Anodic films formed on magnesium in organic, silicate-containing electrolytes

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Abstract

Anodic films were prepared on magnesium in electrolyte solutions consisting of 3.0 M KOH and various concentrations of sodium silicate and aqueous ethylene-glycol solutions. The anti-corrosion properties of the films formed in the ethylene-glycol electrolyte solutions ranging from 10-40 wt% far exceeded that of the anodic film produced using the HAE method. The film formed under optimal conditions had excellent anti-corrosion properties, which were more than 10-fold greater than those of the HAE anodic films. The anodic film consisted of two layers—a heterogeneous porous layer and a barrier layer; moreover, both carbon and silicate were detected in the anodic film.

Keywords: magnesium, anodic film, organic solution, porous film, barrier film

1. Introduction

Magnesium and its alloys have some excellent properties, such as the lowest density of industrial metals, a high strength-to-weight ratio, vibration absorbency, and electromagnetic wave shield characteristics. Because of these properties, magnesium and its alloys can be applied in the manufacture of components for motor vehicles, in housing for electronics, and in the manufacture of sporting goods. In addition, magnesium and its alloys are more easily recycled than synthetic resins [1, 2], which makes these materials eco-friendly. However, the poor resistance of magnesium and its alloys to corrosion has limited the application of these materials in corrosive environments [3-7]. Thus, surface treatments are needed to improve the corrosion resistance of magnesium and its alloys. Anodization is a popular surface-protective treatment for magnesium and its alloys. In contrast to other surface treatments for magnesium, anodization produces a relatively thick, hard, adherent and abrasion-resistant film [7-11]. The most effective anodic coatings are the commercially available HAE [12] and DOW17 [13]; however, toxic substances, such as chromate and fluoride, are present in the electrolytes used in these products, and the materials treated using these methods appear green and brown, respectively, limiting their decorative use.

Recently, a few new environmentally friendly anodizing electrolytes have been developed [8, 9, 10, 11, 14, 15]. Among these newly developed anodizing electrolytes, some additives and their concentrations significantly affect the properties of the anodic films. For instance, Khaselev found that addition of $Al(OH)_3$ to the KOH electrolyte solution caused sparking, and there is a potential of the film to deteriorate as $Al(OH)_3$ concentration increases [10]. Takaya employed secondary ion mass spectroscopy (SIMS) surface analysis to determine the atomic concentration profile of the anodic film formed on a Mg-Mn alloy in a KOH solution and found that the films consisted mostly of MgO [16]. Fukuda et al. anodized an Al-Mg-Zn alloy in an electrolyte solution containing 3 M KOH, Na_2SiO_3 and Mg_2SiO_4, and found that the corrosion resistance of the film formed in a solution of Na_2SiO_3 increased, based on results of an anodic polarization test in 0.1 M KCl [17]. Hsiao et al. investigated the effects of the addition of Na_2SiO_3 and/or 0.15 M $Al(NO_3)_3$ to 3 M KOH, Na_3PO_4 and KF base electrolyte on the properties of an anodic film on AZ91D Mg alloy. The film formed in the electrolyte indicated good corrosion resistance in 3.5 M NaCl [18, 19]. The effects of KOH, Li_4SiO_4, KF and potassium citrate on anodic films on magnesium were investigated, and the anodic film indicated relatively good corrosion resistance in a 240-h salt-spray test [20, 21]. In these reports, aluminum and silicate ions were included in the electrolyte solution, as environmentally friendly additives, to obtain high corrosion resistance; however, addition of fluoride ions to the electrolyte remained necessary. Other research has focused on the selection of electrolytes with additives such as phosphate, silicate, borate, and organic substances [22–26]. In the literature, the addition of oxysalt to an electrolyte has improved the corrosion resistance of magnesium alloys [23, 24, 27]. Secondary oxysalt addition resulted in different anodizing processes, sparking or nonsparking, and sodium silicate was the most favorable electrolyte additive, resulting in anodic film with the strongest corrosion resistance [28].

Silicates are also inhibitors for iron and steel corrosion in cooling water systems. They form protective films composed of a hydrated gel of silica and iron oxide. Sodium silicate (water glass) and phosphate were remarkably effective on zinc corrosion, exhibiting high inhibition efficiencies at around 90% [29]. Trueman et al. investigated the effect of silicates as a sealing step following cerium treatment of a thick aluminum oxide layer [30]. Silica/ceria treatments improve the corrosion resistance due to the formation of protective oxide films that act as a barrier to oxygen diffusion of the metal surface [31].

The effects of the addition of organic solvents to the electrolyte during the anodization of magnesium and its alloys have been reported. An anodic film formed on magnesium in an electrolyte solution containing silicate, potassium salt, a fluoro-chemical and hydrocarbon showed relatively good corrosion resistance in a 240-h salt-spray test [32, 33]. Asoh et al. studied the properties of magnesium anodic films that formed in an electrolyte solution containing ethylene-glycol, water, triethylamine, sodium aluminate and fluorine ammonium. Anodic films that formed in an electrolyte solution containing 10 vol% of water showed good corrosion properties in a 120-h salt spray test [34]. Organic solvents also have been used to obtain anodic films that are highly resistant to corrosion; however, addition of fluoride ions to the electrolytes was necessary in these studies.

In the present study, alkali electrolytes containing both ethylene-glycol, as an organic solvent, and sodium silicate, but without toxic chromate and fluoride, were used to form anodic films on magnesium with satisfactory anti-corrosion properties. Magnesium anodic films were prepared under various current densities in electrolytes consisting of 3.0 M KOH and various concentrations of sodium silicate and ethylene-glycol. The anti-corrosion properties of the anodic films that formed on magnesium were evaluated using electrochemical impedance measurements in a corrosive 0.5 wt% NaCl solution. The surface appearance and cross-sections of anodic films were observed using a scanning electron microscope (SEM) and the anodic film was analyzed using electron probe micro-analysis (EPMA).

2. Experimental

Magnesium of 99.95% purity was used as the test material. A disk-shaped specimen with a diameter of 12 mm and a thickness of 4 mm was cut from the rod. The specimen was polished with emery paper #2000, immersed in a solution of 5 mass% NaOH at 90 ºC for 6 minutes, and immersed in a solution of 8 vol% nitric acid and 1 vol% sulfuric acid at room temperature for 20 seconds, and washed with ion-exchanged water. All samples were connected with a conductive wire in one side and mounted in a sample holder of polyvinylchloride with an exposed area 10 mm in diameter.

Various concentrations of ethylene-glycol, ranging from 0 to 70 wt%, and of Na_2SiO_3, ranging from 0 to 0.5 M, were added to the base electrolyte solution of aqueous 3.0 M KOH for anodization of the specimen. The temperature of the electrolyte solution was maintained at 20 °C and the liquid was stirred with a magnetic stirrer. In the electrolytic cell, a carbon plate was used as the cathode, while magnesium was used as the anode. Pretreated specimens were anodized in various electrolyte solutions under constant current densities, ranging from 25 to 150 A m^{-2}, for 10 min. After anodization, the specimen was washed with a large amount of ion-exchanged water, and then was dried in air. Conventional HAE anodization of magnesium was carried out under a constant current density of 200 A m^{-2} for 8 min for comparison [12].

