

Long-term stability of sulfated hydrous titania-based electrolyte for water electrolysis

Seok-Jun Kim · Takaaki Sakai · Hiroyuki Oda ·
Yuji Okuyama · Yumi Mizutani · Jun-Ichi Hamagami ·
Maki Matsuka · Tatsumi Ishihara ·
Hiroshige Matsumoto

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Abstract The long-term stability in water was investigated for an inorganic proton conductor based on sulfated hydrous titania electrolyte in water electrolysis. Heat treatment temperature in the range of 400–700 °C during synthesis of the material was chosen as the critical parameter for the conductivity and stability in water. Electric resistance of the membrane electrode assembly using the sulfated hydrous titania in water and pH were investigated by the effect of heat treatment temperature on the stability of conductivity and acid detachment. TG, Fourier transform infrared spectroscopy, and energy-dispersive X-ray analysis measurements were performed to understand the amount and state of the sulfate groups on the surface of sulfated

hydrous titania. Heat treatment at 650 °C was found to obtain good conduction behavior for the sulfated hydrous titania and was confirmed to work for a stable water electrolysis.

Keywords Sulfated hydrous titania · Water electrolysis · Long-term stability

Introduction

The emission of carbon dioxide is caused by the continuous consumption of fossil fuels. Thus, the technical investigations

S.-J. Kim (✉) · T. Ishihara
Department of Automotive Science,
Graduate School Integrated Frontier Sciences,
Kyushu University,
744 Motoooka,
Nishi-ku, Fukuoka 819-0395, Japan
e-mail: kim-seok@ifrc.kyushu-u.ac.jp

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

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

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

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

T. Ishihara · H. Matsumoto
International Institute for Carbon-Neutral Energy Research
(I2CNER), Kyushu University,
744 Motoooka,
Nishi-ku, Fukuoka 819-0395, Japan

H. Matsumoto
Next-Generation Fuel Cell Research Center, Kyushu University,
744 Motoooka,
Nishi-ku, Fukuoka 819-0395, Japan

for utilization of renewable energies, such as solar, wind, and geothermal energies, are essentially required to reduce the use of fossil fuels. Hydrogen is one of the effective energy medium to be used in combination with the renewable energies which are fluctuating and uncontrollable and need energy storage to meet the electricity demand. Water electrolysis produces hydrogen from electricity and can be notably recognized as the production method of the storable energy from the renewable energy sources [1–3].

Proton exchange membrane (PEM) electrolysis has been expected to be a simple and environmentally adaptable hydrogen production process [4–8]. PEM water electrolysis cell consists of a membrane (most typically sulfonated fluorocarbons, e.g., Nafion) and gas/water diffusion electrodes, which are in contact with each other to form a membrane electrode assembly (MEA). PEM electrolyte is an important constituent of the water electrolysis cell because this membrane works as a medium for the proton transfer between the electrodes and the separation of produced hydrogen and oxygen.

The authors reported previously that a sulfated hydrous titania, in which proton conduction takes place on the surface of the sulfated titanium oxide nanoparticles, was successfully applied as the electrolyte for water electrolysis, even though its proton conductivity was slightly lower than that of Nafion membrane [9]. The sulfated hydrous titania nanoparticles were used as water-absorbable porous electrolyte, which was found to supply liquid water effectively to the anode. For the practical use in water electrolysis, however, the long-term stability of the electrolyte is also necessary. Since the chemical reaction of the surface of titania nanoparticles with sulfuric acid is the origin of the proton conduction in the sulfated hydrous titania [9, 10], detachment of the chemisorbed sulfuric acid group, probably residing in the form bidentate SO_4 [10, 11], will be concerned to result in time-dependent deterioration of the proton conductivity and contamination of water with sulfuric acid.

