

# Microstructure control of porous alumina film using aqueous sol containing poly(ethylene glycol)

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**Abstract** To fabricate a porous and thick alumina film with large surface area on a substrate by a dip-coating technique, we prepared an aqueous sol containing poly(ethylene glycol) (PEG). The sol was prepared by hydrolysis of aluminum (III) isopropoxide with large amount of water and following peptization to colloidal particle from precipitate. The films were coated on the glass substrate by the dip-coating and then calcined at 500 °C. The maximum thickness of the film prepared by one-run dip-coating was ca. 1,000 nm. The film was an aggregate of alumina particles with a diameter of 30–50 nm and pores were interstices between the particles. The porosity of alumina film can be controlled in the range of 40–59% by changing PEG concentration in the dip-coating solution.

**Keywords** Porous film · Alumina · Sol-gel · Dip-coating · Poly(ethylene glycol)

## 1 Introduction

In porous functional materials like a heterogeneous catalyst and a gas sensor of metal oxide semiconductor, the surface of their materials is a functional site. To enhance their performance, the materials require large specific surface area. The specific surface area is made to enlarge by reducing the size of particles of the materials. In the case of porous film materials, the film requires increasing the film

thickness as well as specific surface area. Generally, the thickness of the film deposited on a substrate by one run of dip-coating using the sol-gel derived solution was limited to 100–200 nm [1]. Although thick films can be prepared by repeating the coating cycle, it is not a practical process from the viewpoint of cost and energy efficiency. To prepare nanoporous and thick titania film, we have developed the new precursor solution comprised of aqueous titania sol and PEG [2, 3]. In the previous process, PEG functioned as a pore forming agent. The pores in the film were formed by the combustion of PEG by heating to over 400 °C. The maximum thickness of the film prepared by one-run dip-coating reached over 1,000 nm.

Alumina has been widely used as support materials for many catalytic applications [4]. In addition, alumina film has been applied to a microreactor [5] and a humidity sensor [6, 7]. In this paper, the addition of PEG to the dip-coating solution, which is an aqueous sol of colloidal alumina particles, is proposed as a new type of aluminum hydroxide sol for control of microstructure in the alumina film. The effects of the addition of PEG to the sol on the thickness and microstructure of the resultant film are investigated.

## 2 Experimental

The dip-coating solutions were prepared by the following method. The powder of aluminum(III) isopropoxide (20.03 g) was put into a flask. The distilled water (3.0 dl) heated at 90 °C was poured into the flask. A white suspension was obtained. PEG (0–3.33 g) was added to this suspension under stirring with magnetic stirrer. A small quantity of concentrated nitric acid (1.0 ml) was added to the suspension and then heated at 90 °C with strong stirring

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to remove organic solvent. During stirring at 90 °C for 3 h, the opaque suspension changed gradually to clear sol by peptization. The clear sol was concentrated to a fixed volume (1.0 dl) with heating at the same temperature. The coefficient of viscosity of the dip-coating solutions was measured using a rotational viscometer at 25 °C. The alumina films were prepared by dip-coating of glass substrates with different pulling rates using the prepared solutions. The glass substrate (38×26×1 mm) was then withdrawn from the solution with the fixed rate, followed by drying at 80 °C for 15 min and heating up to 500 °C for 30 min in an electric furnace. The thickness of the films was measured by a field-emission scanning electron microscopy (FE-SEM).

### 3 Results and discussion

The viscosity of the dip-coating solutions is very important because film thickness depends on the viscosity of the solution at a constant pulling rate of a substrate. Figure 1 shows the coefficient of viscosity of sols measured with a rotary viscometer at 25 °C. The coefficient of viscosity of the sols decreased with the increase in rotation number. It indicates that these sols are a non-Newtonian liquid and a thixotropic sol. Figure 2 shows the change of the coefficient of viscosity of the solutions with PEG contents at 30 rpm. The coefficient of viscosity of the sols increased remarkably with the increase in PEG content.