Electrochemical impedance spectroscopy (EIS) was measured at the OCP in a corrosive 0.5 wt% NaCl solution at 35 °C to evaluate the anti-corrosive properties of the anodic films. The corrosive solution was air-saturated using an air pump. All anodized specimens were connected with a conductive wire on one side and were then mounted in a sample holder of polyvinylchloride with an exposed area 5 mm in diameter. The specimens were immersed in the solution for more than 10 min after the corrosion potential of the specimen stabilized. Impedance spectroscopy of the specimen was performed in a corrosive solution using a carbon counter, Ag/AgCl reference electrodes connected to a potensiostat (HA-150, Hokuto Denko Co.), a frequency response analyzer (5010A, NF Co.), and a personal computer. Measurement data were transferred to the computer using a GPIB interface. Sine-wave voltages (10 mV rms) at frequencies ranging from 20 kHz to 10 mHz were superimposed on a given electrode potential. The difference in impedance values at high and low frequencies was determined to be the polarization resistance, because the phase-shift was nearly 0 at low frequencies.

After anodization, surface roughness was measured using a surface profile meter. The surface morphology and the film thickness was examined using a Joel JSM-5600 scanning electron microscope (SEM) and electron probe micro-analysis (EPMA).

3. Results and Discussion

3.1. The effect of an organic solvent

Fig. 1 shows the voltage during anodization of the magnesium specimen at a constant current density of 100 A m^{-2} in the electrolyte solution comprised of 3.0 M KOH, 0.25 M Na_2SiO_3, and at various concentrations of ethylene-glycol. The voltages in the electrolyte solution containing 0-40 wt% and 70 wt% ethylene-glycol are depicted in the upper and lower panels of the figure. The surface appearances of specimens after anodization in each condition are shown in Fig. 2. The anodizing voltage in the electrolyte with no ethylene-glycol (0 wt%) was very low and did not increase during anodization. The surface of the specimen after anodization had a metallic luster, similar to that of the specimens prior to anodization (Fig. 2). Therefore, it was concluded that an anodic film did not form in the 0 wt% ethylene-glycol electrolyte. In contrast, the voltage increased linearly during the early stage of anodization in the electrolyte containing 10 wt% ethylene-glycol; the rate then decreased at 80 V. As the concentration of ethylene-glycol was increased further, the voltage at which the rate changed shifted towards higher voltages. However, the rate of the voltage increase during the early stages was the same in all electrolytes. The highest final voltage was observed in the electrolyte with the highest concentration of ethylene-glycol. In the second stage, voltage oscillation was observed in the 20 to 40 wt% ethylene-glycol electrolyte solutions. Voltage drops, with maximal values of 30 V, were observed in the 40 wt% ethylene-glycol electrolyte, but the voltage recovered immediately. At this time, white sparking was observed on the specimen surface, moving over the entire surface.

In contrast, the voltage change in the 70 wt% ethylene-glycol electrolyte was markedly different from that observed in the 10 to 40 wt% ethylene-glycol electrolytes. In the 70 wt% ethylene-glycol electrolyte, after reaching 150 V during the early stage of anodization, the voltage decreased sharply to 90 V, at which time it began to oscillate with an amplitude of 50 V. When the oscillation occurred, localized and stationary orange sparking was observed at the surface of the specimen. The film anodized with the 20 wt% ethylene-glycol electrolyte was white, as shown in Fig. 2; similar films were produced using 10 and 30 wt% ethylene-glycol electrolyte solutions. A gray film formed on the surface of the specimen at concentrations of 40, 50 and 60 wt%. In the 70 wt% ethylene-glycol electrolyte, a white, lustrous film, with some apparent defects, formed on the surface of the specimen. Observation of the surface of the specimen during anodization revealed the following: small areas of a black product formed on the specimen where the sparking occurred. Sometimes the product fell into the electrolyte. The surface profiles of specific regions of the specimens anodized in electrolytes containing 20 and 70 wt% of ethylene-glycol are shown in Fig. 3. The roughness of the film formed in 20 wt% ethylene-glycol electrolyte was greater than 1 μm. In contrast, the film formed in the 70 wt% ethylene-glycol electrolyte was relatively smooth; therefore, it was concluded that the luster of the film formed in 70 wt% ethylene-glycol electrolyte was due to surface smoothness.

The anti-corrosion properties of the anodized specimens were investigated. Fig. 4 shows Cole-Cole plots of anodic films, which were formed in 0 and 70 wt% ethylene-glycol electrolytes, in a corrosive 0.5 wt% NaCl solution. The impedance of the anodic films was nearly a semicircle. All anodic films showed a similar diagram. Therefore, the diameter of this depressed semicircle that represents the difference in impedance between high- and low-frequencies was determined to be the polarization resistance of the anodic film to corrosion.

The values for the polarization resistance of the specimens anodized under constant current density of 100 A m^{-2} in the electrolytes comprised of 3.0 M KOH, 0.25 M Na_2SiO_3 and various concentrations of ethylene-glycol are shown in Fig. 5. The closed plot shows the mean value. The polarization resistance of the anodic film formed using the HAE method is shown by the dotted line in the figure for comparison. The polarization resistance of the specimen anodized in the electrolyte without ethylene-glycol (0 wt%) was very low, as an anodic film did not form (see Figs. 1 and 2). However, the polarization resistance of the specimen anodized in 10 wt% ethylene-glycol electrolyte was superior to that of the specimen anodized using the HAE method. As the concentration of ethylene-glycol increased, maximal polarization resistance was observed for the film anodized using the 20 wt% ethylene-glycol solution. At an ethylene-glycol concentration of 50 wt%, the resistance suddenly decreased, similar to that of the pattern observed for the film anodized using the HAE method. The values for polarization resistance of the specimens anodized at concentrations greater than 60 wt% were reduced further, such that these specimens had no anti-corrosion properties.

3.2. Effect of current density

Anodization of magnesium was carried out at various current densities in the electrolyte solution comprised of 3.0 M KOH, 0.25 M Na_2SiO_3, and 20 wt% ethylene-glycol; the film showed excellent anti-corrosion properties. Fig. 6 shows the relationship between anodization time and voltage for specimens anodized in the electrolyte at various current densities. The rate of voltage increase during the early stage was positively related to current density. When the voltage reached approximately 100 V, the slope changed under all conditions; the voltage increased slightly with anodization time. A small voltage oscillation was observed during the second period under all conditions. After 10 min of anodization, the last voltage increased with current density. The polarization resistance of the anodic films is shown in Fig. 7. The closed plot represents the mean values. The resistance of the anodic film at a current density of 25 A m^{-2} was approximately 30 $k\Omega \cdot cm^2$, which was greater than that of the anodic film formed using the HAE method. At a current density of 50 A m^{-2}, the polarization resistance increased further to 90 $k\Omega$ cm^2. As the current density surpassed 50 A m^{-2}, the resistance decreased. As a result, the polarization resistance of anodic film reached its maximal value at a current density of 50 A m^{-2}. The poor anti-corrosion properties of the specimen anodized at a current density of 25 A m^{-2} may result from the low film thickness.