In this study, the stability of the sulfated hydrous titania electrolyte soaked in water was investigated by monitoring the electrolyte resistance and acid dissolubility in water as functions of time. The sulfated hydrous titania was synthesized as a precipitate of titanyl sulfate aqueous solution on warming at around 70 °C, followed by collecting, washing, drying, and final heat treatment at given temperatures [10]. As reported previously, the final heat treatment has different effects to the properties of the sulfated hydrous titania [9, 10]. On one hand, the heat treatment allows chemical bonding of sulfuric acid on to the surface of titania nanoparticles, distinguished by the change in infrared (IR) spectra and resulting in the increase in the proton conductivity. On the other hand, sulfuric acid evaporates at 400–600 °C, as represented later in Fig. 3. Therefore, the heat treatment temperature is a critical parameter for the state and

concentration of sulfate groups remaining in the specimen and the proton conductivity as discussed later in detail and has been taken as a parameter to compare the stability of the sulfated hydrous titania specimens in water in this study. The water electrolysis experiments were conducted potentiostatically and the current was monitored to discuss the long-term stability of selected samples.

Experimental

Sulfated hydrous titania was prepared by thermal hydrolysis of titanyl sulfate ($\text{TiOSO}_4 \cdot n\text{H}_2\text{O}$, $n=1-2$, Kishida Chemical Co., Ltd.) in an aqueous solution in the same procedure described in the previous report [9, 10]. A precipitate generated in 0.17 M TiOSO_4 solution on warming at 70 °C was collected and washed by distilled water using hydrophilic Teflon filter. The resulting powder was heat treated in air at 400–700 °C. The formation of sulfate groups on the surface of the sulfated hydrous titania was analyzed by diffuse reflectance Fourier transform infrared (FT-IR) spectroscopy (FT/IR-610, JASCO Corporation). The energy-dispersive X-ray analysis (EDX, VE7800, Keyence) was performed to examine the change in the amount of absorbed acid groups on the surface of sulfated hydrous titania.

Water electrolysis cells, shown in Fig. 1, were prepared by following the procedure reported previously [9]. The commercial Pt-loaded carbon electrodes (Electrochem Inc., EC-20-10-7, Pt loading 1.0 mg cm^{-2}) was used both for the anode and cathode. The sulfated hydrous titania powder was mixed with Nafion ionomer (20 wt% in aliphatic alcohol solution, Sigma-Aldrich Co., Ltd.) at 10 wt% and 2-propanol as a solvent in mortar, and resulting slurry was painted on to the catalyst side of the Pt-loaded carbon electrode. The top view of the sulfated hydrous titania electrolyte was observed by the scanning electron microscope (SEM, Topcon sm-350). A set of half electrode/electrolyte cells were put together and hot pressed at 140 °C and at 100 kgf cm^{-2} for 1 min to obtain a MEA. As shown in Fig. 1, the MEA consists of the different sizes of half cells for the smooth water absorption into the sulfate hydrous titania electrolyte. The MEA sample was attached with gold lead wires and kept in 50 mL of distilled water. The 2-probe AC impedance technique was performed to measure the electrolyte resistance in the water under an AC voltage of 50 mV and frequency range of 0.1 Hz to 1 MHz by using an impedance analyzer (Versastat3-400, Metek Co., Ltd.). The Nyquist plot in the complex plane typically consisted of one partial arc at high frequencies ($>10^4$ Hz) followed by dispersive rising line (or a large arc). The former arc was attributed to the electrolyte resistance to determine. pH of the water was monitored to evaluate the dissolubility of sulfuric acid in the sulfated hydrous titania.

