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Preparation and Proton Conductivity of Antimonic Acid Films by Electrophoretic Deposition

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Antimonic acid ($Sb_2O_5{\cdot}nH_2O$) films have been successfully prepared on stainless steel and Si(100) substrates by electrophoretic deposition (EPD) using sols formed by a reaction of an H_2O_2 aqueous solution and metallic Sb powder or antimony *i*-propoxide ($Sb(O\text{-}i\text{-}C_3H_7)_3$). Zeta potential measurements reveal that the particles are well dispersed in ethanol or in water, when the sol pH is over ~7. The weight of the $Sb_2O_5{\cdot}nH_2O$ particles deposit on the anode Si(100) substrate linearly increases with current density in the pH = 7. The films are found to consist of fine particles of cubic $Sb_2O_5{\cdot}nH_2O$ single crystal with uniform particle sizes of ~30 nm and ~150 nm. The proton conductivity for the discs consisting of the $Sb_2O_5{\cdot}nH_2O$ particles is discussed in connection with the particle size and the results of $Sb_2O_5{\cdot}nH_2O$ oriented film.
Key words: antimonic acid, electrophoretic deposition, single crystal particles, proton conductivity

1. INTRODUCTION

Cubic antimonic acid ($Sb_2O_5{\cdot}nH_2O$) is known to be a room-temperature proton conductor, for which the conductivity characteristically depends on the ambient humidity.[1] Structurally, there are two polymorphous types of $Sb_2O_5{\cdot}nH_2O$ other than cubic; monoclinic and amorphous.[2] The structure of cubic $Sb_2O_5{\cdot}nH_2O$ is represented by a cubic pyrochlore one and has a three-dimensional framework built up of vertex-linked $(Sb_2O_6)^{2-}$ octahedra.[3] In this framework there are interconnected channels in which water molecules are situated.[3] The proton conductivity of cubic $Sb_2O_5{\cdot}nH_2O$ is considered to occur by a Grotthuss-type mechanism over the hydrogen bond networks of the water molecules.[4]

In $Sb_2O_5{\cdot}nH_2O$, however, the introduction of oxygen vacancies or the desorption of water molecules occur easily under high temperature or high vacuum conditions.[5] Therefore, it is difficult to prepare $Sb_2O_5{\cdot}nH_2O$ films using conventional techniques such as chemical vapor deposition (CVD), vacuum deposition, or sputtering. In fact, to our knowledge, the preparation of $Sb_2O_5{\cdot}nH_2O$ films has been reported in only a few papers.[2,6,7]

On the other hand, electrophoretic deposition (EPD) is a useful technique for producing films of a variety of materials under mild conditions, such as room temperature and atmospheric pressure. There is also an advantage that the density, uniformity and thickness of the films can be controlled relatively easily.[8]

Recently we have successfully synthesized sols in which cubic $Sb_2O_5{\cdot}nH_2O$ single crystal particles with uniform particle sizes are dispersed.[9] In addition, the polycrystalline films of cubic $Sb_2O_5{\cdot}nH_2O$ have been prepared by EPD, using the sols. In this study, it is demonstrated for the first time how the sols and films have been prepared. Next, the proton conductivity of cubic $Sb_2O_5{\cdot}nH_2O$ is discussed in connection with the particle size and the results of (111)-oriented film.

2. EXPERIMENT

The sols were synthesized by a reaction of an aqueous H_2O_2 solution with metallic Sb powder or antimony *i*-propoxide, $Sb(O\text{-}i\text{-}C_3H_7)_3$.[10] Each molar quantity (5×10^{-2} mol) of metallic Sb powder and $Sb(O\text{-}i\text{-}C_3H_7)_3$ was mixed with 30 ml of 30% H_2O_2 solution, then refluxed at ~100 °C for 4 h to give translucent white sols. Subsequently, the excess H_2O_2 in the sols was catalytically decomposed with several Pt foils, and the organic residue was removed by extraction using diethyl ether. Zeta potential and transmission electron microscopy (TEM) measurements were made out on the particles produced in the sols.

$Sb_2O_5{\cdot}nH_2O$ films were prepared on anode electrodes by EPD using the dilute sols containing 1.25×10^{-2} M of $Sb_2O_5{\cdot}nH_2O$. Stainless steel plates (SUS304) and Si(100) wafers with a resistivity less than 10^{-2} Ωcm^{-1} were used as the anode electrodes. A mixture of H_2O and C_2H_5OH having a volume ratio of 1: 3 was used for the sol mediums. EPD was carried out at the sol pH = ~7 by applying dc current from 0 to ~1 mA and 0 to 50 V. The surface morphology of the resulting films was observed with a scanning electron microscope (SEM). The phase and structure were examined by x-ray diffraction (XRD) measurements.