3.3. The effect of sodium silicate

Fig. 8 shows the relationships between anodization time and voltage in electrolyte solutions comprised of various concentrations of sodium silicate and 20 wt% ethylene-glycol at a current density of 50A m^{-2}. When sodium silicate was not added to the electrolyte (0 wt%), the voltage remained unchanged; similarly, voltage remained constant in the absence of ethylene-glycol, as indicated in Fig. 1. However, in the electrolyte solution containing sodium silicate at concentrations greater than 0.1 M, the voltage increased during the early stage of anodization and the rate of increase was similar under all conditions. When the voltage reached a threshold value, the rate decreased. The voltage was lower at higher concentrations of sodium silicate. The electrolyte without sodium silicate did not result in an anodic film; the film without ethylene-glycol was not anodized, as shown in Fig. 1. Thus, both ethylene-glycol and sodium silicate must be present in the electrolyte solution for formation of an anodic film.

The relationship between the polarization resistance of a specimen anodized in the electrolyte containing 0 to 0.5 M Na_2SiO_3, 20 wt% ethylene-glycol and 3.0 M KOH at a current density of 50 A m^{-2} is shown in Fig. 9. The polarization resistance of the specimen anodized in the electrolyte without Na_2SiO_3 was quite low. This result was observed because an anodic film did not form on the surface of the specimen, as indicated in Fig. 8. However, polarization resistance increased with increasing concentrations of Na_2SiO_3; maximal polarization resistance reached 100 kΩ·cm^2 at 0.3 M Na_2SiO_3. Therefore, the optimal Na_2SiO_3 concentration was determined for production of an anodic film with excellent resistance to corrosion.

Fig. 10 shows SEM images of the anodic films formed in the electrolyte containing various concentrations of Na_2SiO_3, 20 wt% ethylene-glycol and 3.0 M KOH at a current density of 50 A m^{-2}. Many pores, 0.5 to 1 μm in diameter, were observed on the surface of the specimen anodized in the electrolyte with 0.2 M Na_2SiO_3. In the 0.3 M Na_2SiO_3 electrolyte solution, larger pores, i.e., 2 μm in diameter, and some cracks were observed on the surface of the anodic film. The pore size of the anodic film that formed in the electrolyte containing 0.5 M Na_2SiO_3 was increased further, and cracks were also observed.

SEM images of cross-sections of specimens anodized in the electrolyte containing various concentrations of Na_2SiO_3 and line analysis of the chemical components, i.e., Mg, C, O, and Si, using EPMA measurements, are shown in Fig. 11. Observation of the cross-sections of these specimens revealed that all anodic films were approximately 1-μm thick with a heterogeneous porous layer. However, due to the distribution of Mg in the depth direction, as determined by EPMA, the level changed until a depth of 4 μm; therefore, the anodic films consisted of a porous layer and a barrier layer. Formation of a porous layer was consistent with the report of Ono [35]. Mg, O, and Si were detected in both layers, with similar distributions. The film of the inner layer appeared to be an oxide of magnesium and silicate, Mg_2SiO_4 [17]. Carbon was also detected in both layers, but it was distributed in the interface between the outer and inner layers and the distribution in the anodic film differed among electrolytes. Formation of carbon was due to decomposition of ethylene-glycol. In the film anodized in the electrolyte containing 0.3 M Na_2SiO_3, carbon was concentrated at the boundary of the inner layer to form Mg_2SiO_4, involving a significant amount of carbon. In contrast to the large amount of carbon in the outer layer, consisting of 0.2 M Na_2SiO_3, only a small amount of carbon was found in the outer layer of 0.5 M Na_2SiO_3. However, no significant films were detected at the boundary of the inner layer in either case. In general, the boundary of the inner layer of the film is primarily responsible for the resistance to corrosion. Therefore, the anodic film that formed in the electrolyte containing 0.3 M Na_2SiO_3 had excellent anti-corrosion properties. Fluorine is used for the formation of films with high resistance to corrosion; insertion of fluoride into the oxide film creates a dense film. The atomic radius of carbon is 0.077 nm, which is similar to the atomic radius of fluorine—0.072 nm. Therefore, it is believed that the dense film formed in the ethylene-glycol solution is the result of a mechanism similar to that found in conventional methods. Consequently, the structure of the anodic film on the magnesium specimen formed in the electrolyte solution containing 20 wt% ethylene-glycol, 0.3 M Na_2SiO_3 and 3.0 M KOH at a current density of 50 A m^{-2} consisted of a porous layer and a barrier layer. It was confirmed that the carbon that was inserted into the oxidation film consisted of magnesium and silicate. In addition, the boundary of the inner barrier layer was dense, although the resistance of the outer porous layer to corrosion was poor, as indicated in Fig. 10.

4. Conclusions

Environmentally friendly anodic films were prepared on magnesium under constant current densities in electrolyte solutions comprised of 3.0 M KOH and various concentrations of sodium silicate and ethylene-glycol aqueous solutions at 20 °C. The anti-corrosion properties of films anodized in the electrolytes were evaluated using the electrochemical impedance method in a corrosive solution of 0.5% NaCl, and the following results were obtained.

1) Both the polarization resistance and the appearance of the resulting anodic films were highly

dependent on the concentration of ethylene-glycol in the electrolyte. The specimens anodized in the electrolytes containing 10 to 40 wt% ethylene-glycol showed excellent anti-corrosion resistance, which was 10-fold greater than that of the anodic film produced using the HAE method. The anodic film formed in the electrolyte containing 20 wt% ethylene-glycol also showed excellent anti-corrosion properties.

2) The applied current density and concentration of sodium silicate in the electrolyte containing 20 wt% ethylene-glycol were optimized, resulting in optimal values of 50 A m^{-2} and 0.3 M of sodium silicate, respectively.

3) The optimized anodic film that formed on magnesium consisted of a porous layer and a barrier layer. Insertion of carbon, consisting of magnesium and silicate, into the anodic film leads to excellent anti-corrosion properties.

Acknowledgement

This research was supported in part by the Research for Promoting Technological Seeds, Japan Science and Technology Agency (No. 12-071).

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Figure captions

Fig. 1. Voltage during anodization of magnesium specimens under a constant current density of 100 A m^{-2} in electrolytes containing various concentration of ethylene-glycol, 3.0 M KOH and 0.25 M Na_2SiO_3.

Fig. 2. Surface appearance of magnesium specimens after anodization at a current density of 100 A m^{-2} in electrolytes containing various concentrations of ethylene-glycol, 3.0 M KOH and 0.25 M Na_2SiO_3.

Fig. 3. Surface profile of magnesium specimens anodized in electrolytes containing various concentrations of ethylene-glycol (20 and 70 wt%), 3.0 M KOH and 0.25 M Na_2SiO_3.

Fig. 4. Cole-Cole plots of anodic films measured in a corrosive solution of 0.5 wt% NaCl solution: the films were anodized in electrolyte solutions containing 0 and 70 wt% ethylene-glycol.