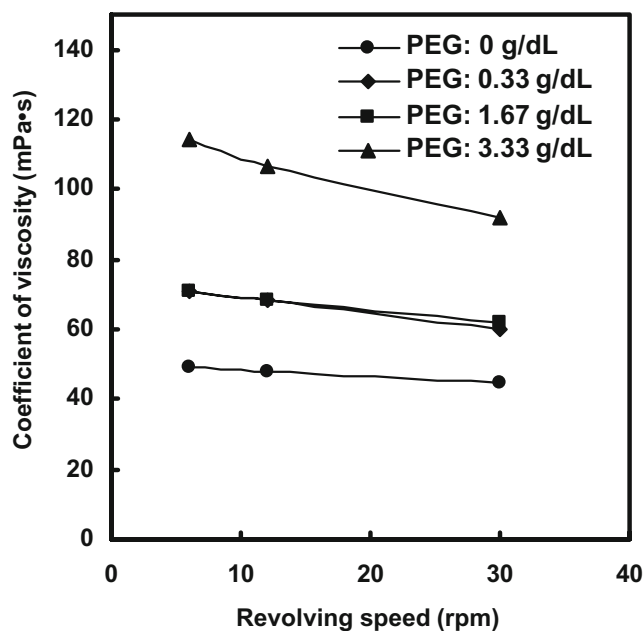


Fig. 1 Coefficient of viscosity of the sols measured by rotary viscometer at 25 °C

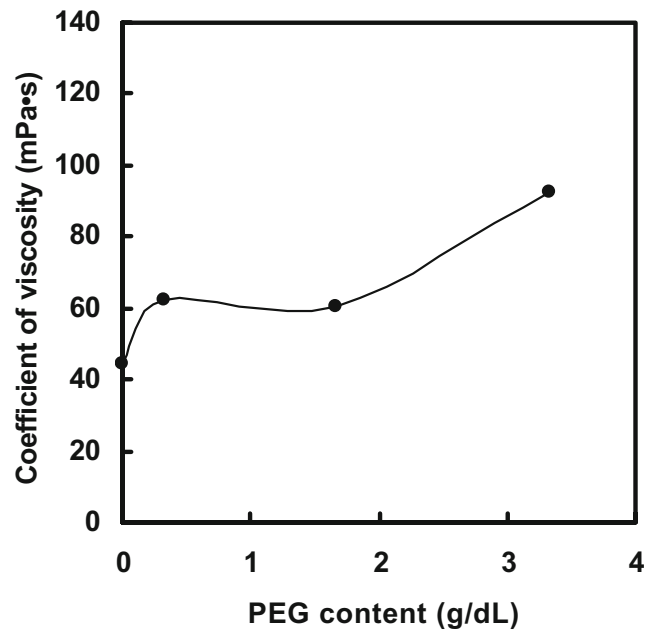


Fig. 2 Relationship between viscosity of sol and PEG content

Figure 3 shows the relationship between a diameter of colloidal particle and PEG content. The diameter of colloidal particle was measured by a dynamic laser scattering method. The diameter of colloid was decreased sharply at 0.33 g/dl of PEG content. Over 0.33 g/dl of PEG content, the diameters of colloid were almost same. The PEG addition caused the sol to increase the degree of dispersion of colloid. It suggested that there was a strong interaction between the colloidal particle and PEG, which

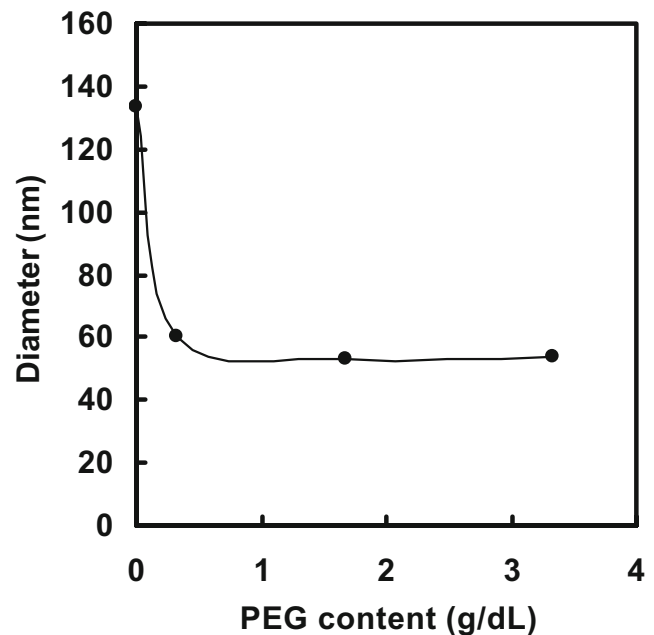


Fig. 3 Relationship between diameter of colloidal particle and PEG content

may be attributed to an adsorption of PEG on the surface of the colloidal particle.

