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Electrophoretic preparation of antimonic acid film

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Electrophoretic preparation has been studied to develop a useful method for the deposition of proton-conductive antimonic acid. The substrate used was ITO–glass coated with a tungsten trioxide thin film and was operated mainly as the anode. Antimonic acid powder, which had been ground beforehand with a ball mill, was dispersed in acetone to prepare the suspension. For preparation of a suitable depositing suspension, ammonium hydroxide and amyl alcohol were effective as the first and second additive, respectively. The applied voltage and time were found to be important factors for the formation of smooth and adhesive films. The amount of deposit or the film thickness was controlled by regulating the quantity of electricity or time.

1. Introduction

Antimonic acid is one of the highly functional materials which can be used for extensive application, e.g. ion-exchangers [1], fuel cells [2], gas separation membranes [3], electrochromic display devices [4] and gas sensors [5]. The compound, in which protons migrate predominantly within the pyrochlore framework [6], is a fast proton conductor at ambient temperature.

Because most proton conductors decompose or change their compositions under high temperature and high vacuum conditions [7, 8], it is considerably difficult to prepare films of such compounds by physical vapour deposition techniques, i.e. vacuum evaporation, sputtering or ion plating techniques. Proton conductors have therefore been used in the forms of thickly pressed plates or tablets [9], sprayed layers [10], pastes or ink sheets [4], etc.

Proton conductors are often required to have smooth, dense and thin forms. In such cases the electrophoresis technique is very useful for film formation on conductive substrates. Films of a wide variety of materials such as metals [11], semiconductors [12] and ceramics [13] have been prepared by the technique. One advantage of the electrophoresis technique is the smoothness of the prepared films, although they are not as fine as those formed by physical vapour deposition. Other advantages are more precise control of the film density and uniformity, and the possibility of unusual and irregularly shaped coatings.

The purpose of this study is to develop a preparation technique of antimonic acid film for use in any heat-free field.

2. Experimental procedure

2.1. Milling of powder

The suspensions used for electrophoretic deposition usually contained a particle size ranging from 0.2 to 20 μm. The antimonic acid powder (Toagosei Chemical Industry Co.) was milled for 1–5 h in an agate container with agate balls using acetone as the suspension medium. The milling conditions were examined by measuring the floating amount of powder in the suspension 10 min after ultrasonic mixing of the ground powder with methanol. The grain size distribution was measured by a granulometer in which the suspension fluid was methanol the ultrasonic mixing time was 120 s and a laser beam of 632.8 nm irradiated the sample.

2.2. Suspension medium and additives

Polar organic liquids are commonly used as suspension media for electrophoretic deposition. The liquid used in this study was acetone because it is volatile and had no influence on the characteristics of the deposited films.

Suspensions could be made to form an adherent deposit by the use of additives. Of several additives studied, a dilute solution of ammonium hydroxide was found to be the most effective [14, 15]. The ammonium hydroxide solution was prepared from concentrated ammonium hydroxide and acetone. In addition, to improve the apparent packing density and adhesion of the deposited films, amyl, octyl, benzyl, isoamyl and sec-butyl alcohols, glycerol, ethylene glycol and 1,3-pentandiol were examined as the second additive or co-additive.

2.3. Suspensions, deposition and characterization

The suspensions were prepared by ultrasonic mixing of the ground powder of antimonic acid, suspension medium and additives. They were tested for deposition characteristics at various concentrations of the additives, various voltages and durations. The electrophoretic deposition experiments were carried out by

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using a substrate holder and two electrodes as shown in Fig. 1. The substrate was an ITO-coated glass plate (20 mm × 20 mm) on which a tungsten trioxide film (450 nm thick) was deposited by vacuum evaporation. The substrates thus prepared were used for both the anode and the cathode in the electrophoresis. Deposited samples scraped from the substrate were analysed by infrared spectroscopy (i.r.) with potassium bromide tablets and by X-ray diffraction (XRD) using CuK_α radiation. Using the deposited films with the substrate, the d.c. conductivity was measured and cyclic voltammetry was performed at a sweep rate of 40 mV s^{-1}.

