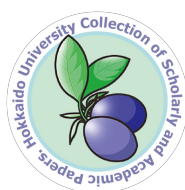




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Highly increased breakdown potential of anodic films on aluminum using a sealed porous layer

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Abstract

The growth of a uniform barrier-type anodic film on aluminum is usually terminated by electric breakdown, which is controlled by the resistance of electrolyte or anion concentration. In this study, highly resistive porous layers have been introduced by anodizing aluminum in sulfuric acid electrolyte followed by boiling water treatment to examine their influence on the electric breakdown potential. The pores of the porous alumina film are sealed by forming hydrated alumina (pseudo-boehmite) after the boiling water treatment. The breakdown potential increases to over 1500 V for the pore-sealed aluminum specimens on anodizing in sodium tungstate electrolyte. The electrochemical impedance spectroscopy measurements revealed an increased resistance of the porous layer after the pore-sealing treatment. GDOES depth profile analysis disclosed that the sealed porous layer impedes the incorporation of tungsten species into the barrier layer. The introduction of a highly resistive layer that also suppresses the anion incorporation on aluminum is effective in increasing the breakdown potential of anodic films.

Keywords: Anodizing, aluminum, anodic film, pore sealing, electric breakdown

1 Introduction

2 Valve metals, such as aluminum, hafnium, niobium, tantalum, and zirconium, produce a compact “barrier-type”
3 anodic film at high efficiency in the appropriate electrolyte. Aluminum, niobium and tantalum form amorphous
4 anodic oxides, and their growth involves cooperative transport of cations (outwards) and anions (inwards) under
5 a high electric field of $\sim 10^6 \text{ V cm}^{-1}$, forming film material both at the film/electrolyte and metal/film interfaces,
6 respectively [1]. Such anodic oxide films are of practical importance as dielectric layers in capacitor industry
7 [2-6] and memristive films for nonvolatile memory devices [7, 8].

8 In galvanostatic anodizing of aluminum, niobium and tantalum, the anodizing potential rises linearly with
9 anodizing time because of the constant thickening of the anodic film. However, the potential rise is terminated
10 by electric breakdown, which often involves sparking [9, 10]. Thus, it is important to know the factors
11 controlling the breakdown potential, E_B , to grow relatively thick anodic films. Early studies demonstrated that
12 the E_B increases linearly with the logarithm of the electrolyte resistivity, ρ , as follows [11, 12]:

$$13 \quad E_B = A + B \log \rho \quad (1)$$

14 where A and B are the constants depending on the electrolyte composition and the anodizing metal. Yaholom
15 and Hoar reported the importance of the type and amount of electrolyte anion in the E_B [10]. Later, Kato *et al.*
16 reported that E_B decreases linearly with an increase in the logarithm of anion concentration at a fixed solution
17 resistivity [13]. In contrast, the current density, electrolyte temperature, stirring of electrolyte, surface
18 topography, and history of anodic oxides have little influence on the breakdown [9, 14, 15]. The mechanism of
19 the electric breakdown of anodic oxides has often been discussed by an “electron avalanche” model proposed
20 first by Ikonopisov [16] and later modified by Albella [17].

21 Several attempts have been made to increase the E_B of anodic oxides. Increased E_B is of practical
22 importance in the fabrication of electrolytic capacitors with high withstand potentials. As shown in Equation (1),
23 the E_B increases with the increase in the electrolyte resistivity. Li *et al.* reported that the anodizing potential for
24 high purity aluminum increased to $\sim 1800 \text{ V}$ in diluted $5 \text{ mmol dm}^{-3} \text{ H}_3\text{BO}_3$ electrolyte. However, anodizing in
25 this electrolyte involved gas generation above 1000 V , and the anodic film contained many flaws [18]. In diluted
26 KOH and NaOH electrolytes, the anodizing potential exceeded 1000 V , but above 850 V , non-uniform anodic

films with a scalloped metal/film interface were developed [19].