The alumina films were prepared by dip-coating of glass substrates with different pulling rates using the dip-coating solutions containing PEG. All films prepared on the glass substrates were transparent, uniform and crack-free. These films showed a weak peak of  $\gamma$ -alumina (440) in a XRD measurement. Figure 4 shows the pulling rate dependence of the thickness of the alumina films, which were heated at 500 °C. The thickness of the film was increased with the increase in the pulling rate. In the case of the sol containing PEG (3.33 g/dl), the maximum thickness of the film obtained by one-run dip-coating was ca. 1,000 nm. The film thickness was increased also with the increase in PEG content, because the viscosity of the sols was increased with the increase in PEG content.

Figure 5 shows the SEM photograph of the cross section of the thick alumina film deposited on the substrate using the sol containing PEG (3.33 g/dl). From this observation, it is obvious that the film is an aggregate of alumina particles with a diameter of 30–50 nm and interstices between the particles are characteristically existing. It is observed that the nanoparticles deposited uniformly along the direction perpendicular to the surface.

Figure 6 shows that the relationship between the porosity of alumina films and PEG content in the solution. These alumina films were coated on the glass substrate at 0.60 mm/s of pulling rate. The porosity  $\varepsilon$  of the films were estimated by the following equation.

$$\varepsilon = (1 - d/D) \times 100$$

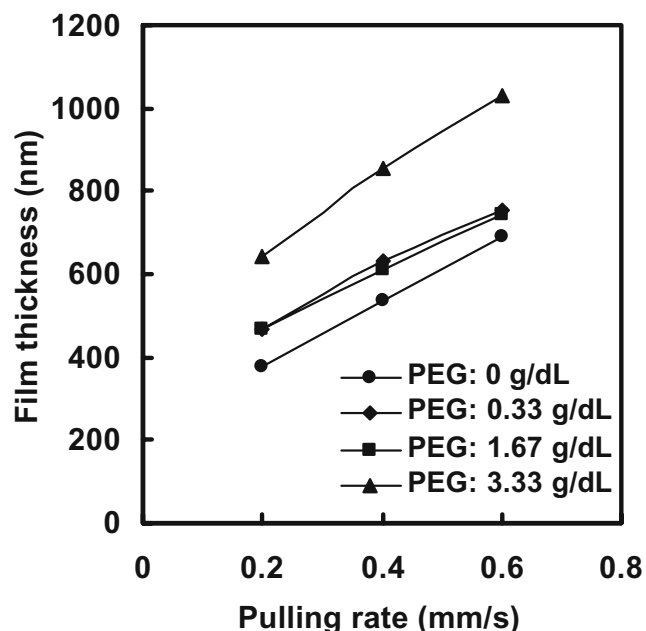


Fig. 4 Relationship between film thickness and pulling rate

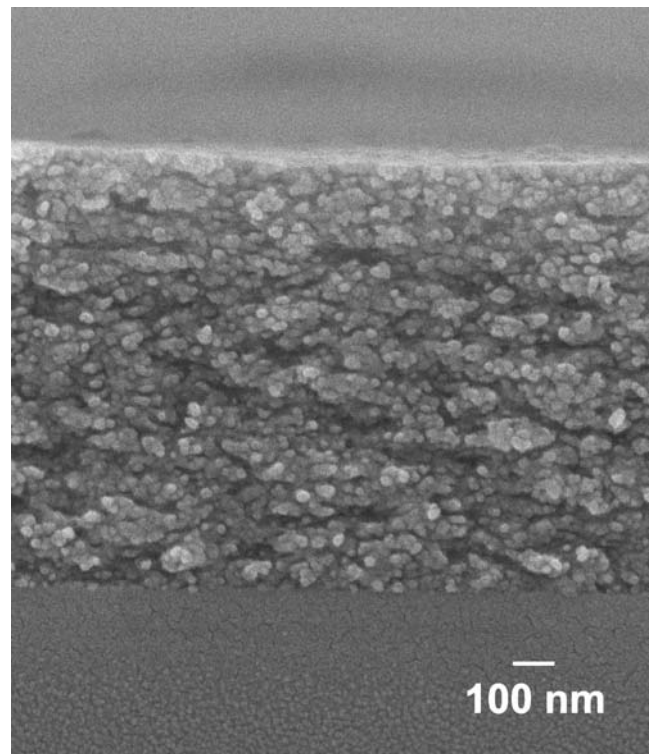


Fig. 5 SEM photograph of cross section of the alumina film prepared from the sol containing PEG (3.33 g/dl)

Film density  $d$  was calculated using thickness, coated film area and weight of the film. True density  $D$  of  $\gamma$ -alumina was 3.72 g/cm<sup>3</sup>. The porosity of the film prepared from the sol containing PEG (0.33 g/dl) decreased than the

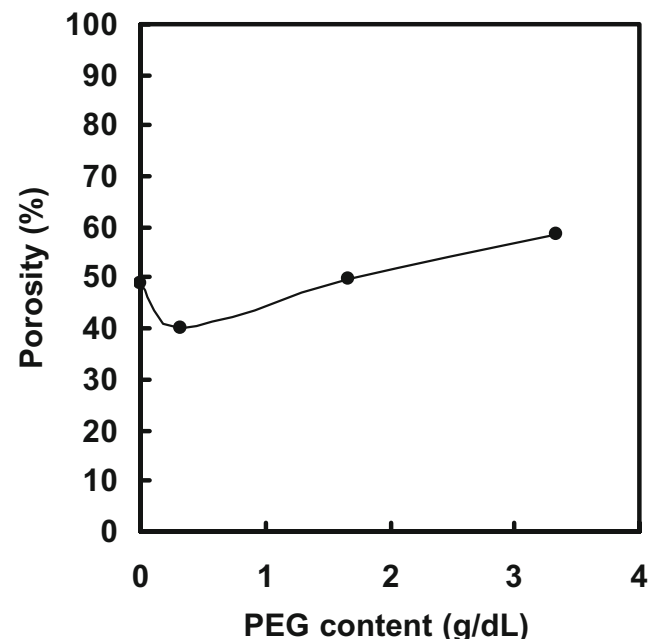


Fig. 6 Relationship between porosity and PEG content