Fig. 5. Polarization resistance of magnesium specimens anodized at a current density of 100 A m^{-2} in electrolytes containing various concentrations of ethylene-glycol, 3.0 M KOH and 0.25 M Na_2SiO_3. Dotted line shows the polarization resistance of the specimen anodized using the HAE method.

Fig. 6. Relationship between anodization time and voltage for specimens anodized in the electrolyte containing 20 wt% ethylene-glycol, 3.0 M KOH and 0.25 M Na_2SiO_3 at various current densities.

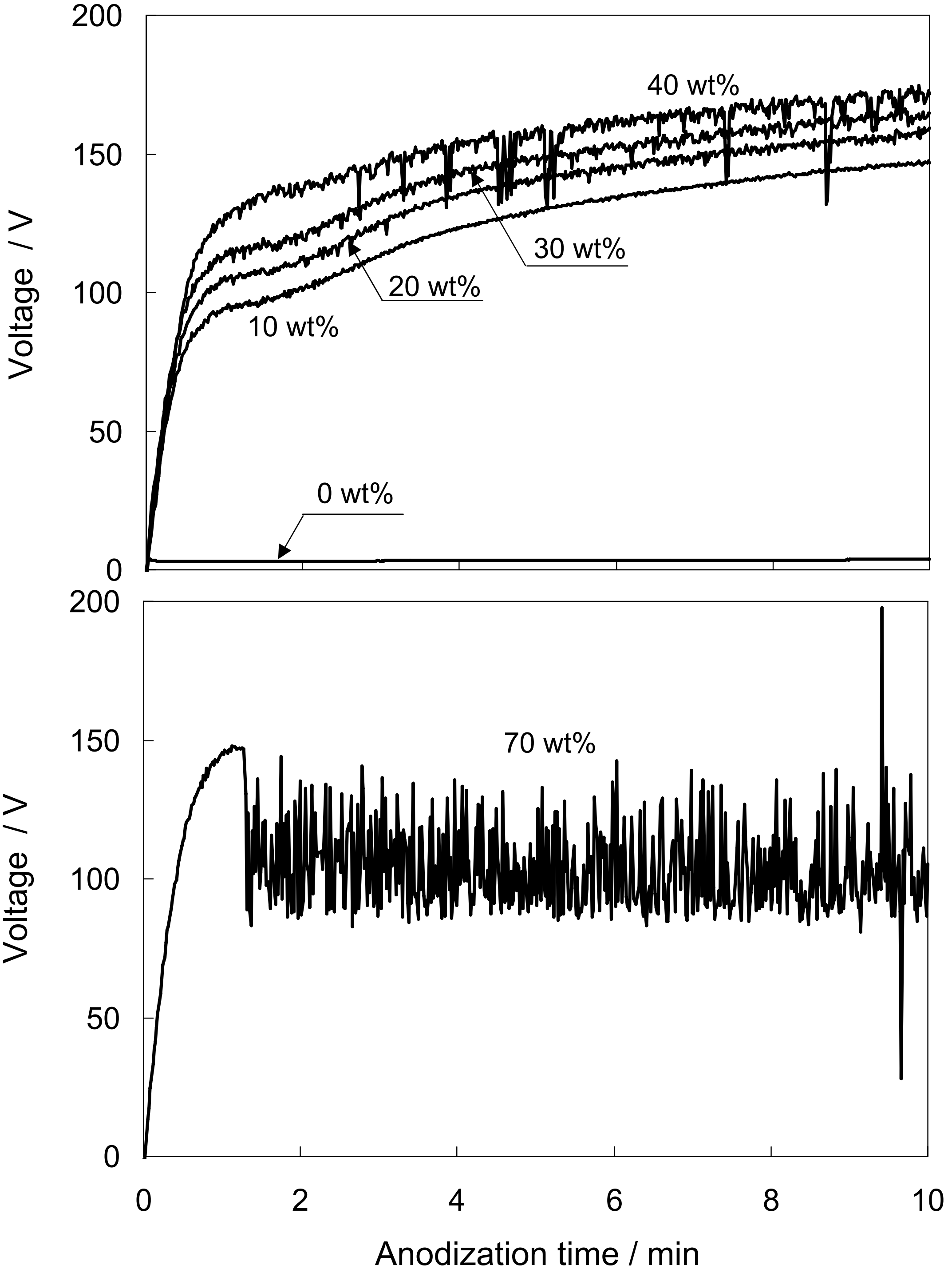
Fig. 7. Polarization resistance of magnesium specimens anodized under various current densities in the electrolyte containing 20 wt% ethylene-glycol, 3.0 M KOH and 0.25 M Na_2SiO_3. Dotted line shows the polarization resistance of specimens anodized using the HAE method.

Fig. 8. Relationship between anodization time and voltage in electrolyte solutions containing various concentrations of Na_2SiO_3, 20 wt% ethylene-glycol at a constant current density of 50 A m^{-2}.

Fig. 9. Polarization resistance of magnesium specimens anodized in electrolytes containing various concentrations of Na_2SiO_3, 20 wt% ethylene-glycol and 3.0 M KOH at a constant current density of 50 A m^{-2}. Dotted line shows the polarization resistance of specimens anodized using the HAE method.

Fig. 10. SEM images of anodic films formed in electrolyte containing various concentrations of Na_2SiO_3, 20 wt% ethylene-glycol and 3.0 M KOH under a constant current density of 50 A m^{-2}.

Fig. 11. SEM image of cross-sections of magnesium specimens anodized in electrolytes containing various concentrations of Na_2SiO_3 20 wt% ethylene-glycol and 3.0 M KOH under a constant current density of 50 A m^{-2}. Lines in the figure are results of the line analysis of the chemical components, i.e., Mg, C, O and Si, using EPMA measurements.



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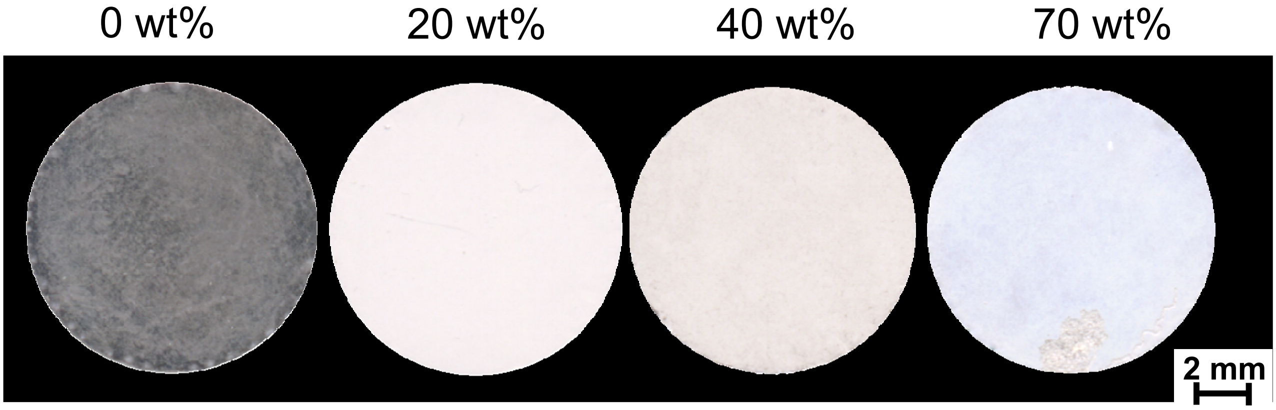

