



Sulfated zirconia nanoparticles as a proton conductor for fuel cell electrodes

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ABSTRACT

Sulfated zirconia nanoparticles are evaluated as a possible alternative for a solid proton conductor in a fuel-cell catalyst layer. Two methods are applied for the synthesis of the nanoparticles, *i.e.*: (i) a conventional method treating ZrO₂ particles in sulfuric acid, and (ii) a solvent-free method directly synthesizing sulfated zirconia nanoparticles through the thermal decomposition of a mixture of ZrOCl₂ and (NH₄)₂SO₄. The nanoparticles synthesized by the solvent-free method have a size of 5–10 nm and an amorphous structure, and moreover their properties are promising in view of the application. In particular, the proton conductivity of the nanoparticles is high enough, *i.e.* of the 10⁻² S cm⁻¹ order, to be comparable to that of Nafion. Even though they possibly reduce the activity of Pt catalyst, layers containing sulfated zirconia as a proton conductor prove to be active as catalyst in fuel cell prototypes. Compared with conventional, Nafion-based cells, the maximum power density of the cells using sulfated zirconia is about one third. We believe that improvement in the preparation procedures for catalyst layers and membrane electrode assemblies will improve the cell performance. Therefore sulfated zirconia can be a valid proton conductor for fuel cell application.

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1. Introduction

Due to their environmental friendliness and high energy-conversion efficiency, fuel cells have attracted great interest in view of a proper exploitation of sustainable energy sources. Among the various possible types, fuel cells using a polymer electrolyte membrane, *i.e.* polymer electrolyte fuel cells (PEFCs), are particularly attractive because of their operation at low temperature (<100 °C). In these cells, the polymer electrolyte is used not only as the electrolyte membrane separating the anodic and cathodic compartments, but also as the proton conductors in the catalyst layers. Generally, NafionTM (DuPont), or a sulfonated tetrafluoroethylene copolymer, has been the polymer of choice because of the high ionic conductivity and the excellent chemical and mechanical stability.

However, the thermal performance and particularly, the cost of this type of polymers are still far from being ideal for the commercialization of fuel cells.

Numerous efforts have been devoted to synthesize polymers alternative to Nafion, including the Nafion-based composites [1–4], and hydrocarbon polymers [4–6]. However, almost all the studies on the electrolyte for fuel cells so far reported were limited to the characterization of the membranes, and thus their applications to the catalyst layers are doubtful. For example, most hydrocarbon membranes seem to be unstable in PEFC electrodes, because of their oxidation by Pt catalysts. To be suitable for PEFC electrodes, a proton conductor must fulfill several requisites, including (i) high conductivity, (ii) high stability, (iii) high dispersibility, and (iv) low cost. Some of these are valid also for the use as membrane, but they should be optimized in the case of catalyst layer use. In this respect, sulfated zirconia nanoparticles are very promising materials.

Sulfated zirconia, *i.e.* a solid acid of zirconia modified with sulfate on its surface [7,8], has been widely studied in terms of their catalyst properties and of their preparation methods [8]. Generally, this material is synthesized just by impregnating zirconia with sulfate, followed by a calcination at about 600 °C, this making it

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attractive in terms of cost and resources. Since sulfated zirconia is an excellent proton conductor, *i.e.* at the same level as Nafion [9], our and several other laboratories researchers have studied its application as an electrolyte membrane for fuel cells [2,3,10,11]. We found that a composite membrane of Nafion and sulfated zirconia had a high conductivity ($>10^{-2}$ S cm $^{-1}$) in a 60–150 °C temperature range [10]. This value is even better than that of Nafion, and thus, sulfated zirconia is a promising material as an electrolyte membrane in fuel cells. Almost all the studies so far reported have focused on this use, while few attention has been devoted to sulfated zirconia as a proton conductor in the catalyst layers, excepting a brief report [12]. Thus, we have tried to fill this gap by undertaking a detailed study of sulfated zirconia as a proton conductor in fuel cell electrodes.

In this work, sulfated zirconia in the form of nanoparticles was synthesized, because the smallest particles are expected to be the highest proton conductivity (ionic conductive groups of sulfated zirconia exist on its solid surface) and the best dispersibility in the electrodes. The sulfated zirconia nanoparticles synthesized in this work were evaluated in terms of electrochemical stability and of influence on electrochemical reactions on a Pt catalyst. Furthermore, porous electrodes containing sulfated zirconia were prepared and evaluated.

2. Experimental

2.1. Synthesis of sulfated zirconia nanoparticles

Sulfated zirconia nanoparticles were synthesized by using two different methods. One was the well-known method using a solvent (*e.g.*, a H₂SO₄ aqueous solution and a (NH₄)₂SO₄ aqueous solution) to modify the surface of zirconium oxide particles [7,8]. In this paper, this sample is referred to as “S-SZ”. The other was a solvent-free method proposed by Sun et al. [13], and referred to as “SF-SZ”.

2.1.1. Solvent method

1.0 g of commercial ZrO₂ nanoparticles (20–30 nm, Aldrich) were stirred in 100 mL of 2.5 M (NH₃)₂SO₄ (Wako) aqueous solution for 2 days. The mixture was dried at 150 °C for 1 day, and calcined according to the following sequence: (i) heated up to 350 °C at 1 °C min $^{-1}$, (ii) kept at 350 °C for 2 h, (iii) heated up to 620 °C at 1 °C min $^{-1}$ and then (iv) kept at 620 °C for 2 h [14].