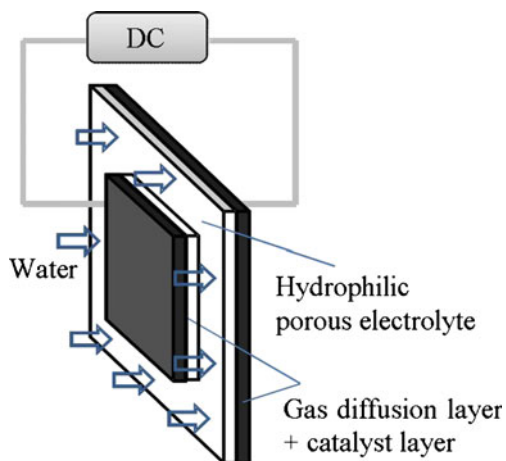
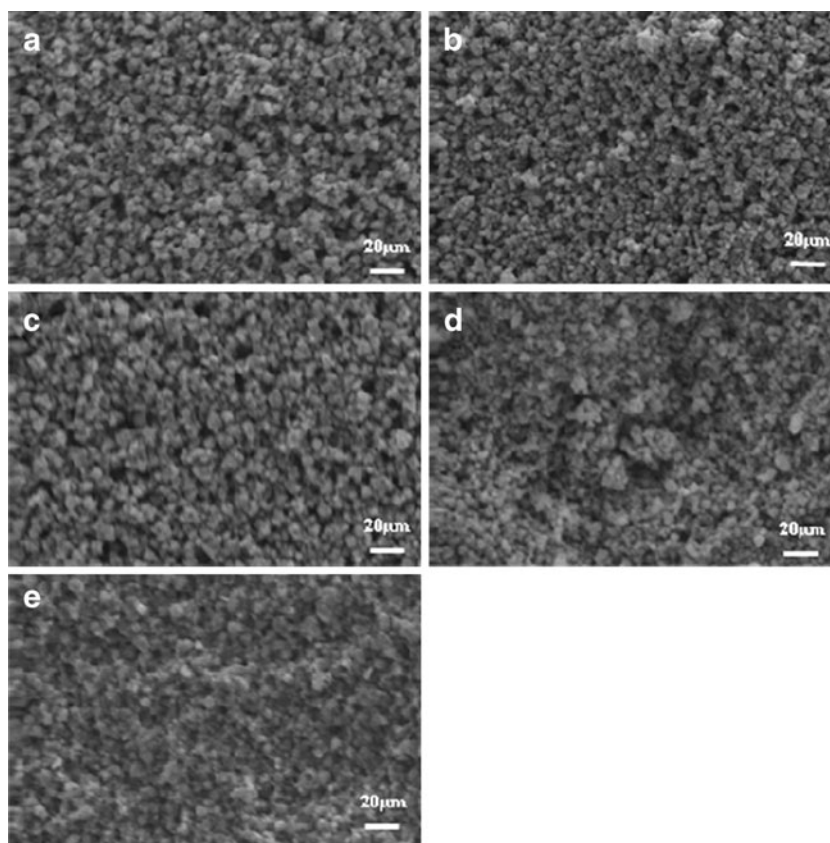


Fig. 1 Illustration of the water electrolysis cell structure utilized in this study

The water electrolysis was also performed for the evaluation of i - V characteristics. The laboratory-made gas diffusion electrodes with Pt loading amount of 2.5 mg cm^{-2} [9] were used to fabricate the electrolysis cells for the long-term cell tests at 25°C . The direct current was passed through the cells potentiostatically using a DC power supply (HA-151B, Hokuto denko Co., Ltd.) and the current was monitored as a function of time.

Fig. 2 SEM images of the top view of sulfated hydrous titania electrolyte with different heat treatment temperature: **a** 400°C ; **b** 500°C ; **c** 600°C ; **d** 650°C ; and **e** 700°C



Result and discussion

Effect of heat treatment temperature on the stability of sulfated hydrous titania in water

The SEM images of a top view of sulfated hydrous titania electrolyte heat treated at various temperatures on GDL with 10 % contents of Nafion were shown in Fig. 2. The all electrolytes appeared to have a quiet homogenous distribution and particles of sulfated hydrous titania were uniformly dispersed with Nafion in the electrolyte. The all electrolytes, which have a porous structure, show no structural cracks, even though the heat treatment temperature is different with each other.

The MEAs prepared with sulfated hydrous titania heat treated at 400 , 500 , 600 , 650 , and 700°C were soaked in water at 25°C and their resistances were measured. The time course of electrolyte resistance after soaking in water is shown Fig. 3a. It is apparent that the electrolyte resistance at an initial period was minimized when the sample was treated at 400°C and the samples heat treated at 400 – 600°C ; the resistance increased with time and reached several $10 \Omega \text{ cm}^{-2}$ in 3 days. The observed variation of the electrolyte resistance was not stable in water. In contrast, the sample heat treated at 650°C presented steady conduction behavior in water, i.e., the resistance changed only slightly from 23.4 to $17.0 \Omega \text{ cm}^{-2}$ in