A pore-filling method was used to raise the E_B of anodic alumina films. Prior to a barrier-type film growth on aluminum, a porous anodic alumina film was formed in sulfuric acid or oxalic acid electrolyte. The subsequent anodizing in either diluted H_3BO_3 or KOH electrolyte formed new film material at the pore base, which filled the pores by outward migration of Al^{3+} ions, in addition to the film formation at the metal/film interface by inward migration of O^{2-} ions [20, 21]. The E_B by pore-filling method was higher by 100-200 V than that of the anodic alumina [22]. This was obtained by avoiding the local concentration of the current flow under the presence of alumina micropores.

A sol-gel coating on aluminum is also an effective way to grow a uniform anodic alumina film to >1000 V [23]. Anodizing SiO_2 -coated aluminum in $0.5 \text{ mol dm}^{-3} H_3BO_3$ electrolyte at 293 K formed a composite oxide film, consisting of an outer SiO_2 layer, an intermediate Al_2O_3 - SiO_2 composite layer, and an inner alumina layer. The thickness of the outer SiO_2 layer was reduced while the composite and alumina layers thickened with an increase in the anodizing potential. It was also found that less-defective anodic films were formed to 1000 V by SiO_2 coating, but the E_B increased from 1150 V to 1200 V.

The findings from the past studies indicate that the E_B can be increased by using highly resistive electrolyte for anodizing. However, the high resistivity is likely to be needed only on the surface region of the metal and not in the bulk electrolyte. The introduction of a highly resistive layer on aluminum may increase the E_B effectively. Thus, in the present study, an attempt has been made to increase the E_B by introducing a boiling-water-sealed porous anodic alumina layer prior to growing a barrier layer to high potentials.

Experimental

An aluminum foil (99.99% purity) of 0.1 mm thickness was used in this study. The foil was first electropolished at 20 V in a mixed solution of 60% $HClO_4$ and ethanol (1:4 volume ratio) below 283 K for 5 min. Porous alumina films of 4.8 μm to 26 μm were formed by anodizing the electropolished aluminum foil at 25 V in $0.3 \text{ mol dm}^{-3} H_2SO_4$ (SA) electrolyte at 288 K. A two-electrode cell with an aluminum foil as a counter electrode was used to form the porous alumina films. Hereafter, the specimens with anodic films of 4.8, 11, and 26 μm

thickness are denoted as SA4.8, SA11, and SA26, respectively. The pore-sealing treatment was then conducted by immersing the aluminum foil with a porous alumina film in boiling water for 10 min. The boiling-water-treated specimens are denoted, for instance, as SA4.8-BW. This treatment induced the precipitation of pseudo-boehmite (hydrated alumina) in the nanopores of the alumina films [24]. The barrier-type anodic alumina films were grown at a constant current density of 50 A m^{-2} in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{WO}_4$ electrolyte ($\text{pH} = 7.8$) at room temperature. A two-electrode cell with a platinum wire as a counter electrode was used to grow the barrier layer.

Surfaces and fracture cross-sections of the specimens were observed using a field-emission scanning electron microscope (either JEOL, JSM-6500F or Zeiss, Sigma-500). The electrochemical impedance spectroscopy (EIS) measurements of the anodized specimens were performed using an Ivium, Compactstat with a frequency response analyzer. A three-electrode cell with a Pt counter electrode and an Ag/AgCl (saturated KCl) reference electrode were used for the EIS measurements. A salt bridge was used to suppress the contamination of the electrolyte by chloride ions. The measurements were conducted at an open circuit potential with an AC amplitude of 100 mV in the frequency range of 10^5 Hz to 0.1 Hz .

Results and Discussion

Scanning electron micrographs of the surface and cross-section of aluminum anodized in SA for 30 min (Figs. 1a and 1b) disclose the formation of nanoporous anodic alumina films, which were developed to the direction normal to the metal/film interface (Fig. 1b). The porous alumina film was uniform in thickness, i.e., $4.8 \text{ }\mu\text{m}$, and the pore diameter was 10-15 nm. The film thickness increased almost linearly with anodizing time at a rate of $0.18 \text{ }\mu\text{m min}^{-1}$. Thus, the film thickness was readily controlled by anodizing time.

