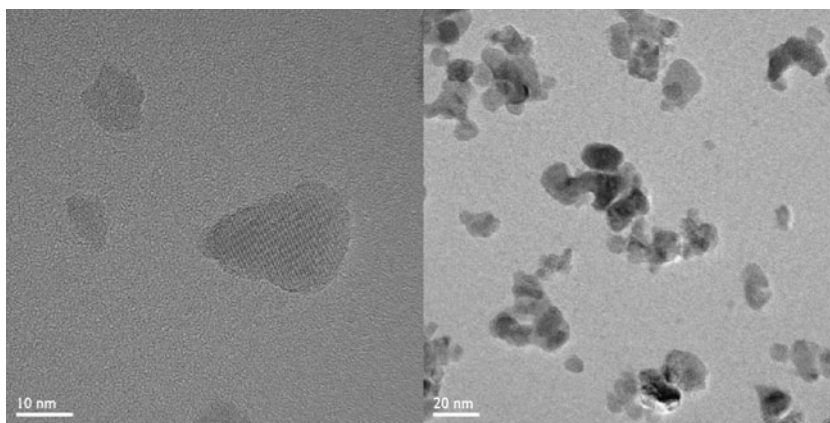

Fig. 1 Conceptual diagram of a proton conductor, *acid-modified nano oxide* [11]. The *shaded regions* in the respective figure are filled with large amounts of water molecules

Fig. 2 XRD pattern of nano-titania synthesized by sol–gel method

Fig. 3 TEM image of nano-titania synthesized by sol–gel method

frequency range of the impedance measurement was 5 Hz to 1 MHz with an applied voltage of 0.1 V using an impedance analyzer (Model 1260, Solartron Analytical). Usually, only one flat semi-circle was observed in the impedance measurement.

Results and discussion

The XRD pattern of the nano-titania powders after being calcined at 400 °C is shown in Fig. 2. The structure of the nano-titania powders was a mixed phase of anatase and brookite. Thus, the structure of the nano-titania prepared by sol–gel method was slightly different from that prepared by hydrolysis of titanyl sulfate (hydrous sulfate nano-titania) that consisted only of the anatase phase [11]. The crystallite size of nano-titania was estimated to be about 8 nm from the Scherrer equation [12, 13].

The TEM image of the nano-titania is shown in Fig. 3. TEM measurement was performed at up to 590,000-fold magnification with acceleration voltage of 200 kV (EN-002B, TOPCON Corp.). The numerous particles of about 10 nm in diameter can be seen in the pictures, even though the particles agglutinated with each other. Thus, by TEM

measurement, the particle size of the nano-titania prepared by sol–gel method was estimated to be about 10 nm.

The conductivity of nano-titania after being modified by sulfuric acid (sulfuric acid-impregnated nano-titania, 0.97 mmol/g sulfate groups) is shown in Fig. 4. The conductivity was measured with decreasing temperature from 350 to 30 °C after the temperature had been initially increased to 350 °C. For comparison, the conductivity of hydrous sulfate nano-titania with 1.1 mmol/g sulfate groups is also shown in Fig. 4 [11]. The conductivity of sulfuric acid-impregnated nano-titania was almost the same as that of hydrous sulfate nano-titania, suggesting that nano-titania with sulfuric acid groups on its surface exhibits high protonic conductivity and its conduction mechanism does not differ between the specimens prepared by either method.

The conductivity of the nano-titania samples increased with decreasing temperature due to the dependence of the conductivity on relative humidity: the relative humidity in Fig. 4 decreases with increasing temperature since P_{H2O} was fixed at 2.3 kPa [11]. It has been reported by Chan et al. that the large amount of protons was inserted into TiO_2 bulk when in contact with H_2SO_4 or $CsHSO_4$ due to space charge effect, and high proton conduction will occur due to protons
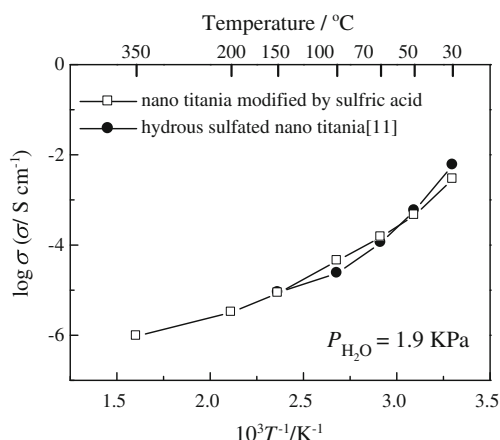