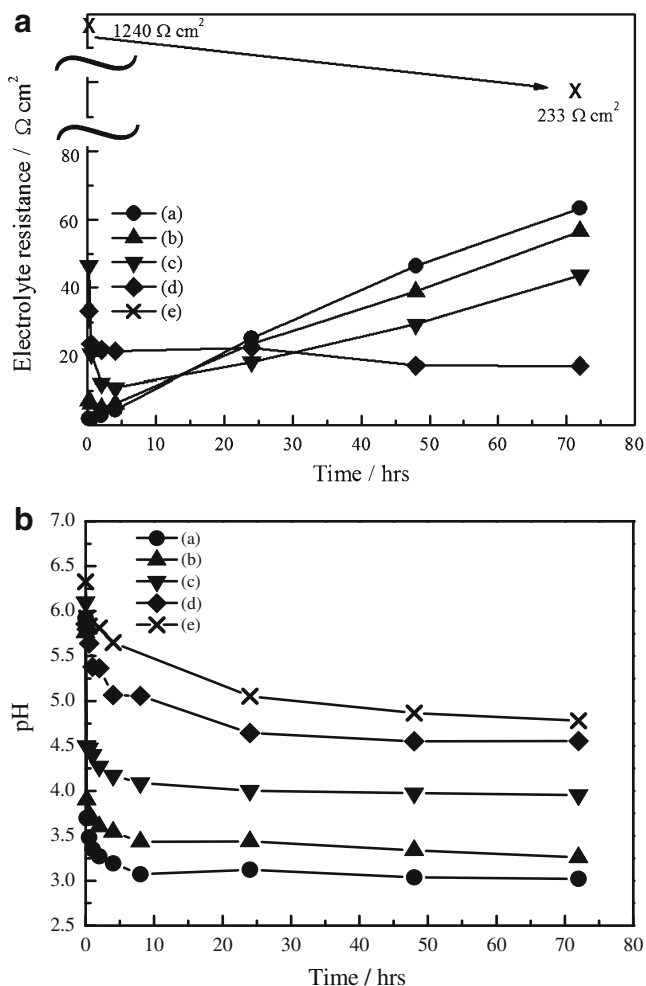


Fig. 3 **a** Time courses of electrolyte resistance in which the MEAs prepared with sulfated hydrous titania are heat treated at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 650 °C, and (e) 700 °C during soaking in water for 3 days. **b** Time courses of pH of water in which the MEAs prepared with sulfated hydrous titania are heat treated at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 650 °C, and (e) 700 °C during soaking in water for 3 days

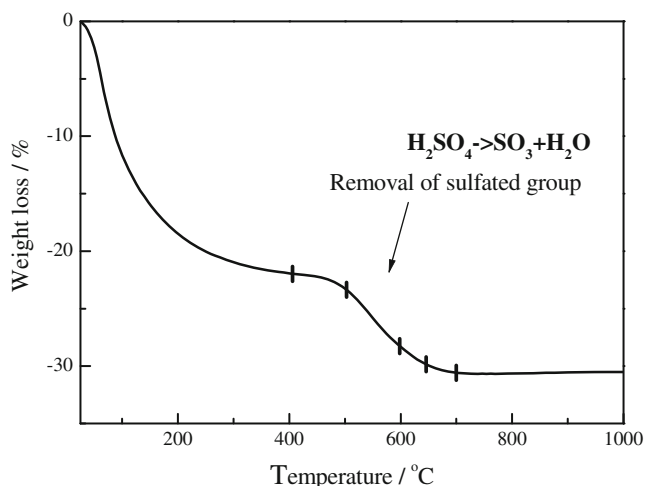


Fig. 4 TGA result of sulfated hydrous titania. The bars indicate the heat treatment temperature in this study. TGA curve is reproduced from ref. [10]

3 days. The heat treatment at 700 °C resulted in extremely high resistance. Conclusively, the heat treatment at 650 °C was effective to stabilize the conductivity of sulfated hydrous titania in water. The effective temperature range is narrow: The heat treatment at 400–600 °C resulted in time-dependent deterioration of the conductivity and the sample as heat treated at 700 °C largely lost the proton conductivity in water.