one prepared from the sol without PEG addition. However, the porosity of films increased with the increase in PEG content over 0.33 g/dl of PEG content. Therefore, the porosity is found to be controllable in the range of 40 to 59% by changing PEG content.

The porous and thick alumina film was successfully prepared by the addition of PEG to the coating solution. Commonly, the thickness of the film deposited on the substrate by one run of dip-coating using the sol-gel derived solution was limited to 100–200 nm, because cracking and detachment from the substrate during the heating process can easily occur in the thicker film coated on the substrate. However, these damages were prevented by the addition of PEG to the solution in this technique. PEG (mean molecular weight: 2,000) used as an additive has a melting point of 44 °C. It is considered that the stress induced by the shrinkage of the film during the heating process is relaxed by the plasticity provided to the film by the melting of PEG. The PEG was burned out during heating at 500 °C in the furnace, and resultantly, pores formed in the films. In Fig. 4, the thickness of the films prepared with the same pulling rate increased with the increase in PEG content. The increase of thickness was attributed to the increase of pore volume in the film as well as the increase of viscosity of the sol, because the porosity of the film was increased in the increase of PEG content as shown in Fig. 6. The pore volume in the film was reflected by the volume ratio of PEG to alumina sol in the dried film. It suggested that the PEG addition suppressed the sintering

between the alumina particles and was effective for keeping the porosity of the alumina film.

#### 4 Conclusions

The porous and thick alumina film has been prepared by the dip-coating technique using the aqueous sol containing PEG. Film thickness was controlled by the PEG content and pulling rate. The maximum thickness of the film prepared by one-run dip-coating reached over 1,000 nm. Furthermore, the porosity of the film was controllable in the range of 40 to 59% by changing PEG content. PEG was found to have some positive effects on the fabrication of the porous and thick alumina films.

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