Fig. 4 Proton conductivity of nano-titania modified by sulfuric acid impregnation (*open square*)
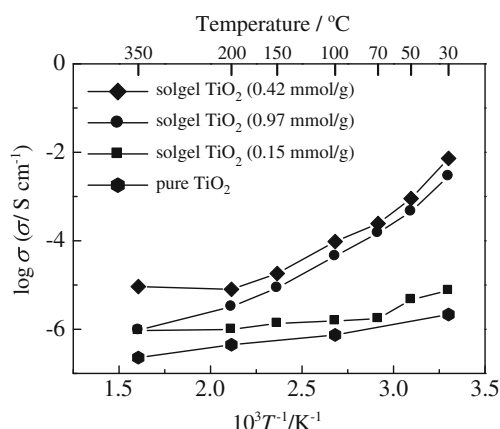

Fig. 5 Proton conductivity of nano-titania with various amounts of adsorbed sulfate groups
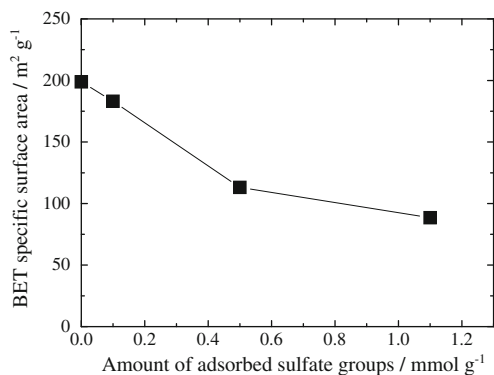
Fig. 6 Relation between the BET-specific surface area of the modified nano-titania and the amount of adsorbed sulfate groups

Fig. 8 Proton conduction mechanism of sulfuric acid-modified zirconia and sulfuric acid-modified titania [2]

inserted at a higher-temperature region [14, 15]. In this work, increase in conductivity at high temperature region was not observed. Thus, in this measurement condition, the effect of surface proton conduction was larger than that of the bulk proton conduction.

The dependence of the conductivity of the impregnated nano-titania on the amount of adsorbed sulfate groups is shown in Fig. 5. The conductivity of nano-titania tended to increase with the amount of adsorbed sulfate groups. However, the highest conductivity was obtained at an adsorbed sulfate group amount of 0.42 mmol/g, not 0.97 mmol/g. This indicates that the enhancement of conductivity with increasing amount of adsorbed sulfate groups is limited.

The BET-specific surface area of nano-titania with various amounts of sulfate groups is shown in Fig. 6. The BET-specific surface area decreased with increasing amount of adsorbed sulfate groups, suggesting that the apparent surface area was decreased due to the excess sulfuric acid.

Figure 7 shows the diffuse reflectance FT-IR spectra of nano-titania. In the case of the sulfuric acid-modified samples, the peaks were observed at around 3,500, 1,650, and 980–1,250 cm^{-1}. Arata et al. attributed the peaks at 980–1,250 cm^{-1} to bidentate sulfate coordination on the titania surface (980–990, 1,040, 1,130–1,150, and 1,210–

1,230 cm^{-1}) [16]. These peaks were clearly observed in the spectra of the sample with sulfate group amounts of 0.42 and 0.97 mmol/g, suggesting that the high conductivity of these samples was also caused by the formation of the bidentate sulfate coordination, similar to the case of hydrous sulfated nano-titania [11], while the peaks of the sample with sulfate groups of 0.15 mmol/g were not clearly observed (rather, these peaks seem to shift to the low frequency range).