Proton conductivity measurements were made out by an ac impedance method in the frequency range 100 Hz – 15 MHz, using a Hewlett-Packard 4194 analyzer. In this study, compact polycrystalline discs were used as samples for the conductivity measurements, since the measurement for thin films prepared on conducting substrates required relatively difficult and advances techniques. The discs of diameter 13 mm, thickness ~1 mm, and relative density ~60% were prepared by pressing cubic $Sb_2O_5{\cdot}nH_2O$ powder at 147 MPa.[2] The powder was formed by evaporation of the sols at 120 °C. Nickel sponges of diameter ~11 mm were attached as electrodes to both sides of the discs by pressing, and platinum wires were connected to the nickel sponges using silver paste. The conductivity measurements were carried out at 19.5 °C under various degrees of relative humidity.

3. RESULTS AND DICCUSSION

Figure 1 is a typical bright-field TEM micrograph and a selected area diffraction pattern of the $Sb_2O_5{\cdot}nH_2O$ particles prepared by the reaction of an aqueous H_2O_2 solution with metallic Sb powder for 1 h. The bright-field imaging shows that the particles have facets. The selected area diffraction pattern corresponds to that of a cubic $Sb_2O_5{\cdot}nH_2O$ single crystal. Such single crystals are considered to begin growing in the initial stage of the reaction. It has been also confirmed that the particles prepared by reacting an aqueous H_2O_2 solution with $Sb(O\text{-}i\text{-}C_3H_7)_3$ are cubic single crystals.

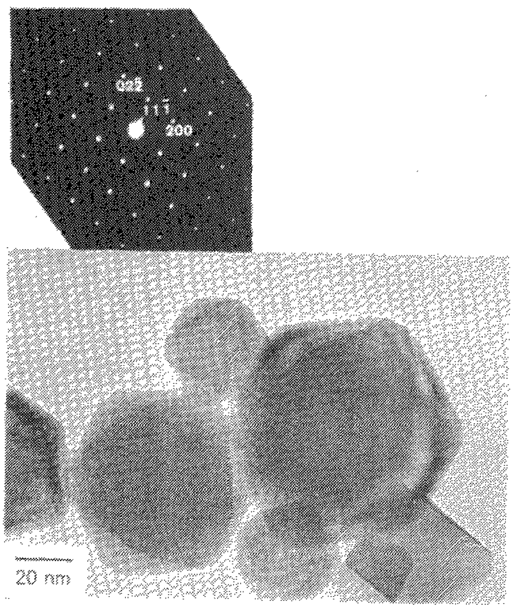

Fig. 1. Bright-field TEM micrograph of the $Sb_2O_5{\cdot}nH_2O$ particles together with a selected area diffraction pattern. The particles were prepared by a reaction of an aqueous H_2O_2 solution and metallic Sb powder at ~100 °C for 1 h.

In Fig. 2, zeta potentials are plotted as a function of sol pH. The isoelectrical points are found to be in the pH range 2 – 3.5. Moreover, the particles are negatively charged (-30 to -20 mV) in the pH range 7 – 13, which indicates repulsion forces between the particles. As a result, it has been observed that the $Sb_2O_5{\cdot}nH_2O$ particles are well dispersed in both water and ethanol for a pH > 7.

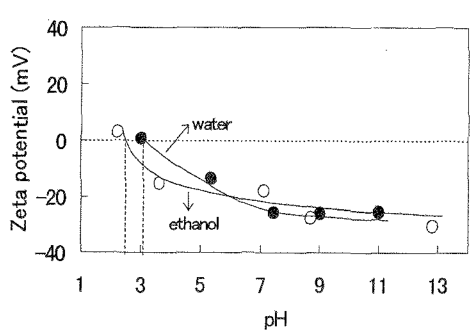

Fig. 2. Zeta potentials of the cubic $Sb_2O_5{\cdot}nH_2O$ particles plotted as a function of pH. The particles were dispersed in water or in ethanol at a concentration of ~3 $\times 10^{-5}$ M.