3. Results and discussion

3.1. Powders of antimonic acid

In order to determine the appropriate milling conditions, the grinding effect was examined by measuring the residual proportion of ground powder in the supernatant liquid. According to this method, the higher the residual proportion, the better the milling conditions. Table I summarizes the amount of suspension medium, milling time, and the residual proportion, where 10 g of individually ground powder was used as the starting sample. The results suggest that the main factor influencing the milling efficiency was not the milling time but the amount of suspension medium, and that the combination of 20 ml of acetone and 5 h of time was best. Fig. 2 shows the integration curve of the grain size obtained with the best milling conditions. The diameters for 10 and 90% of undersize were 0.25 and 0.79 μm, respectively, and the median size was 0.45 μm. These values indicate that the ground powder was sufficiently fine to be used for electrophoretic deposition.

3.2. Effect of additives

If the acetone solution of ammonium hydroxide as the additive was not added to the suspension, the antimonic acid powder coagulated and sedimented, and the deposition on the electrode was very little. In contrast, when the additive was used the powder deposited on the anode or on the cathode according to the concentration of the additive. The variation of deposition behaviour with additive concentration is shown in Fig. 3. The pH of the suspension gradually increased with increasing additive concentration and it suddenly jumped at 0.1 g l^{-1} of additive. This concentration seems to give the isoelectric point (i.p.) to the sample powder [14]. In the region lower than the i.p., deposition exclusively occurred on to the anode, while in the region higher than the i.p. the powders entirely deposited on to the cathode. According to observation by a scanning electron microscope, the homogeneity and adhesion of the deposited film were best at 1.62 × 10^{-2} g l^{-1} in anodic deposition. In cathodic deposition at about 10 g l^{-1} of additive the deposit was apparently very little. The result seems to be caused by very poor adhesion of the powder to the substrate, accompanied by slip-down on taking the electrode out of the suspension bath.

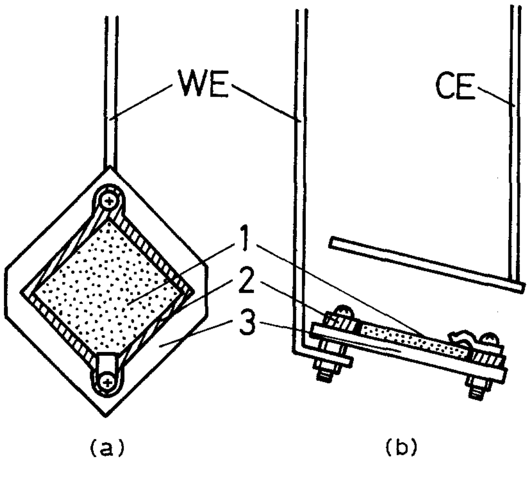

Figure 1 (a) Substrate holder and (b) electrodes used for electrophoretic preparation of antimonic acid film: (1) substrate, (2) conductive holder contacting with the substrate, (3) working electrode contacting with the conductive holder.

TABLE I Effect of the amount of suspension medium and milling time on residual proportion of ground powder in the supernatant liquid 10 min after ultrasonic mixing

Suspension medium (ml)	Time (h)	Residual proportion (%)
10	1	69
10	5	76
20	1	89
20	3	91
20	5	93
40	5	87

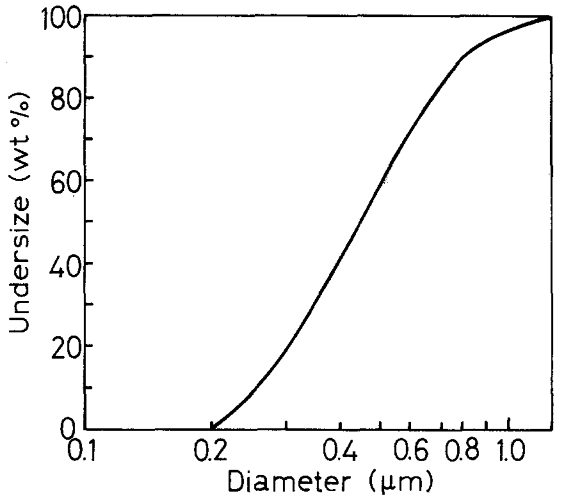

Figure 2 Grain size distribution measured after ultrasonic mixing of the ground antimonic acid powder and methanol for 120 s.