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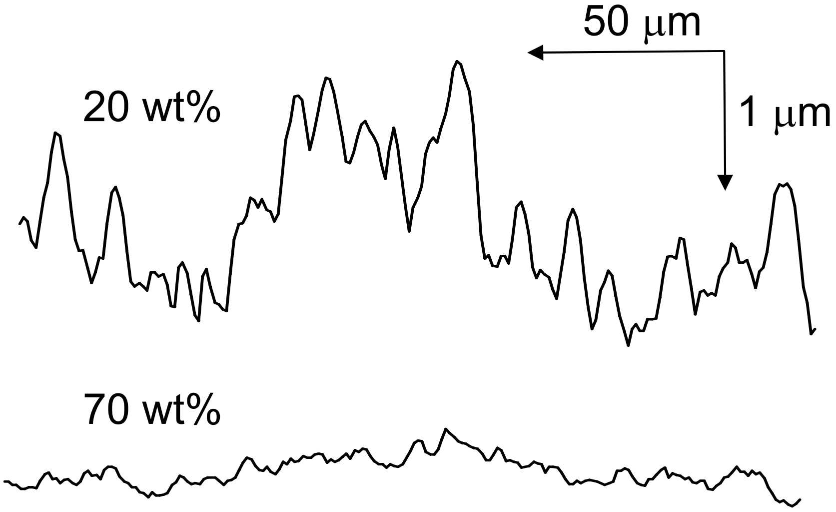

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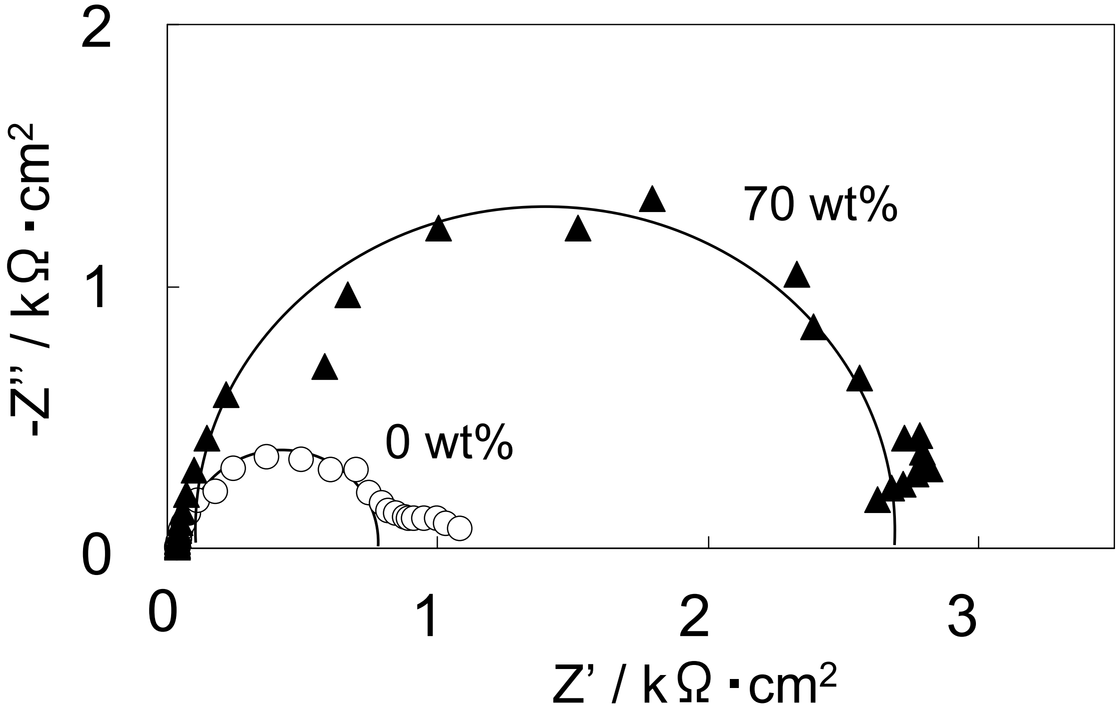

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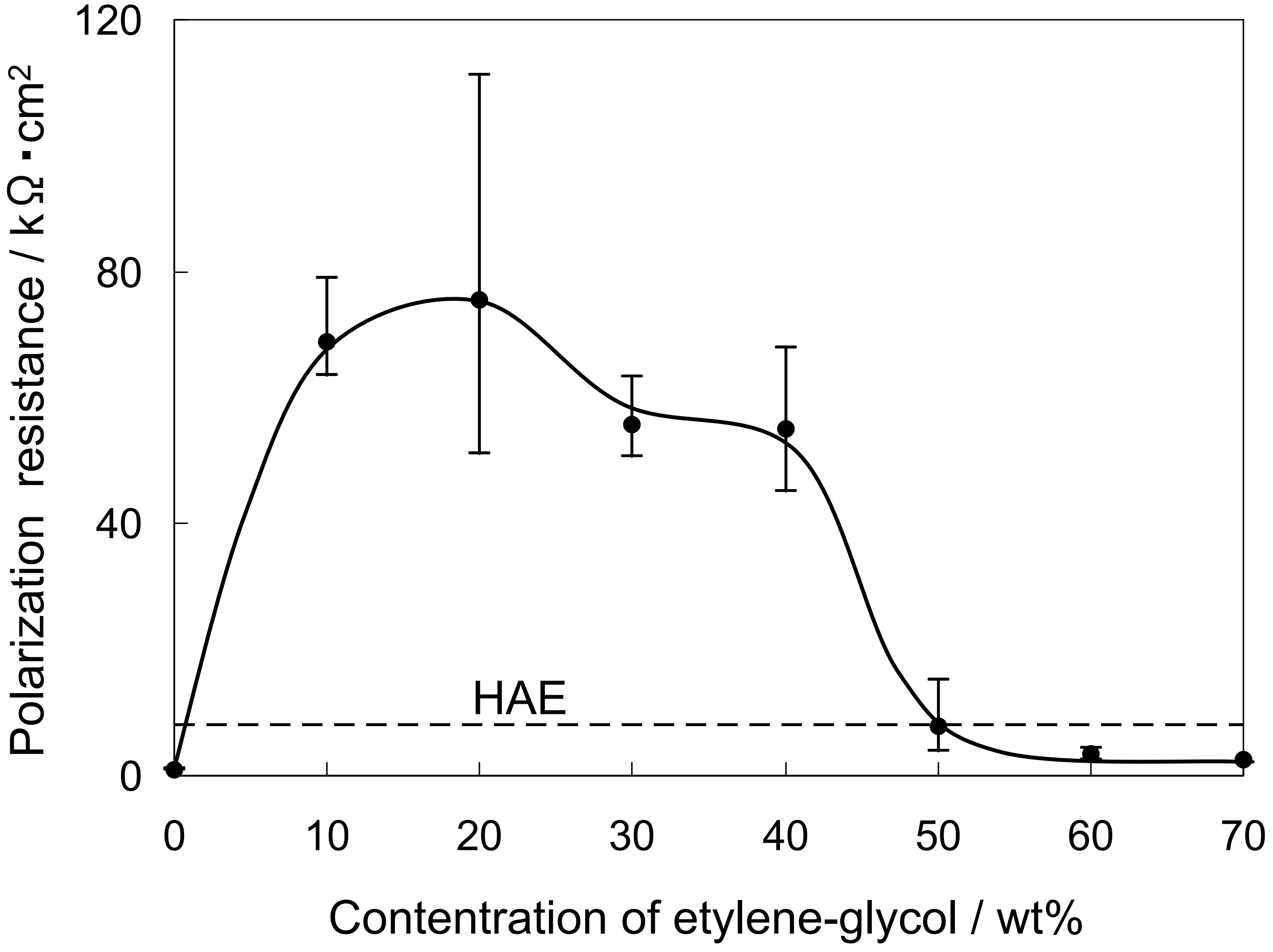