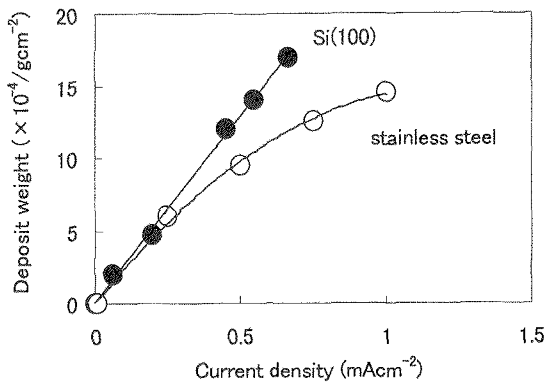

Fig. 3. Relationship between the current density and the deposit weight of the particles on the anode substrates. The sols used for EPD were prepared by reacting an aqueous H_2O_2 solution with metallic Sb powder.

The EPD experiments were carried out at the sol pH = ~7 for 5 min, using the sols prepared by reacting an aqueous H_2O_2 solution with metallic Sb powder. Figure 3 shows the relationship between the weight of the $Sb_2O_5{\cdot}nH_2O$ deposit on the anode substrates and the current density. It should be noted that the weight of the

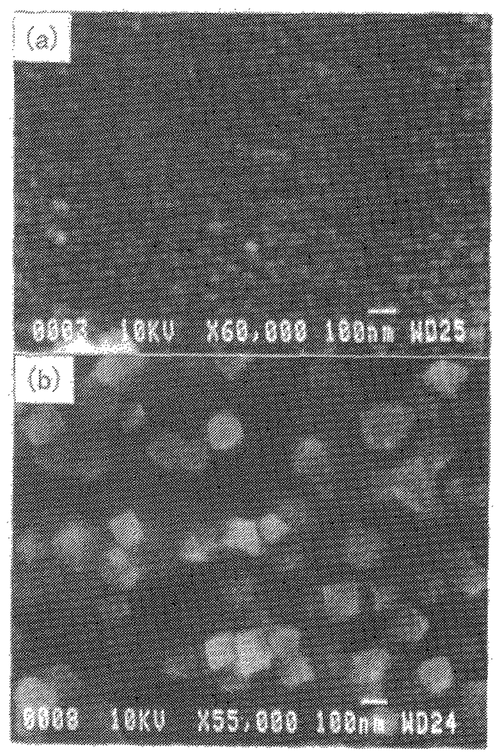

Fig. 4. SEM images of the $Sb_2O_5{\cdot}nH_2O$ film surfaces. The films were fabricated on Si(100) substrates by EPD, using the sols prepared by reacting an aqueous H_2O_2 solution with $Sb(O\text{-}i\text{-}C_3H_7)_3$ (a) or metallic Sb powder (b).

deposit on a Si(100) substrate increases linearly with the current density in the range 0 – 0.67 mAcm-2, which is in accordance with Faraday's law. On the other hand, slight deviation from Faraday's law is observed for a stainless steel substrate, which may be attributed to the electrolysis of water in the sol.[11]

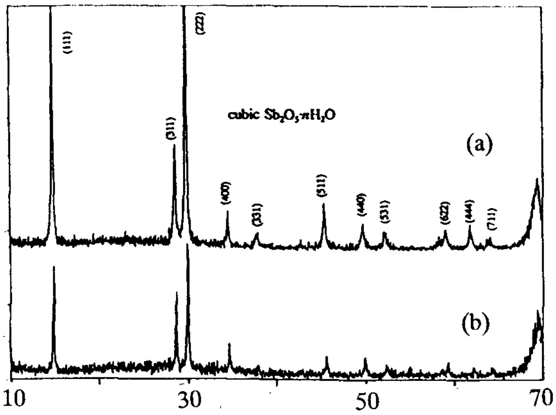

Fig. 5. XRD profiles of the $Sb_2O_5{\cdot}nH_2O$ films. The films were prepared on Si(100) substrates by EPD, using the sols prepared by reacting an aqueous H_2O_2 solution with $Sb(O\text{-}i\text{-}C_3H_7)_3$ (a) or metallic Sb powder (b).