Figure 3b shows the time courses of pH of water in which the MEAs are soaked. It started from around pH=6 which resulted from dissolution of carbon dioxide in air in the laboratory distilled water. The values decreased for the first time and reached almost constant, apparently resulted from the detachment of sulfate groups from the surface of titania

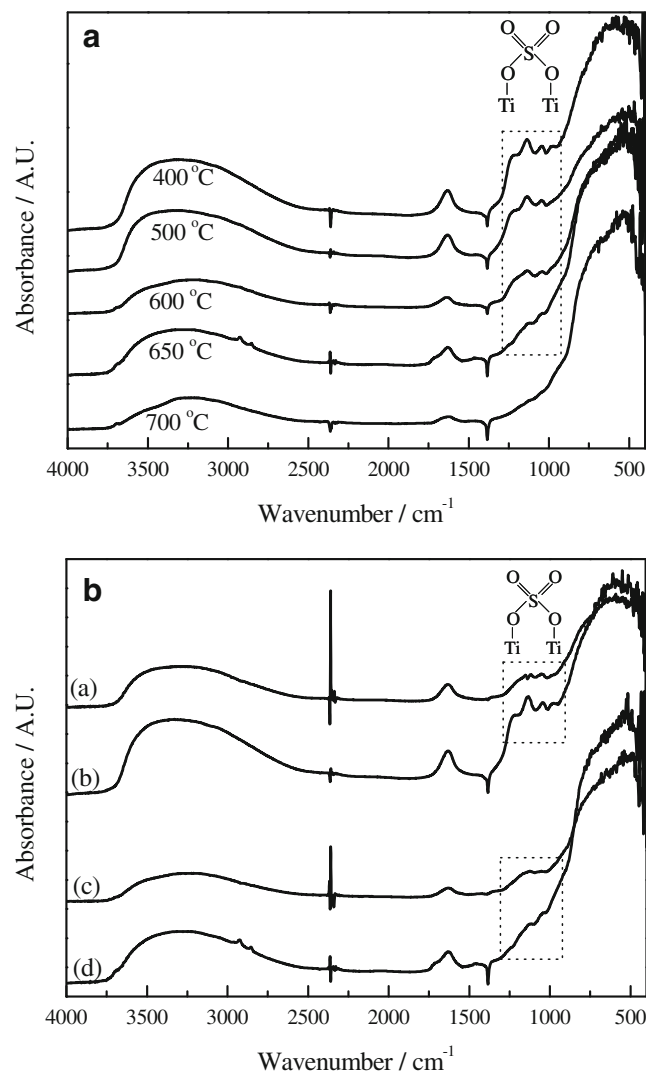


Fig. 5 **a** Diffuse reflectance IR spectra of the sulfated hydrous titania. **b** Comparison of the change in IR spectra of (a) sulfated hydrous titania heat treated at 400 °C measured after soaking in water for 3 days, (b) sulfated hydrous titania heat treated at 400 °C measured before soaking in water, (c) sulfated hydrous titania heat treated at 650 °C measured after soaking in water for 3 days, and (d) sulfated hydrous titania heat treated at 650 °C measured before soaking in water

Table 1 EDX results of sulfated hydrous titania before and after soaking in water for 3 days; the samples were heat treated at either 400 °C (HT400) and 650 °C (HT650)

	Ti (atomic %)	O (atomic %)	S (atomic %)	S/Ti ratio
HT400 before soaking in water	31.5	64.4	4.1	0.13
HT400 after soaking in water for 3 days	29.0	68.8	2.2	0.075 (↓ 42 %)
HT650 before soaking in water	38.4	61.2	0.4	0.010
HT650 after soaking in water for 3 days	26.0	73.8	0.2	0.0089 (↓ 11 %)

particles. The stationary pH lowers as the heat treatment temperature is lowered. As reported previously [10], thermo gravimetric analysis, represented as Fig. 4, suggests that the sulfate groups on the surface of titania start to evaporate at 400 °C and disappears at 700 °C. The stationary pH values primarily reflected the initial amount of sulfate groups residing in the specimen. The pH value of the sample heat treated at 650 °C showed almost 5.0 after 3 days. The reason of pH decrease in sample heat treated at 700 °C might be caused by the small amount of sulfated group from the mixed Nafion and all heat-treated samples at various temperatures are slightly affected in water. This result indicates that the amount of detached sulfuric acid from the sample was very small and is consistent with the stable conductivity observed in Fig. 3a, b.