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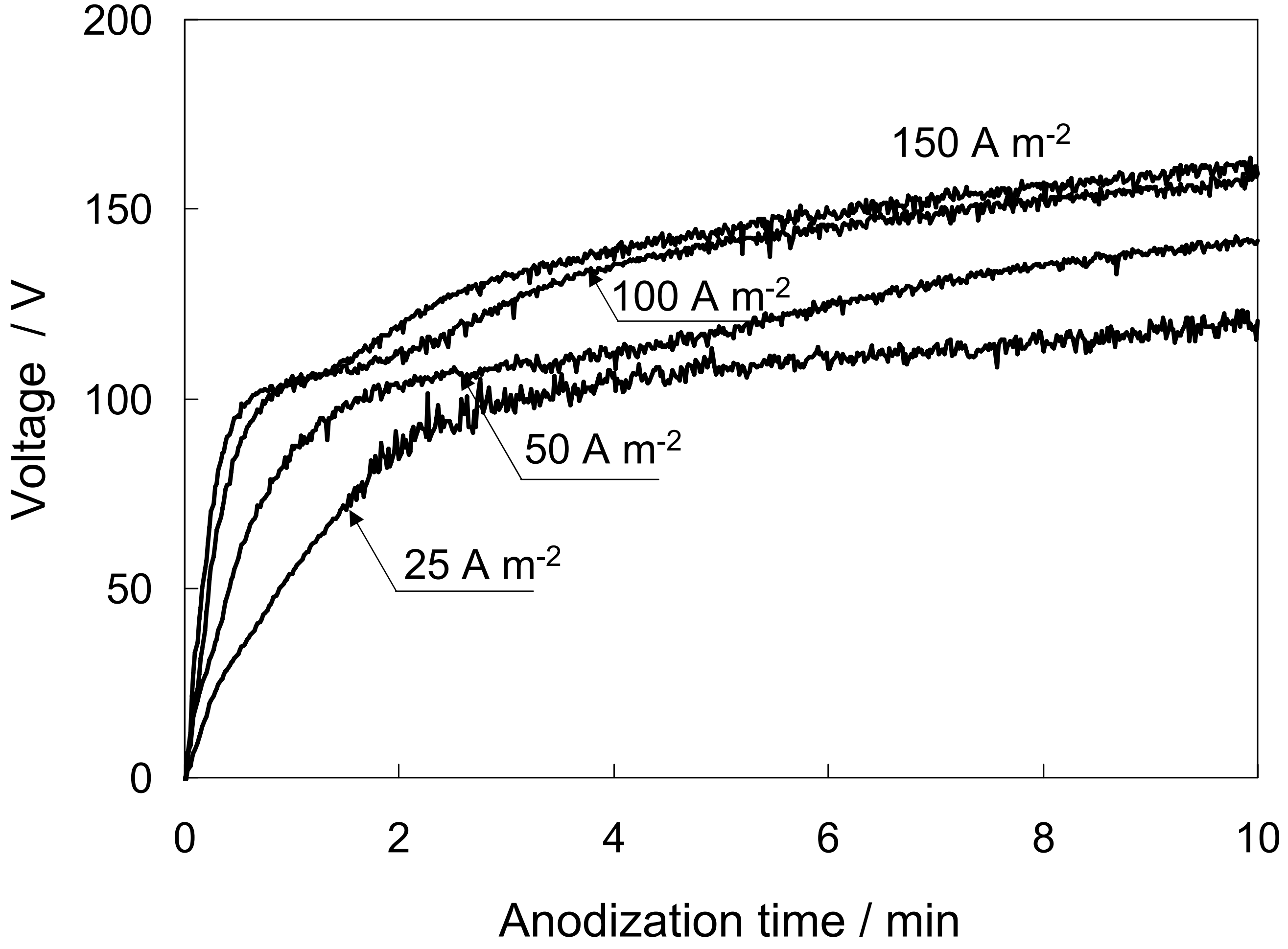