SEM images of the film surfaces deposited on Si(100) substrates are shown in Fig. 4, and XRD profiles of the films in Fig. 5. We can see that both films have very few pores and cracks. Moreover, it is found that the films consist of many octahedral particles with uniform particle sizes of ~30 nm (Fig. 4(a)) and ~150 nm (Fig. 4(b)). These particles are cubic $Sb_2O_5{\cdot}nH_2O$ single crystals, as determined by TEM characterizations. It has been also confirmed that the thickness of the films is proportional to the current density and deposition time. However, the appearance of many cracks on the films is observed as the current density increased over 0.5 $mAcm^{-2}$. The XRD patterns of both films are identical to that of a cubic $Sb_2O_5{\cdot}nH_2O$ powder specimen.[12] There is also no significant difference in the cubic lattice parameter.

Figure 6 indicates the proton conductivity of the polycrystalline discs as a function of relative humidity. In Fig. 5, the results of (111)-oriented film of cubic $Sb_2O_5{\cdot}nH_2O$ are shown at the same time.[2] The discs consist of cubic $Sb_2O_5{\cdot}nH_2O$ single crystal particles with uniform particle sizes of ~30 nm and ~150 nm, as mentioned above. It has been confirmed that the ionic transference numbers of both discs are over 0.98, using dc electrical conductivity measurements.[13] We can see that the conductivity of the discs depends on the relative humidity and increases by about one order of magnitude as the relative humidity increases from ~10% to ~85%. Furthermore, it should be noted that the conductivity of the material with larger particle size is at least twice as high as that of the material with smaller particle size. It has been shown that the proton conductivity of cubic $Sb_2O_5{\cdot}nH_2O$ is influenced significantly by the number of water molecules located in the channel structures.[14] In addition, we have reported that the number of the water molecules is affected not only by the relative humidity but also variation of the channel size with the cubic lattice parameter.[15] However, there is no difference in the lattice parameter of the particles for the discs, as investigated in the XRD measurements. Thus, it is likely that a factor other than the water content plays a part in the conductivity differences of two materials. We suggest that the differences reflects the effects of grain boundary conductivity, for which the proton migration of a Grotthuss-type mechanism is considered not to occur as easily as compared to in the bulk.[4] On the other hand, in Fig. 5, the conductivity of the (111)-oriented film is approximately one order of magnitude, or more, larger than that of the polycrystalline discs. The (111)-oriented film consists of cubic $Sb_2O_5{\cdot}nH_2O$ single crystal particles with uniform particle size ~150nm. The result suggests that the conductivity of cubic $Sb_2O_5{\cdot}nH_2O$ is influenced not only by the particle size but also by the arrangement of the channels between particles.

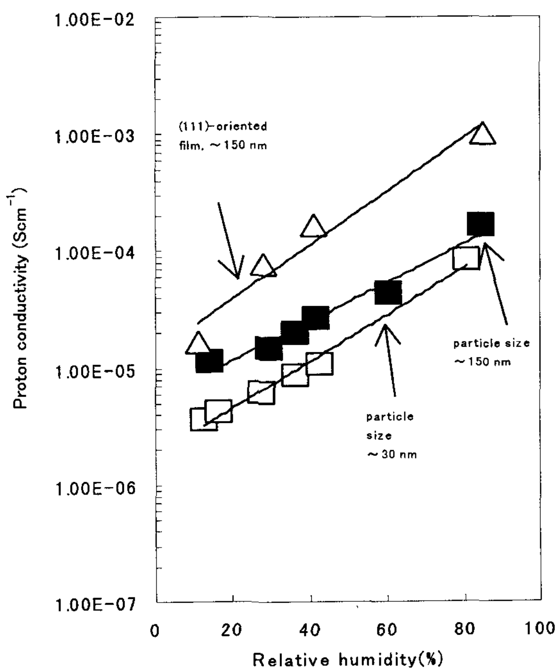

Fig. 6. The proton conductivity at 19.5 °C of the polycrystalline cubic $Sb_2O_5{\cdot}nH_2O$ discs as a function of relative humidity. The discs consist of cubic $Sb_2O_5{\cdot}nH_2O$ single crystal particles with uniform particle sizes of ~30 nm and ~150 nm. The results of (111)-oriented film are shown at the same time.[2]

4. CONCLUSIONS

It has been demonstrated that the preparation of the sols in which cubic $Sb_2O_5{\cdot}nH_2O$ single crystal particles with uniform particle sizes of ~30 nm and ~150 nm are dispersed. Furthermore, the preparation of the films consisting of the particles using EPD is also demonstrated. The results of the conductivity measurements reveal that the particle size and the arrangement of the channels most likely influence the proton conductivity of cubic $Sb_2O_5{\cdot}nH_2O$.

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