The i.r. spectra of the anodic and cathodic deposits are displayed in Fig. 4 together with the spectrum of the original antimonic acid powder. The anodic deposit had almost the same transmittance curve as the original powder, while the cathodic deposit contained two absorption peaks other than the peaks of the original powder. One peak near 1400 cm^{-1} originates

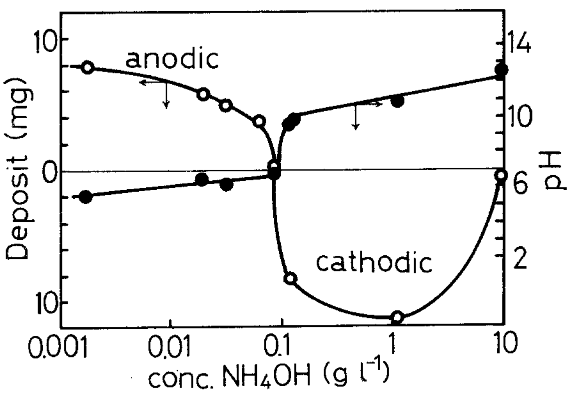

Figure 3 Addition effect of acetone solution of concentrated ammonium hydroxide on anodic and cathodic deposits and pH. The apparent concentration of antimonic acid was adjusted to 1.0 g l^{-1} in every electrophoresis.

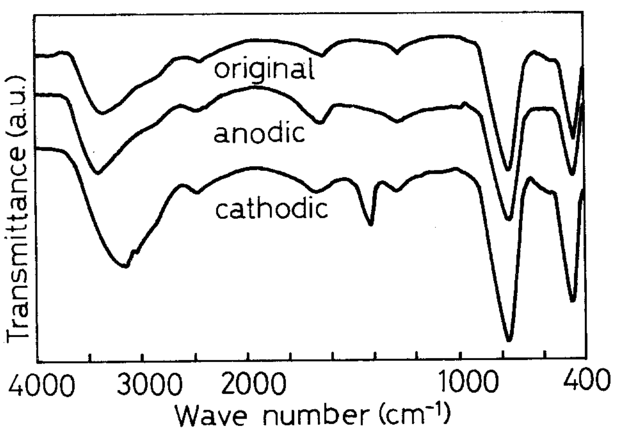

Figure 4 Infrared spectra of original antimonic acid powder, anodic deposit and cathodic deposit.

in the N–H bending vibration and the other peak at 3150 cm^{-1} results from the N–H stretching vibration. This result suggests that ammonium ions were incorporated into the cathodic deposition film by partial replacement of protons of antimonic acid with ammonium ions [14]. Therefore, cathodic operation is not appropriate for electrophoretic preparation of the antimonic acid film.

3.3. Current and voltage effects

Fig. 5 shows the change in the amount of deposit on the anode with increasing quantity of electricity or charge. At low charges the deposit increased in proportion to the charge. The rate of increase of the deposit slightly decreased at high charges. This was probably caused by gradual consumption of antimonic acid particles in the suspension at high charges. It is worthy of notice that the amount of deposit was almost independent of the applied voltage. However, the smoothness was best at the voltage of 300 V. On the basis of this observation, the deposition behaviour was examined by changing the electrophoretic period at 300 V. A relation between the film thickness and time is shown in Fig. 6. As can be seen, after the thickness linearly increased up to about 2 min, the rate of increase slowed down at 4 min. The curvature of the plot also seems to relate to the consumption of sample particles in the suspension. It was found from the results shown in Figs 5 and 6 that the amount of deposit or the thickness of the deposited film is optionally controlled by regulating the charge below 40 mC or the period below 2 min at 300 V in this experimental configuration.