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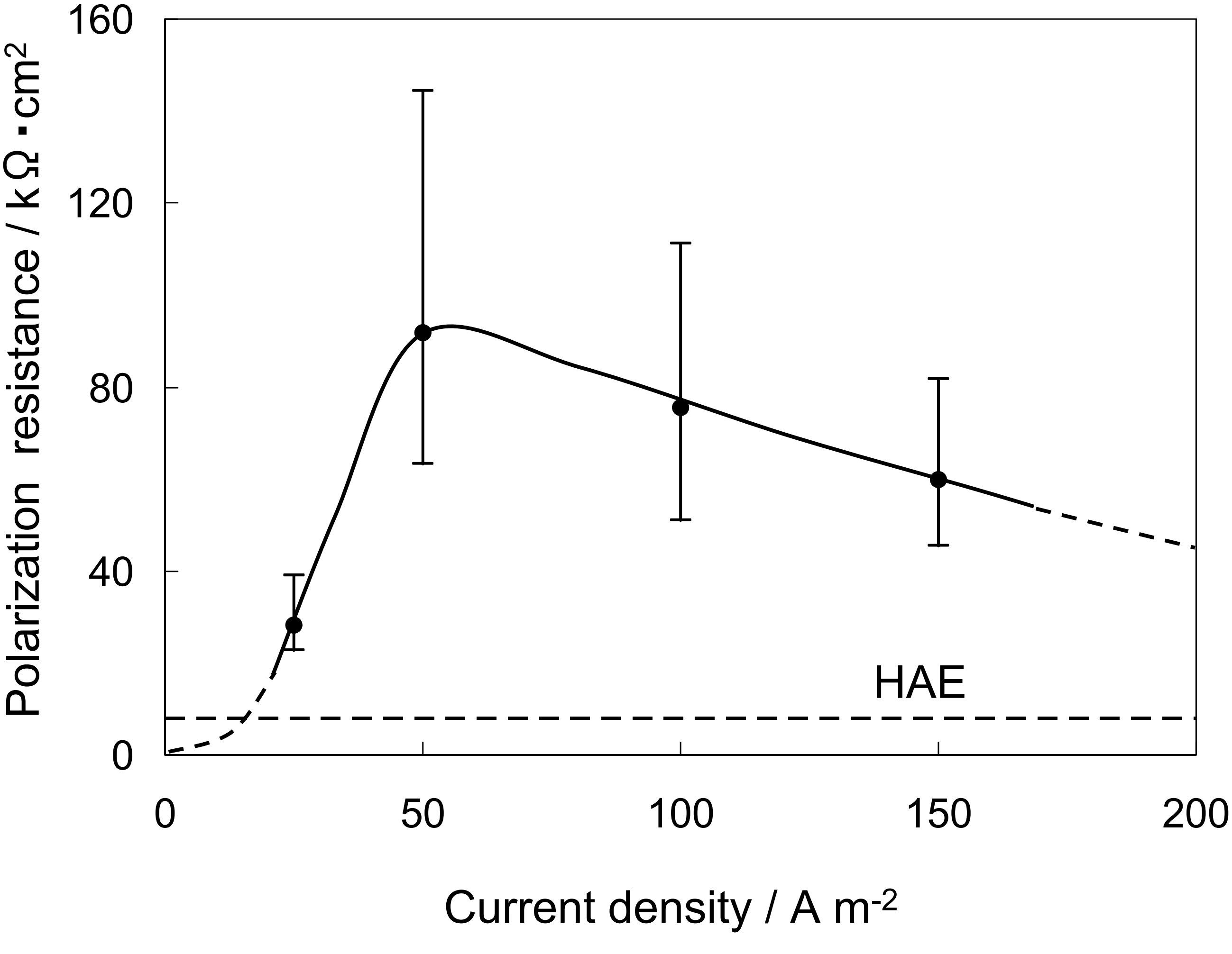

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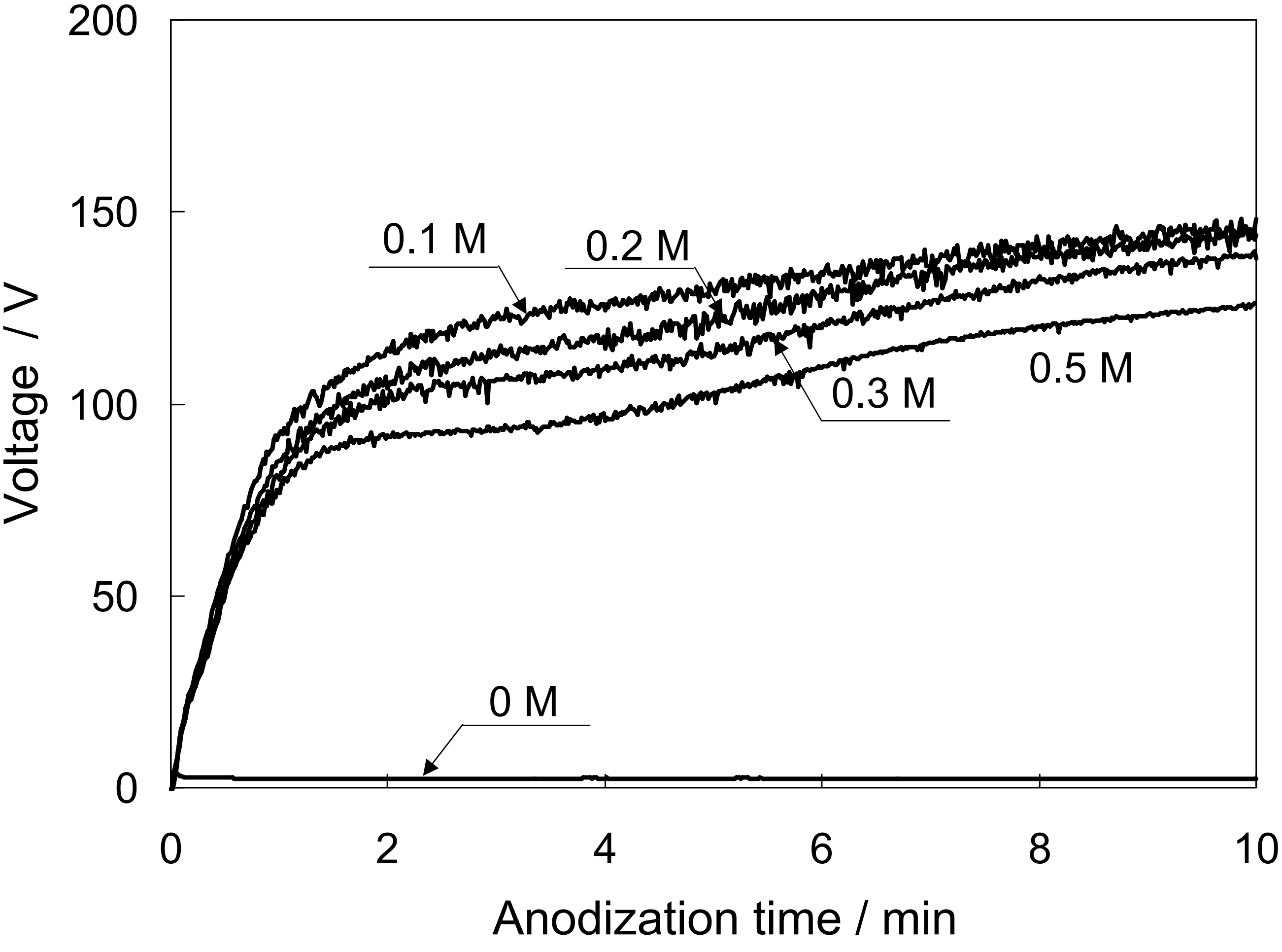

Fig. 8 Akihiro Yabuki et. al.