2.1.2. Solvent-free method

ZrOCl₂·8H₂O (Aldrich) and (NH₄)₂SO₄ were separately ground for 10 min and then mixed in a ratio of 29 wt.% ZrOCl₂·8H₂O for over 10 min until reaching the state of a sticky paste. The mixture was aged for over 18 h at room temperature and then calcined at 600 °C for 5 h under continuous air flow (400 mL min $^{-1}$); finally, the temperature was gradually decreased to room temperature still under air flow.

2.2. Characterization of synthesized sulfated zirconia

The synthesized powders were characterized in terms of (i) particle size, (ii) composition, (iii) acidity strength, (iv) surface group and (v) crystal structure. The particle size was carefully estimated by a transmission electron microscope (TEM) (Hitachi H8100A) at 100 kV, by a scanning TEM (STEM) (Hitachi S5500) at 30 kV, and by a high-resolution scanning electron microscope (HR-SEM) (Hitachi S5500) at 30 kV. The composition was determined by energy dispersive X-ray spectroscopy (EDXS) at 10 kV. The acidity strength was determined by using a Hammett indicator (*m*-nitrochlorobenzene) dissolved in anhydrous cyclohexane (1 g L $^{-1}$), after drying the samples at 300 °C in nitrogen for 1 h [7,15]. The surface group was

investigated by means of Fourier transform infrared spectroscopy (FT-IR) in a KBr pellet, after washing the samples with pure water. The crystal structure was analyzed by X-ray diffractometry (XRD) (RINT-UltimaIII, Rigaku) applying Cu K α radiation at 40 kV and 40 mA under ambient conditions.

2.3. Evaluation of sulfated zirconia as a proton conductor

The electrochemical characteristics of sulfated zirconia nanoparticles were evaluated in terms of three fundamental properties, namely ionic conductivity, electrochemical stability, and influences on catalytic activity.

2.3.1. Ionic conductivity

Pellets of SF-SZ were formed at 880 kgf cm $^{-2}$. Their ionic conductivities were evaluated by AC impedance method (PARSTAT 2273) at 30 °C in 100%-RH, by sandwiching the samples between two Au electrodes. Moreover, the ionic conductivity of an aqueous dispersion of SF-SZ (20.4 g L $^{-1}$) was evaluated.

2.3.2. Electrochemical stability

Cyclic voltammetry (CV) was conducted by scanning a Pt electrode in a conventional three-electrode cell using the sulfated zirconia dispersion as electrolyte from –0.2 to 1.0 V, *i.e.* in the potential range of interest for fuel cell operation. The response was recorded on a computer-controlled potentiostat (PARSTAT 2273), used platinum as the counter electrode and a silver/silver chloride (Ag/AgCl) electrode as the reference electrode.

2.3.3. Influence on catalytic activity

Methanol oxidation and oxygen reduction on a Pt electrode were investigated using the aqueous dispersion as the supporting electrolyte. The reaction rates were evaluated by linear sweep voltammetry (LSV) using a rotating-disc-electrode (RDE) at 1000 rpm. The cell configuration was the same as for the CV test.

2.4. Preparation of catalyst layers

Three types of porous electrodes (catalyst layers) containing a different proton conductor (*i.e.* S-SZ, SF-SZ and Nafion, respectively) were prepared. For assuring comparison and reproducibility [16], all the three electrodes contained the same loading (0.6 mg_{Pt} cm $^{-2}$) of carbon supported Pt catalyst (Pt/C) (47 wt.% Pt, Tanaka Kikin-zoku). To avoid leaching out from electrodes, S-SZ nanoparticles were immobilized through electrostatic interaction with silanol groups of fumed silica (Aldrich) [17]. Since silica particles cannot immobilize SF-SZ, a hydroxide gel with more electrostatic charge, or zirconium hydroxide (a protonic gel in acid) [18–20] was applied in the case of SF-SZ.

2.4.1. Catalyst layers with S-SZ

Pt/C (50 mg) and S-SZ (36 mg) were mixed in pure water (0.115 mL), followed by adding fumed silica (25 mg) treated in water vapor at 150 °C for 1 h [21,22]. The mixture was further mixed with a poly(tetrafluoroethylene) (PTFE) suspension (50 μ L, 5 vol.%, Aldrich), and then cast on a carbon paper (TGP-060, Toray). The catalyst layers were slowly dried under ambient conditions and then further dried at 140 °C in nitrogen for 30 min.

2.4.2. Catalyst layers with SF-SZ

SF-SZ (50 mg) was mixed with 2.2 mM ZrOCl₂ (1.38 mL) and then washed with excess of pure water by using centrifugation. The SF-SZ with zirconium hydroxide gel was mixed with Pt/C (50 mg) in water (12 mL), and then centrifuged to improve the contact with the gel and Pt/C. The deposit was re-dispersed in water (0.85 mL)