The peak at around 3,500 cm^{-1} corresponds to the stretching vibration mode of water molecules and was also observed in the pure nano-titania sample. The peak of the samples at around 1,650 cm^{-1} is attributed to the bending mode of water molecules adsorbed on the Ti^{4+} site [17], and this peak decreased when the amount of adsorbed sulfate groups increased. It is likely that water adsorption on the Ti^{4+} site was prevented by the excess sulfuric acid when the amount of sulfate groups became higher. This decrease in water adsorption on the Ti^{4+} site might be the reason why the conductivity did not increase with increasing sulfate group amounting from 0.42 to 0.97 mmol/g. Miyayama et al. have proposed a model for the proton conduction mechanism of sulfuric acid-modified zirconia as shown in Fig. 8: when a water molecule is adsorbed on the Zr^{4+} site coordinated with a bidentate sulfate group, the hydroxyl group of the water molecule is incorporated in the oxide structure, and the proton of the water becomes a Brönsted acid involved in proton

Fig. 7 Diffuse reflectance FT-IR spectra of the sulfuric acid-modified nano-titania

conduction. If this model is also applied to sulfuric acid-modified titania as shown in Fig. 8, there is a possibility that the limitation on the conductivity increase was caused by insufficient water molecule adsorption on the Ti^{4+} site.

Conclusion

The proton conduction properties and proton conduction mechanism of sulfuric acid-modified nano-titania synthesized by impregnation of sulfuric acid were investigated in this study. The crystallite size of the nano-titania powders used was about 8 nm, and the nano-titania structure was a mixed phase of anatase and brookite. The conductivity of the impregnated nano-titania was almost the same as that of hydrous sulfated nano-titania. Although proton conductivity tended to increase with the amount of adsorbed sulfate groups, the highest conductivity was obtained at 0.42 mmol/g, not 0.97 mmol/g. This limitation on the conductivity increase might be caused by insufficient water molecule adsorption on the Ti^{4+} site coordinated with a bidentate sulfate group.

References

1. Costamagna P, Srinivasan S (2001) J Power Sources 102:242–252
2. Hara S, Miyayama M (2004) Solid State Ionics 168:111–116
3. Munakata H, Chiba H, Kanamura K (2005) Solid State Ionics 176:2445–2450
4. Carriere D, Moreau M, Lhalil K, Barboux P, Boilot JP (2003) Solid State Ionics 162–163:185–190
5. Kozawa Y, Suzuki S, Miyayama M (2009) J Electrochem Soc 156: B1401–B1405
6. Nogami M, Matsushita H, Goto Y, Kasuga T (2000) Adv Mater 12:1370–1372
7. Li G, Nogami M, Abe Y (1996) Solid State Ionics 83:209–214
8. Matsuda A, Kanazaki T, Tadanaga K, Tasumisago M, Minami T (2001) Electrochim Acta 47:939–944
9. Matsuda A, Kanazaki T, Tadanaga K, Tsumisago M, Minami T (2001) Solid State Ionics 145:161–166
10. Tsuru T, Yagi Y, Kinoshita Y, Asada M (2003) Solid State Ionics 158:343–350
11. Sakai T, Kajitani S, Kim SJ, Hamagami J, Oda H, Matsuka M, Matsumoto H, Ishihara T (2010) Solid State Ionics 181:1746–1749
12. Scherrer P (1918) Nachr Ges Wiss Göttingen 26:98–100
13. Milligan WO, Morriss RH (1968) J Am Chem Soc 86:3461–3466
14. Chan WK, Borghols WJH, Mulder FM (2008) Chem Comm 47:6342–6344
15. Chan WK, Haverkate LA, Borghols WJH, Wagemaker M, Picken SJ, Van Eck ERH, Kentgens APM, Johnson MR, Kearly GJ, Mulder FM (2011) Adv Func Mater 21:1364–1374
16. Arata K, Hino M (1990) Mater Chem Phys 26:213–237
17. Takeuchi M, Anpo M (2006) Mater Integr 19(7):35–42 (in Japanese)