After the boiling water treatment, the surface morphology was found to change as shown in Fig. 1c. Flaky hydrated alumina layer was formed, which is typical of the boiling-water-treated alumina film [24]. The cross-section image (Fig. 1d) discloses that the nanopores were filled with hydrated alumina precipitates, although there is small porosity even after the boiling water treatment. It was reported that the boiling water treatment involves the dissolution of anhydrous alumina from the pore walls, the formation of a hydrated

alumina gel inside the pores, and the saturation and subsequent precipitation of alumina hydrates, which takes place in the entire length of pores [25, 26].

Then, the specimens were anodized at 50 A m^{-2} in Na_2WO_4 electrolyte to examine the influence of the pretreatments on E_B . Anodizing was repeated several times to see the reproducibility of the results. For instance, the slope of the potential rise varied up to 0.1 V s^{-1} . The potential-time curves of the aluminum specimens as-polished, anodized in SA for 30 min (SA4.8) and anodized in SA for 30 min followed by boiling water treatment (SA4.8-BW), revealed the marked change in the E_B (Fig. 2). The as-polished aluminum shows a linear potential rise of 2.3 V s^{-1} to $\sim 200 \text{ V}$. The electric breakdown with sparking occurs at $\sim 240 \text{ V}$, terminating any further rise of potential. The SA4.8 specimen also shows a linear potential rise but at a greater rate of 11.2 V s^{-1} . The increased rate is associated with the existence of the preformed alumina film, and the slope is related to the porosity, α , of the porous alumina film. Studies have previously reported [1] that a barrier-type anodic alumina film grows both at the metal/film and film/electrolyte interfaces due to the migration of O^{2-} ions toward aluminum substrate and Al^{3+} ions toward the electrolyte, respectively. Under the presence of porous alumina layer, Al^{3+} ions migrating to the pore base form newly formed alumina, filling pores from the pore base. Thus, the new film material during the barrier film growth under the presence of an outer porous layer develops at the pore base as well as at the metal/film interface. The porosity of the porous layer influences the rate of pore filling by alumina, changing the slope of the potential rise during anodizing in tungstate electrolyte at a constant current density. The slope can be correlated with porosity using the following equation [21, 27]:

$$\alpha = \frac{\beta t_{\text{Al}^{3+}}}{1 - \beta t_{\text{O}^{2-}}} \quad (2)$$

where β is the ratio of the slope for electropolished aluminum to that for aluminum with a porous alumina film. $t_{\text{Al}^{3+}}$ and $t_{\text{O}^{2-}}$ are the transport numbers of cations and anions, respectively. Assuming the $t_{\text{Al}^{3+}}$ value is 0.4 [28], the porosity of the SA4.8 specimen is estimated to be 9.4%. The linear potential rise of the SA4.8 specimen continues up to 595 V, which is remarkably higher than that of the electropolished aluminum. After reaching 595 V, the potential decreases to $\sim 450 \text{ V}$, at which sparking can be observed by the naked eye.

The boiling water treatment is effective in increasing the E_B further. Anodizing of the SA4.8-BW specimen shows an initial potential surge of 150 V at the commencement of anodizing, probably reflecting the formation of the dense hydrated alumina precipitates at the pore base of the porous alumina film. Following the potential surge, the linear potential rise can be as high as 1100 V, at which film breakdown occurs and the potential drops to ~450 V. Despite the hydrated alumina precipitation in the pores, the slope of the potential rise is reduced to 6.6 V s⁻¹. The reduced slope by sealing of the porous alumina film in hot water has been reported previously [29], and the slope reduction was discussed based on the change in the transport number of cations. From Equation (2), the transport number of cations can be estimated using the α and β values for the SA4.8-BW specimen. It can be assumed that the α value is unchanged even after boiling water treatment. This is because of the reduced porosity of the porous alumina film by the boiling water treatment owing to the volume expansion in the conversion of amorphous alumina to pseudo-boehmite (hydrated alumina, such as Al₂O₃·2H₂O). The reduced porosity by the hydration increases again by dehydration in the growth of a barrier layer [29]. It is also worth mentioning that no dissolution of alumina occurs during the boiling water treatment of aluminum with a porous alumina film [30]. By using $\alpha = 0.094$ and $\beta = 0.34$, the $t_{Al^{3+}}$ is estimated to be 0.20 for the SA4.8-BW specimen. The reduced transport number of cations may be related to the formation of a crystalline barrier film as shown later.