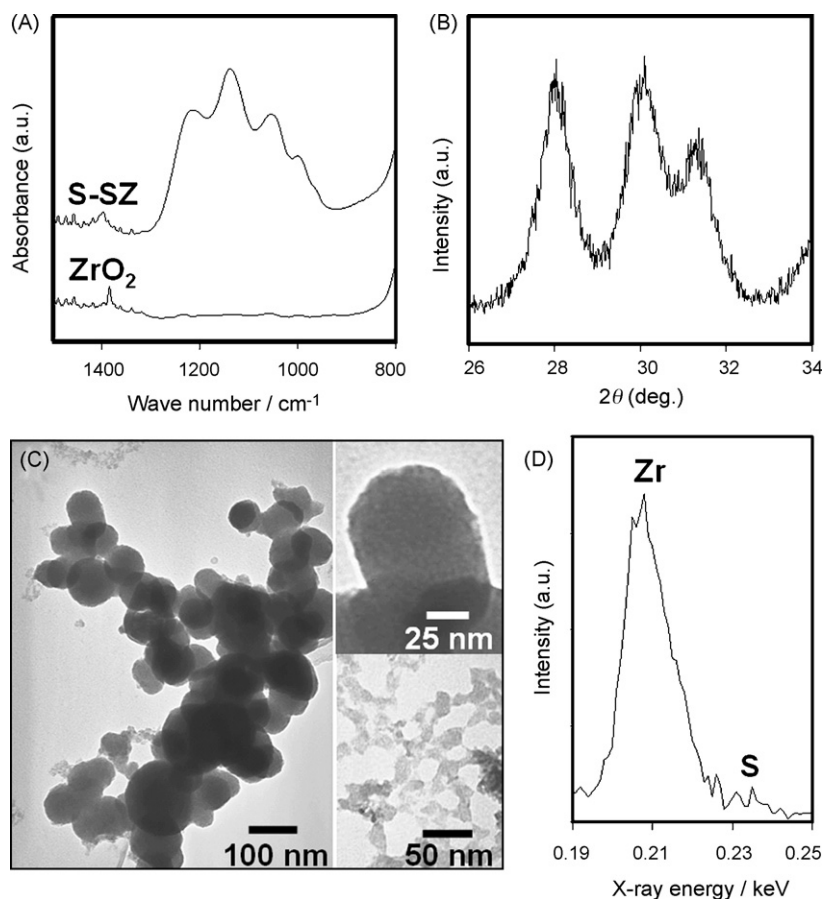


Fig. 1. Characterization of sulfated zirconia prepared by the solvent method (S-SZ). (A) FT-IR spectra of S-SZ and its precursor, i.e. ZrO₂ nanoparticles. (B) XRD pattern. (C) TEM images. The particles are in 50–100-nm range (left, upper right). Partly, smaller aggregated particles are observed as shown in lower right. (D) EDX spectrum.

followed by adding a PTFE suspension (15 vol.%, 20 μ L). The mixture was cast on a carbon paper and then dried in the same above described way.

2.4.3. Catalyst layers with Nafion

This catalyst layer was prepared as described in the previous works [16,23]. In brief, Pt/C was mixed with a Nafion ionomer solution (5 wt.%, Aldrich) in ethyleneglycol dimethyl ether and then cast on a carbon paper.

2.5. Evaluation of catalyst layers

The catalyst layers were evaluated in terms of microstructure, methanol oxidation property and fuel cell performance.

2.5.1. Microstructure

The catalyst layers were observed with a SEM (Hitachi, S-4800). The immobilization of the sulfated zirconia particles was confirmed by X-ray photoelectron spectroscopy (XPS) (JPS-9010TR, JEOL) after the catalyst layers were immersed in water for several days.

2.5.2. Methanol oxidation

To evaluate the feasibility of sulfated zirconia as a proton conductor in fuel cell electrodes, the methanol oxidation on the catalyst layers was tested by CV scanned in an electrochemical cell previously proposed by us [16,23]. In this cell, the intrinsic ionic conductivity of the catalyst layer significantly influences the oxidation current due to the absence of supporting electrolyte into the methanol solution.

2.5.3. Cell performance

Fuel cell performance was evaluated using a direct methanol fuel cell system as a preferred sample device. The cell was operated at 25 $^{\circ}$ C with the passive supply of 1 M methanol to anode and under air-breathing conditions for the cathode. Membrane electrode assemblies (MEAs) consisted of a catalyst layer with sulfated zirconia as the anode, a catalyst layer with Nafion ionomer as the cathode and a Nafion 112 membrane as the electrolyte. The cathode was hotpressed with the Nafion membrane at 25 kgf cm⁻² (135 $^{\circ}$ C, 3 min), while the anode was in physical contact with the membrane. For comparison purpose, a MEA with two catalyst layers containing Nafion ionomer was also prepared. In this case, both electrodes were hotpressed with Nafion 112.

3. Results and discussion

3.1. Characterization of sulfated zirconia

Both the two samples, i.e. S-SZ and SF-SZ, were characterized as sulfated zirconia nanoparticles. Comparing the two samples, SF-SZ appears more suitable for application as a fuel cell electrode due to its higher content of sulfate groups and smaller particle size. Details of the characterization of these samples are described below.

3.1.1. Solvent method

S-SZ was confirmed to be a typical sulfated zirconia, i.e. a superacid material composed of SO₄ groups and a crystalline zirconia. The acidity strength of S-SZ was determined by the Hammett indicator test to be at least -13.16 , that is, stronger than that of 100%

Table 1
Ionic conductivity of the sulfated zirconia synthesized with the solvent-free method (SF-SZ)

	Ionic conductivity ^a (mS cm ⁻¹)	Ionic conductivity ^b (mS cm ⁻¹)	pH
SF-SZ	13 ± 3	17 ± 3	1.1
Nafion	26	–	–
H ₂ SO ₄ (0.1 M)	–	39	1.1

^a The values were obtained for solid samples (SF-SZ: pellet, Nafion: membrane of Nafion 112) at 30 °C and 100% RH.