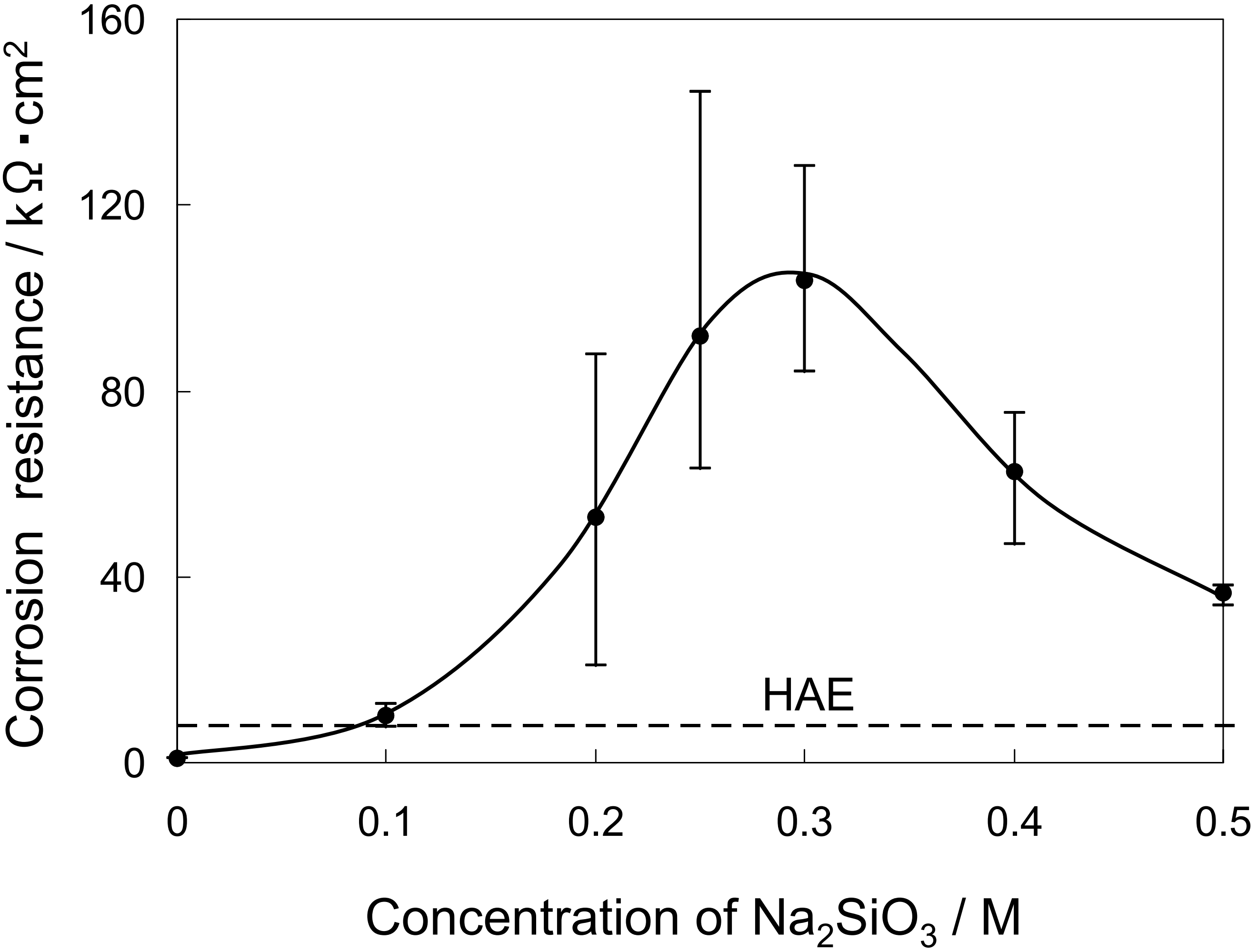

Fig. 9 Akihiro Yabuki et. al.

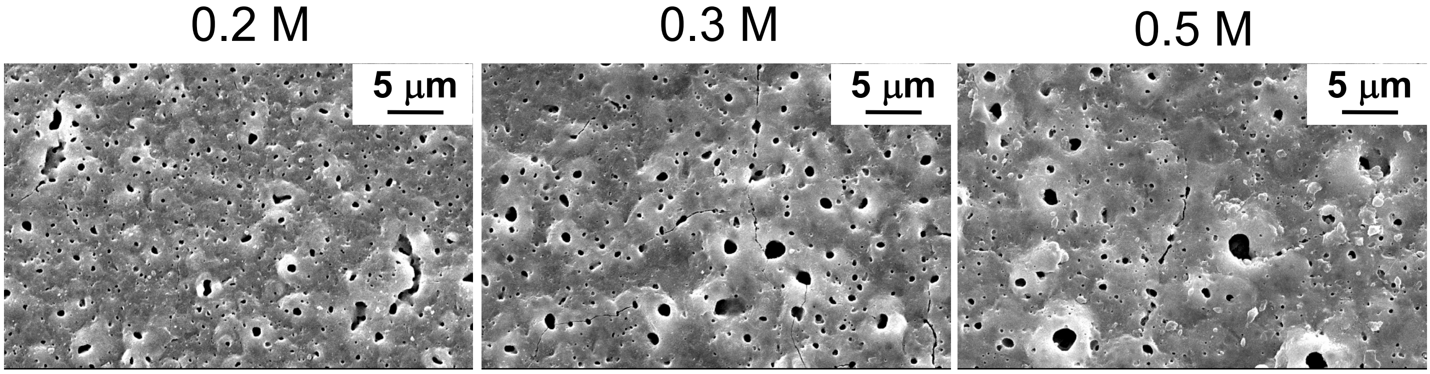

Fig. 10 Akihiro Yabuki et. al.

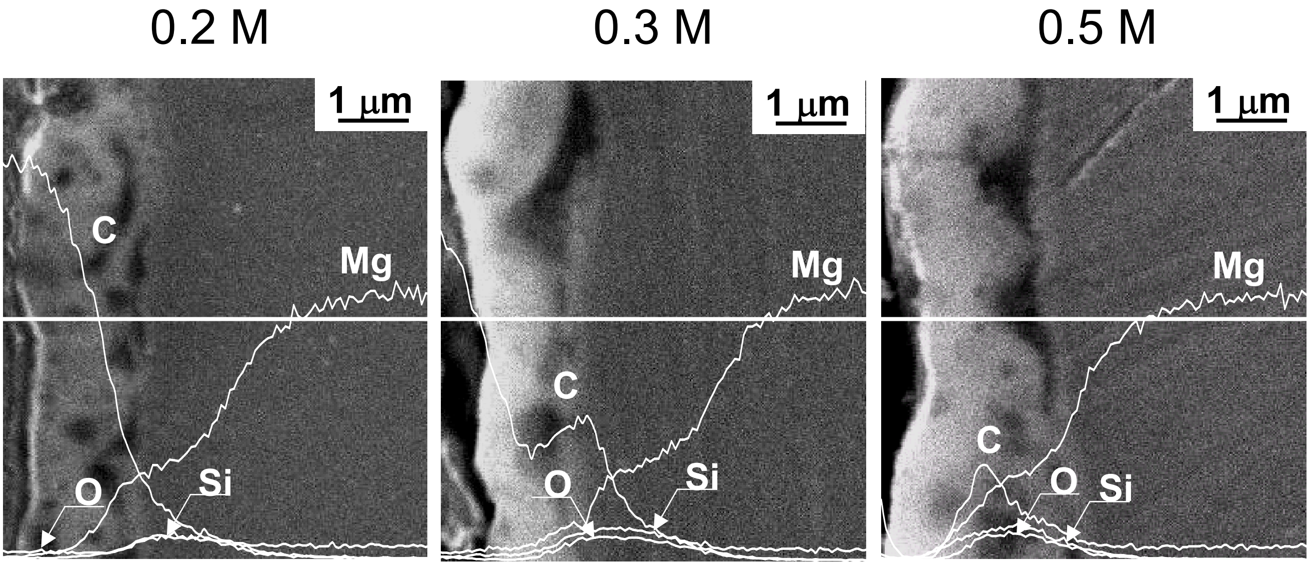

Fig. 11 Akihiro Yabuki et. al.