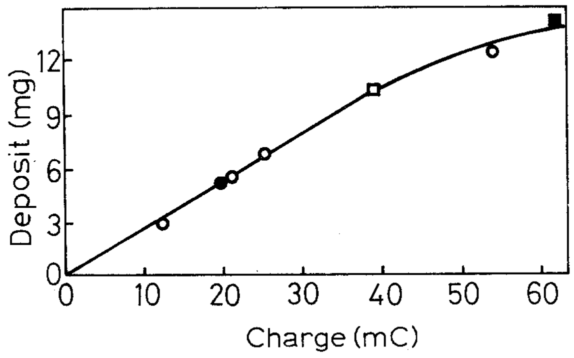

Figure 5 Deposit versus charge relation obtained at several voltages: (●) 200 V, (○) 300 V, (□) 500 V, (■) 700 V.

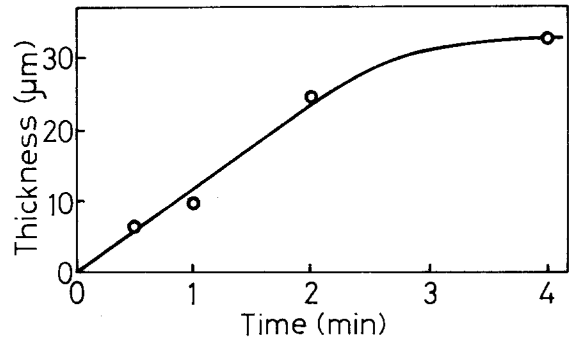

Figure 6 Dependence of thickness on electrophoresis time.

3.4. Co-additive effects

Of eight kinds of additive examined, only three reagents, i.e. amyl, octyl and benzyl alcohols, gave some effective results. By using the co-additive, the reproducibility of the electrophoretic deposition was raised and the deposition films became fairly uniform. Fig. 7 shows the XRD profiles of the deposited films obtained with and without amyl alcohol. The diffraction intensity of the film formed with the co-additive is clearly stronger than that of the film deposited without the alcohol. The result implies that a denser film was formed by the use of the co-additive. At 300 V, the current passing through the suspension increased on the addition of amyl alcohol. This fact suggests that the conduction of the suspension liquid was increased by the co-additive. The co-additive effect corresponds to the effect of increasing the applied voltage without the co-additive.

3.5. Estimation of conductivity

Two sheets of the antimonic acid films deposited on the anode using the additive and co-additive were combined and the symmetric cell ITO/WO_3/X/WO_3/ITO was fabricated to measure the resistance of the deposition film, where X is the antimonic acid. The resistance was estimated by the d.c. method to be 1 kΩ from the applied voltage and the current. Using the surface area and thickness of the film, a conductivity of the order of about 10^{-6} S cm^{-1} was obtained. Because this value contains not only the resistance of the tungsten trioxide films but also the contact resistance at the interfaces for the configuration WO_3/X/WO_3, the net conductivity of antimonic acid film must be larger than the order of 10^{-6} S cm^{-1}. Considering the reports [6, 16] that the conductivity of an antimonic acid sample varies from 10^{-7} to 10^{-4} S cm^{-1} with the amount of sorbed water, the conductivity estimated in this work lies in the range of the literature values and the deposited film seems to contain rather sorbed water.

3.6. Cyclic voltammetry

Finally, it is necessary to examine whether the deposited film can be used as a proton conductor or not. One method for checking the proton conduction in the film is to form the cell ITO/WO_3/X/WO_3/ITO and to analyse cyclic voltammograms. When the proper current flows through the measuring system according to the potential sweep and stable cycles are obtained on repeated operation, the sample film may be regarded as a practical proton conductor because the film contains no mobile ions other than protons. Moreover, when the current waves at oxidation and reduction are large and sharp and the end currents at the two edge potentials are close to zero, the film used is considered to be excellent.