FT-IR and EDX analysis

Figure 5a shows the diffuse reflectance IR spectra of the sulfated hydrous titania. Peaks at around 3,500 and 1,650 cm^{-1} are attributed to the stretching and bending vibration of OH bonds. Peaks in the range of 1,000–1,250 cm^{-1} originated from the sulfate groups. In our previous report, these peaks were attributed to the bidentate sulfate coordination on the surface of titanium oxide, according to the literature [11], and the sulfate groups in such a state was considered

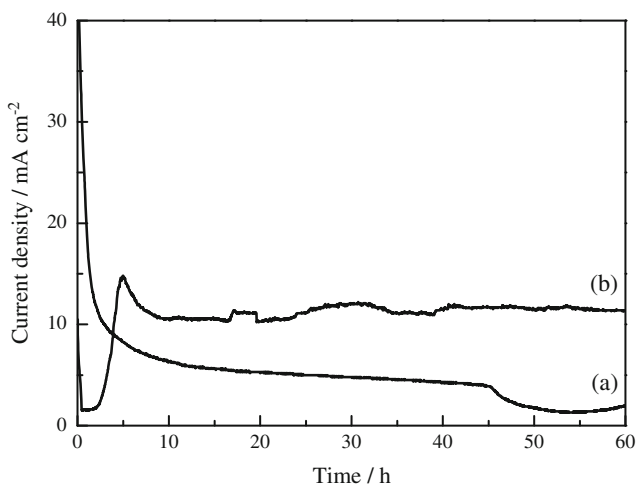


Fig. 6 Long duration test of MEA prepared with sulfated hydrous titania heat treated at (a) 400 °C, (b) 650 °C under a constant voltage of 1.8 V at 25 °C

to be the proton source for the conduction [10]. The idea is consistent with the magnitude of the peaks in Fig. 5a, i.e., the peaks shrank with increasing heat treatment temperature and almost disappeared in the sample heat treated at 700 °C that indicated very high resistivity. Figure 5b compares the change in IR spectra of sulfated hydrous titanias heat treated at 400 and 650 °C measured before and after soaking in water for 3 days. The peaks originated from the sulfate groups (1,000~1,250 cm^{-1}) were obviously collapsed after soaking in water for 3 days, which is caused by the detachment of sulfuric acid from the oxide. In contrast, the shape of the absorption peaks was nearly unchanged before and after soaking in water for 3 days for the sample heat treated at 650 °C. This result suggests that the heat treatment at 650 °C fixed the sulfate groups tightly on to the oxide surface. This idea is quantitatively supported by the result of EDX analysis as summarized in Table 1. Before soaking in water, the sample heat treated at 400 °C had an atomic ratio of S to Ti of 0.13 which decreased to 0.075, and 42 % of sulfur was lost in water during 3 days.