^b The values were obtained for liquid samples (SF-SZ: dispersion) at room temperature (~25 °C).

sulfuric acid [7,8]. Such super-acidity is a typical property of sulfated zirconia. The IR-spectrum of S-SZ (Fig. 1A) shows the peaks in the wave number range from 900 to 1200 cm⁻¹ which are typical of SO₄²⁻ groups [24]. Since these peaks were obtained after rinsing the sample with water, one may conclude that surface groups are to some extent stable in water. XRD results (Fig. 1B) show that the crystal structure of S-SZ is a mixed crystalline form of the monoclinic phase of zirconia (28.3° and 31.5°) and the tetragonal phase of zirconia (30.2°), that is, the typical crystal structure of sulfated zirconia reported by many researchers [7,8].

Fig. 1C shows the TEM analysis of the S-SZ sample. The particle size was determined to be in the range of 50–100 nm, even though smaller particles (ca. 20 nm) are also detected (lower right). Judging from the size of the precursor (ZrO₂, 20–30 nm), the latter are possibly identified as unreacted precursors or non-coagulated resultant materials.

Sulfur content of S-SZ was determined as ca. 3 wt.% by the EDXS of S, Zr, and O atoms (Fig. 1D). Assuming that one sulfur atom becomes one acidic site, this sulfur content corresponds to an acid content of ca. 0.9 mmol g⁻¹, i.e. a value comparable to that of Nafion 1100 (0.91 mmol g⁻¹).

3.1.2. Solvent-free method

SF-SZ was also confirmed to be sulfated zirconia by Hammett indicator (acidity strength: min –13.16) and by IR spectrum (Fig. 2A). However, its crystal structure was not that typical of sulfated zirconia, that is, a completely amorphous form was indicated by X-ray analysis as shown in Fig. 2B. Sun et al., who proposed the solvent-free process for preparation of sulfated zirconia, reported that crystal structure of their sample was tetragonal phase [13]; thus, we speculate that some trivial difference in synthetic procedure, for example, grinding method and mass of the precursors, resulted in the different crystal structure. In view of the fact that crystallization temperature of zirconia depends on particle size [25], the amorphous structure probably suggested that our particles were smaller than those prepared by Sun et al. Further, detailed investigation is certainly needed to confirm this aspect.

The particle size of SF-SZ samples was determined to be 5–10 nm by TEM, STEM, and SEM observation (Fig. 2C and D), even though larger particles (20–40 nm) are also detected (Fig. 2D). To be noticed that the smallest particles (5–10 nm) could not be observed by TEM at high accelerating voltage (e.g., 100 kV) but only by STEM at 30 kV and by HR-SEM, see Fig. 2C (images in the same region of the sample). These observations clearly show that the small particles dominate the SF-SZ samples.

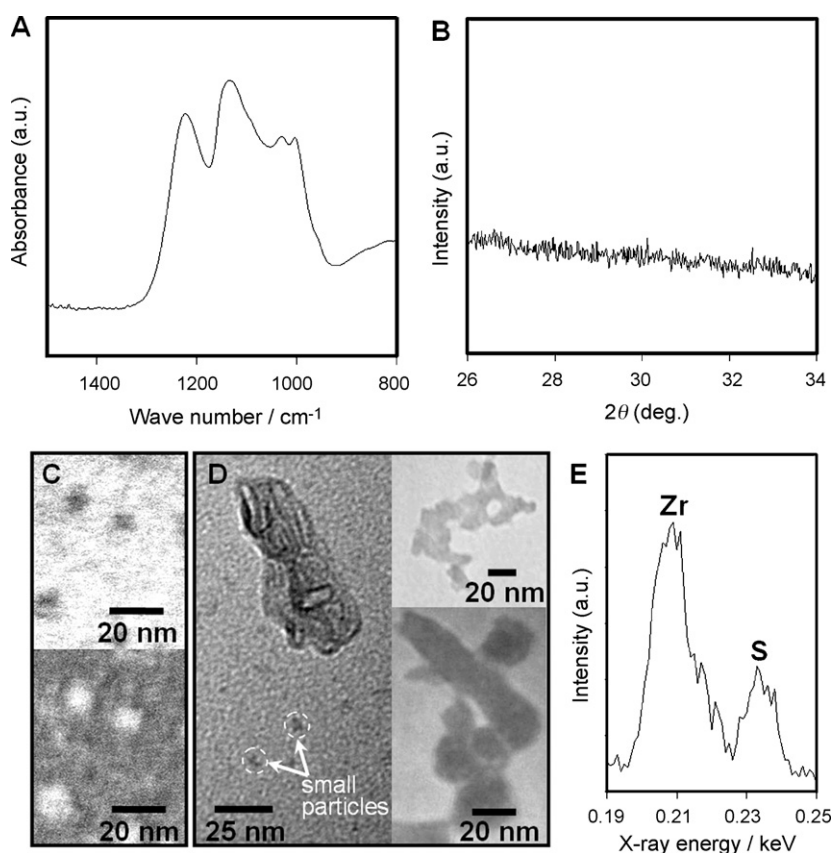


Fig. 2. Characterization of sulfated zirconia prepared by the solvent-free method (SF-SZ). (A) FT-IR spectrum. (B) XRD pattern. (C) STEM image (upper), and SEM image (lower) corresponding to the STEM image. The acceleration voltage was 30 kV. The particles are in 5–10-nm range. (D) TEM images at high acceleration voltage (left: 80 kV; right: 100 kV). Large particles (left, lower right) and aggregated particles (upper light) are clearly observed. Smaller particles are obscurely observed in the left image. (E) EDX spectrum.