Fig. 8 shows the cyclic voltammograms of cells with the deposited films obtained using several co-additives. All the voltammograms are nearly symmetrical with respect to the origin of the current–voltage coordinates. However, the oxidation and reduction peak currents differ from cell to cell according to the co-additive. The voltammogram for a film obtained without co-additive is the standard voltammogram in this experiment. The film with amyl alcohol had a voltammogram remarkably similar to that of the film without co-additive. The film with octyl alcohol displayed low peak currents and somewhat high end currents, and the film with benzyl alcohol showed high peak currents but again somewhat high end currents. The high end currents may be capacitative and are undesirable in this work. Considering the waveforms of the cyclic voltammograms as well as the features of the deposited films, the electrophoretic film of antimonic acid obtained by the use of amyl alcohol in addition to ammonium hydroxide was found to be the best of all.

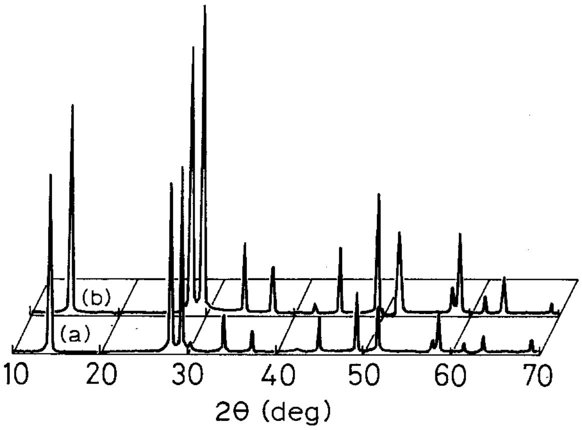

Figure 7 XRD patterns of anodic deposits (a) without and (b) with amyl alcohol as co-additive in addition to ammonium hydroxide as the main additive.

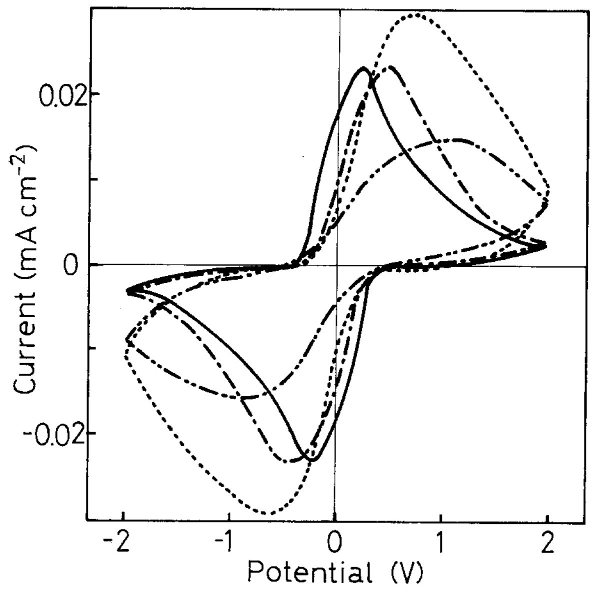

Figure 8 Cyclic voltammograms of electrochromic cells with antimonic acid film anodically deposited using co-additives: (——) no additive, (— - —) amyl alcohol, (—— - ——) octyl alcohol, (- - -) benzyl alcohol.

4. Conclusion

Electrophoretic preparation has been shown to be a useful technique for the deposition of antimonic acid film. First, factors important in the preparation of suitable plating suspensions were the choice of suspension medium (acetone), additive (ammonium hydroxide) and co-additive (amyl alcohol), as well as the milling conditions of the sample powder. Second, important factors in the formation of smooth, adherent deposits were the applied voltage (300 V) and duration (60 s). By examining the conductivity and the waveform of cyclic voltammograms, the antimonic acid film deposited on the anode is regarded as a practical proton conductor.

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