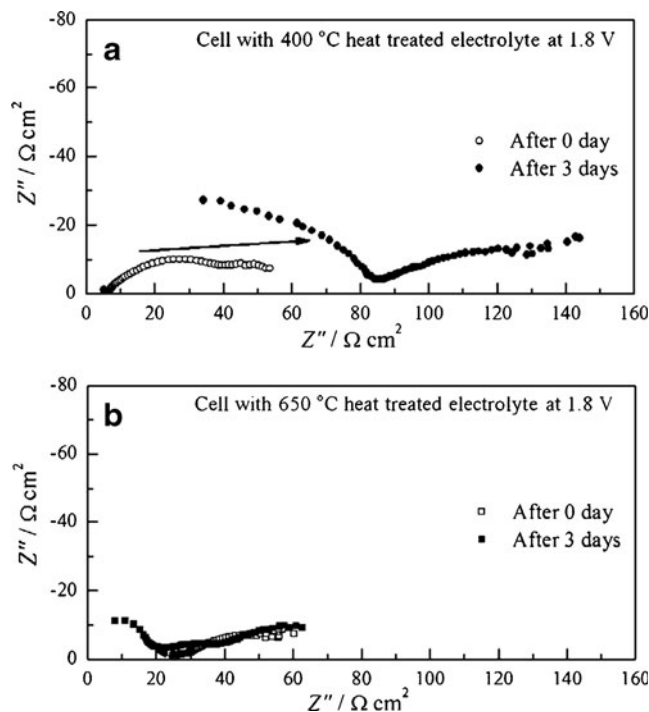


Fig. 7 Comparison with the impedance spectrum of the cells using sulfated hydrous titania at the applied voltage at 1.8 V after 0 day and 3 days. **a** Cell with 400 °C heat-treated electrolyte and **b** cell with 650 °C heat-treated electrolyte

The S/Ti ratio was 0.010 in the sample treated at 650 °C, much smaller than the former case, but 89 % remained during the soaking in water for 3 days. EDX possibly interferes with one another and the absolute values of S/Ti ratio will not be reliable. However, this result, as well as the IR spectra in Fig. 5b, means that less amount of sulfate groups are originally contained in the sample heat treated at 650 °C but is less dissolving into water. This is the most important information provided from the above-mentioned experiments. On the other hand, the above-mentioned results suggests that the chemical state of sulfate groups on the titania surface will not be unique but is dependent on the heat treatment temperature, governing the dissolution tendency. This feature is important to manage the conductivity and stability of the sulfated hydrous titania. The chemical states of the sulfate groups are not yet clarified in this study and are to be investigated for the future report.

Long-term stability of water electrolysis

Water electrolysis experiment was conducted using the samples heat treated at 400 and 650 °C for the affirmation the long-term stability in the above results and discussion. As shown in Fig. 6, long duration test was carried out at 25 °C and constant voltage of 1.8 V with monitoring the current. In the case of the cell using sulfated hydrous titania as heat treated at 400 °C, a rapid decay of the current during water electrolysis was observed for 3 days. On the other hand, the cell using sulfated hydrous titania heat treated at 650 °C showed a steady current flow during water electrolysis, although the small decay of current for a short time was observed due to the slow water transport through the electrolyte.

In order to discuss what is the main reason for the stable cell performance, the impedance spectrum of water electrolysis cells using the 400 and 650 °C heat-treated electrolyte at the voltage of 1.8 V are shown in Fig. 7a, b, respectively. The impedance spectroscopy generally provides the information on the electrolyte resistance and electrode overpotential. In Fig. 7a, the electrolyte resistance which contributes to IR potential drop between the anode and cathode drastically increased during water electrolysis after 3 days. The cell using sulfated hydrous titania heat treated at 650 °C showed nearly unchanged electrolyte resistance after 3 days in Fig. 7b. The electrode overpotential was not largely different in the spectra of both electrolysis cells. Therefore, different electrolysis performance can be attributed to the electrolyte resistance which is dependent on the dissolution of sulfated groups on the surface of titania into water. This result indicates that the loss of conductivity of the electrolyte is the major reason for the long-term stability of water electrolysis cell.

The electrolyte using sulfated hydrous titania heat treated at 650 °C reveals the stable conductivity with extremely small detachment of acid groups in water. The sulfated hydrous titania heat treated at 650 °C has a long-term stability, leading to the stable cell performance for water electrolysis.

Conclusion

The sulfated hydrous titania heat treated at 650 °C showed the stable conduction behavior and low acid dissolubility in water. The effective temperature range for the heat treatment was narrow, i.e., heat treatment at lower temperatures causes time-dependent deterioration of the conductivity accompanied by much dissolution of sulfate groups into water, while the higher temperature treatment leads to the loss of conductivity. TG, FT-IR, and EDX measurements suggest that the heat treatment at 650 °C leads to the partial evaporation of sulfate groups and tight bonding of the remaining ones to allow stable conduction behavior. Stable current–voltage characteristics could be also observed in water electrolysis experiment and the choice of the suitable heat treatment temperature is crucial for the preparation of the proton conducting sulfated hydrous titania for use in water electrolysis.

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