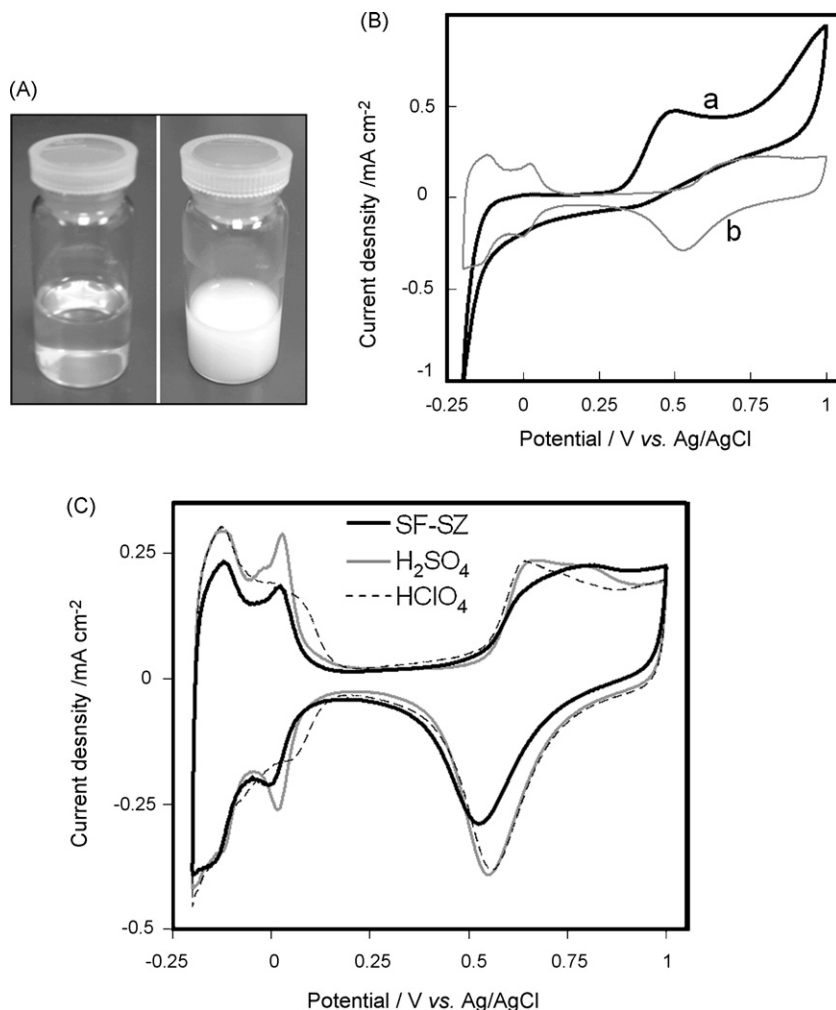


Fig. 3. Evaluation of electrochemical stability of the sulfated zirconia using its dispersion (SF-SZ). (A) Photographs of the dispersion just after preparation (left), and after aging for 1 day (right). (B) CVs of a Pt electrode in a dispersion of sulfated zirconia: (a) as-prepared dispersion, and (b) the dispersion treated by drying (150 °C) followed by re-dispersing procedure. (C) The CV of sulfated zirconia was compared with those of sulfuric acid (0.1 M) and of perchloric acid (0.2 M). Electrolyte: purified dispersion saturated with nitrogen. Scan rate: 100 mV s⁻¹.

By EDXS (Fig. 2E), the sulfur content of SF-SZ was determined to be 9.5 ± 1 wt.%, *i.e.* a value higher than that of S-SZ. The acid content was calculated to be *ca.* 3.0 mmol g⁻¹, *i.e.* a value remarkably higher than that of Nafion. These values were not changed even after the purification process for the electrochemical measurements, *i.e.* a process of dispersing in water followed by drying at 150 °C. Furthermore, our thermogravimetric analysis (data was omitted) exhibited two weight losses, which are typical for sulfated zirconia, assigned to the removal of water (25–400 °C) and the removal of surface sulfate groups (600–1000 °C) [13], indicating that SF-SZ did not contain residual precursor ((NH₄)₂SO₄) though the sulfur content was high.

3.2. Evaluation of sulfated zirconia as a proton conductor

The fundamental properties of sulfated zirconia as a proton conductor in fuel cell electrodes were evaluated using the sample having the smallest particles, *i.e.* SF-SZ. These samples were evaluated in terms of ionic conductivity, electrochemical stability and catalytic activity.

3.2.1. Ionic conductivity

The ionic conductivity of SF-SZ is high and comparable even around room temperature to those of Nafion and of 0.1 M sulfuric

acid (Table 1). The conductivity is roughly ten times higher than that of hydrated zirconia [26], this confirming the positive effect of sulfation.

3.2.2. Electrochemical stability

The electrochemical stability of sulfated zirconia in the potential range of the interest for fuel cell operation was evaluated by CV using a SF-SZ dispersion. The as prepared dispersion was transparent, but then gradually turned into a white suspension (Fig. 3A). This change was reproduced by drying the suspension (at >300 °C) and redispersing it, this meaning that dried sulfated zirconia, which is Lewis acid, becomes a transparent dispersion and then it may gradually turn into Brønsted acid to be a white suspension. Thus, the color change was probably attributed to agglomeration of the nanoparticles caused by electrostatic interaction originating from Brønsted acidic sites.

Preliminary CV tests of a Pt electrode showed that the suspension contained electrochemically active species (Fig. 3B, curve “a”). Also on the basis of literature results [27,28], we speculate that these are oxygen-unsaturated sulfur compounds, *e.g.*, sulfur dioxide (SO₂). SO₂ not only reacts on electrodes but it is also a poison for platinum catalysts. Thus, to remove SO₂, the suspension was heated at 150 °C until drying and then redispersed in water. As a result, the CV of the redispersed solution is the typical one of a Pt electrode

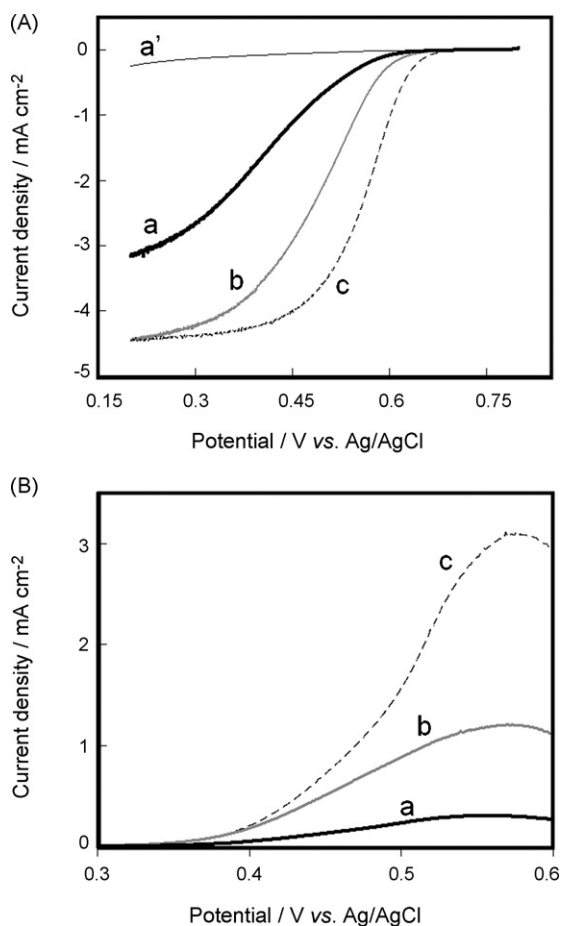


Fig. 4. LSVs for evaluating influences of sulfated zirconia on the fuel-cell reactions using a Pt-RDE at 1000 rpm: (A) oxygen reduction in an electrolyte solution saturated with oxygen (1 mV s^{-1} , $0.8\text{--}0.2 \text{ V}$, 25°C), and (B) methanol oxidation in an electrolyte solution containing 0.1 M methanol (5 mV s^{-1} , -0.1 to 1.0 V , 25°C). Catalytic activities were compared using different supporting electrolytes: (a) sulfated zirconia (SF-SZ) dispersion, (b) sulfuric acid (0.1 M), and (c) perchloric acid (0.2 M). Data using sulfated zirconia dispersion without the drying procedure was also shown as (a').

in acidic media (Fig. 3B, curve “b”), and moreover the voltammogram shows that sulfated zirconia is electrochemically stable in the potential range (from -0.2 to 1.0 V vs. Ag/AgCl) of interest to fuel cell reactions, *i.e.* oxygen reduction, methanol oxidation and hydrogen oxidation. This stability is of great importance for the application as electrolyte in fuel cell electrodes.

Next, the CV response was compared with those in sulfuric acid (0.1 M) and in perchloric acid (0.2 M). The trend approaches that in 0.1 M sulfuric acid (see Fig. 3C), although the hydrogen peaks (-0.2 , 0 V) and the oxide peaks (0.55 V for reduction, 0.6 V for oxidation) are somehow smaller. Since these currents are related to the reactions of Pt surface, the reduction of currents can be attributed to the adsorption of something onto the surface. In view of this and the fact that the solutions possessed the same pH, the difference in peak height is attributable to the difference in the anionic species, and thus to the adsorption of sulfated zirconia (and/or of some impurities) onto the Pt surface. Influences of anionic species are also observed in the cases of the responses of sulfuric acid and perchloric acid around 0 V , as already reported [29,30].

3.2.3. Catalytic activity

Compared with sulfuric acid and perchloric acid, sulfated zirconia unfortunately degraded oxygen reduction (Fig. 4A) and

methanol oxidation as well (Fig. 4B). In the case of oxygen reduction, not only the current in the kinetically controlled region, but also that in the diffusion controlled region, are lower than those of sulfuric acid. This decrease in current is attributed to an increase in adsorption of anion (and/or of some impurities) and also to a low solubility of oxygen [31]. In the case of methanol oxidation, the current density is clearly lower than that in sulfuric acid, see Fig. 4B. Judging from the decrease of oxidation current in the CV response of Fig. 3C (around 0.55 V), this current decay might be attributed to the decrease of OH groups on the electrode surface. Though this in turn might be caused by the super-acidity of sulfated zirconia, further study is needed to confirm this hypothesis, also considering that the decrease in activity may be also attributed to the residual of a small amount of SO_2 poison [27].

3.3. Evaluation of the catalyst layer containing sulfated zirconia

Catalyst layers containing sulfated zirconia as a proton conductor were evaluated in terms of microstructure, methanol oxidation, and cell performance in a direct methanol fuel cell prototype.

3.3.1. Microstructure

SEM images of the catalyst layers containing sulfated zirconia are compared with that of a conventional catalyst layer containing Nafion ionomer (Fig. 5) (the cross-sectional images were almost the same as those of the top images and thus are omitted). As shown in Fig. 5A, the catalyst layer with S-SZ is granular and less porous than the others. This type of microstructure is expected, since the catalyst layers contain only nanoparticles (S-SZ, Pt/C, fumed silica, PTFE). As shown in Fig. 5B, the catalyst layer with SF-SZ consists of agglomerates in the $100\text{--}300\text{-nm}$ range as well as of pores in the sub-micrometer range. This non-uniform microstructure is possibly attributed to the addition of the hydrogel. One may speculate that the agglomerates are covered with the zirconium hydroxide gel containing SF-SZ. The existence of SF-SZ in this layer was confirmed by XPS (S 2p), see inset of Fig. 5B. Compared with the catalyst layer containing Nafion (Fig. 5C), the agglomerates are smoother and the pores are smaller.

3.3.2. Methanol oxidation

Fig. 6 shows that the methanol oxidation current considerably increases when passing from simple PVdF-HFP electrodes to sulfated zirconia added electrodes, and this proves the role of sulfated zirconia as a proton conductor, because the electrochemical cell can clarify the difference in the intrinsic ionic conductivity of catalyst layers as shown by the inset of Fig. 6. This proof of concept is quite attractive in terms of fuel-cell operation without the expensive ionomer, Nafion. Comparing the two catalyst layers containing sulfated zirconia, the performance of that containing SF-SZ is quite higher than that containing S-SZ, and this may result from higher sulfur-group content and smaller particle size of SF-SZ. Actually, the acid content in the catalyst layer with SF-SZ ($\sim 4 \mu\text{mol cm}^{-2}$, $1.3 \text{ mg}_{\text{SZ}} \text{ cm}^{-2}$) was found to be higher than that with S-SZ ($\sim 0.8 \mu\text{mol cm}^{-2}$, $0.92 \text{ mg}_{\text{SZ}} \text{ cm}^{-2}$) from the calculation using the composition of catalyst inks and the sulfur contents from EDXS results. However, though the acid content of the catalyst layer with Nafion was lower, $\sim 0.3 \mu\text{mol cm}^{-2}$ ($0.31 \text{ mg}_{\text{Nafion}} \text{ cm}^{-2}$), its performance in the potential region of $>0.4 \text{ V}$ was higher than those of the layers containing sulfated zirconia. This may indicate that Nafion can form better ion-conductive paths than sulfated zirconia.

The performance of the catalyst layers containing sulfated zirconia is comparable to that containing Nafion in the kinetically controlled region ($<0.4 \text{ V}$); thus, in view of the results of methanol oxidation shown in Fig. 4B, one may speculate that the adsorption of sulfated zirconia on the catalyst surface might be reduced in

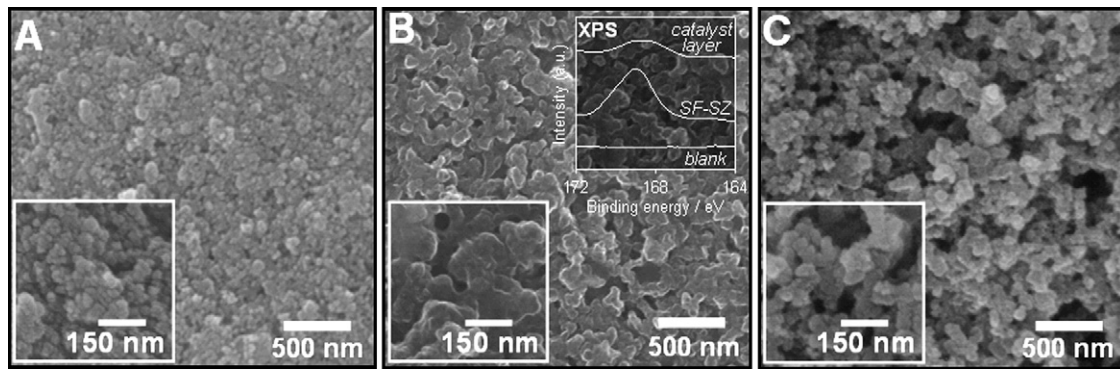


Fig. 5. SEM surface images of the catalyst layers containing different proton conductors: (A) S-SZ, (B) SF-SZ, and (C) Nafion ionomer. The inset spectra in "B" is XPS of S 2p (top: catalyst layer with SF-SZ; middle: SF-SZ; bottom: catalyst layer without SF-SZ (blank)).

catalyst-layer tests and/or that SO_2 poison was diffused out from the layers. In addition, the current density of the layer containing SF-SZ was slightly higher than that containing Nafion. This can be attributed to increase in catalytic activity and/or in catalyst utilization. The former might be caused by the inorganic additives, *i.e.* fumed silica and zirconium hydroxide gel, and the latter might be caused by the difference in microstructure. However, further analysis is required to consider in detail the difference in performance.

3.3.3. Cell performance

Polarization curves of the MEAs using the catalyst layers based on sulfated zirconia are compared with those of conventional MEAs using Nafion ionomer in Fig. 7 [16,32]. The maximum power density for the cell with S-SZ MEA is *ca.* 0.2 mW cm^{-2} and that with the SF-SZ MEA is *ca.* 0.8 mW cm^{-2} . These performances are lower than that of the cell with Nafion MEA (*ca.* 2.3 mW cm^{-2}). These decays in performance of the catalyst layers containing sulfated zirconia can be attributed to their microstructure (or preparation method) as well as to the interface between the catalyst layer and the Nafion membrane. Actually, since the sulfated zirconia catalyst layers did not contain Nafion and were not hotpressed with the Nafion membrane, this possibly resulted in a high ionic resistance in the layers and also at the interface between the layer and the membrane. Thus, the improvements in preparation procedures for catalyst layers and MEAs are expected to greatly improve the performance. However,

even under the present conditions, the results confirm that sulfated zirconia can operate as a proton conductor in fuel cell electrodes.

In addition, we evaluated MEAs with the catalyst layers containing sulfated zirconia also at the cathode side. The performance was almost the same as that shown in Fig. 7, except for a slight decrease in voltage around open circuit. This result suggests that the catalyst layers based on sulfated zirconia might be suitable for cathode use in direct methanol fuel cells (or at low current operation), though some concern remains on flooding due to the hygroscopicity of sulfated zirconia.

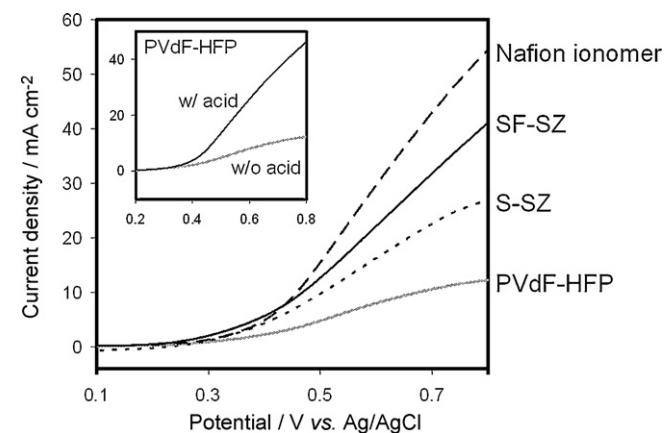


Fig. 6. Methanol oxidation on catalyst layers with a different proton conductor: S-SZ, SF-SZ, Nafion ionomer. For comparison, a catalyst layer without proton conductors (PVdF-HFP as binder) is also shown. The inset demonstrates that methanol oxidation on a catalyst layer without proton conductors significantly improved by adding sulfuric acid (0.5 M) into the methanol solution. The cell configuration was described in our previous paper [23].

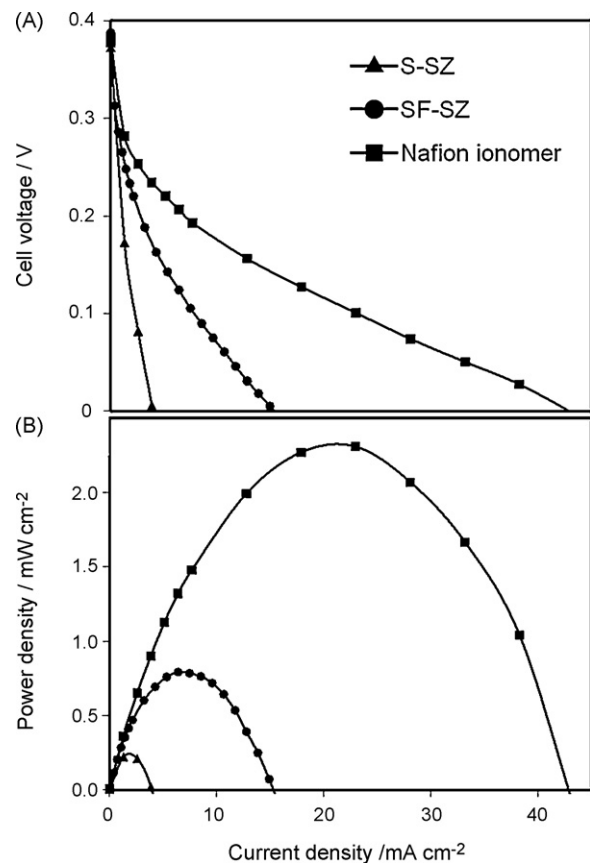


Fig. 7. Performances of fuel cells with an anode catalyst layer containing different proton conductors: (▲) S-SZ, (●) SF-SZ, and (■) Nafion ionomer. All the cathode catalyst layers contained Nafion ionomer. (A) Current–voltage curves and (B) current–power curves. Pt/C was used for both anode and cathode (0.6 mg cm^{-2}). Fuel: 1 M methanol solution (passive feed); oxidant: oxygen from air (air-breathing); room temperature.

4. Conclusions

Sulfated zirconia nanoparticles were evaluated as proton conductors in catalyst layers of fuel cells. We showed that the ionic conductivity and the electrochemical stability are suitable for the application. Even though with performance still lower than that of standard Pt catalyst, the sulfated zirconia-based catalyst layers still had a very promising response, this proving the feasibility of sulfated zirconia as new types of proton conductors. We believe that improvement in the preparation of the catalyst layers will result in a net improvement of the cell performance, thus finally placing sulfated zirconia as a valid alternative material for fuel cell applications.

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