The influence of the porous film thickness on E_B was also examined. Figure 3a shows the potential-time curves of aluminum with porous alumina films of three different thicknesses during anodizing at 50 Am⁻² in the tungstate electrolyte. All three specimens showed a linear potential rise with the same slope of 11.2 Vs⁻¹, indicating a similar porosity of 9.4% for all the porous alumina films. The E_B was found to increase from 595 V to 894 V with the increase in the porous film thickness. The boiling water treatment of thicker porous alumina films further enhanced the E_B , as shown in Fig. 3b. The SA26-BW specimen showed no film breakdown up to 1500 V, which was the maximum potential of the power supply used in this study. No breakdown was also found for the SA16-BW specimen up to 1500 V. Thus, the E_B successfully exceeded 1500 V by pore-sealing of the porous alumina films of thicknesses ≥ 16 μ m.

To clarify the role of sealed porous layers on the enhanced E_B , the EIS measurements were taken. Figure 4 shows the Bode plots of the as-polished aluminum, SA4.8 and SA4.8-BW specimens before anodizing in the tungstate electrolyte. The impedance modulus changes linearly with the frequency with a slope close to -1 in the double logarithmic plot below 100 Hz and 1000 Hz for the as-polished and SA4.8 specimens, respectively, being characteristic of metals covered with an insulating layer. A constant impedance modulus of $500 \Omega \text{ cm}^2$ at a high-frequency region reflects the electrolyte resistance. Even though a porous layer is present on a thin barrier layer for the SA4.8 specimen, the Bode diagram shows only one time constant. This is due to the negligibly small resistance of the electrolyte in pores in comparison with that of the thick electrolyte between the specimen and the counter electrode. In contrast, the SA4.8-BW specimen shows two time constants; the impedance modulus decreases linearly with frequency in the low-frequency region and then, becomes almost constant followed again by a linear decrease with the increase in the frequency. The phase shift also changes from -85° to a peak of -20° , followed by a negative peak of -60° with an increase in frequency. The EIS spectra of these three specimens were fitted using equivalent circuits shown in Figs. 4b and 4c, in which R_s is the electrolyte resistance, $(\text{CPE})_b$ and R_b are the constant phase element and resistance of the barrier layer, respectively. $(\text{CPE})_h$ and R_h are the constant phase element and resistance of the sealed porous layer, respectively. The constant phase element was used to consider the non-ideal capacitive behavior of the anodic films [31]. The impedance of a CPE is given by:

$$Z_{\text{CPE}} = 1/[Q(j\omega)^n] \quad (3)$$

where ω is the angular frequency, and Q and n ($0 \leq n \leq 1$) are CPE parameters, being independent of frequency. The capacitances, C , of the barrier layer and the sealed porous layer were estimated using the following equation [32]

$$C_i = Q^{1/n} R_i^{(1-n)/n} \quad (i = b \text{ or } h) \quad (4)$$

The simulated curves are fitted well for all three specimens in Fig. 4. The capacitance of the thin oxide film formed by electropolishing on the as-deposited aluminum is $2.7 \mu\text{F cm}^{-2}$, which is reduced to $0.22 \mu\text{F cm}^{-2}$ for the SA4.8 specimen. The thickness of the electropolishing film formed on aluminum is usually 2-3 nm while the barrier layer between the porous layer and metal substrate formed at 25 V in sulfuric acid is ~ 25 nm. Since the

capacitance is inversely proportional to the thickness of the oxide layer, the reduced capacitance by anodizing of the electropolished aluminum is mainly associated with film thickening. The capacitance of the barrier layer for the SA4.8-BW specimen slightly increased to $0.26 \mu\text{F cm}^{-2}$ after the boiling water treatment owing to the partial conversion of alumina in the barrier layer to hydrated alumina, which results in slight thinning of the barrier layer.

The resistance of the sealed porous layer was $1.0 \times 10^5 \Omega \text{ cm}^2$ for the SA4.8-BW specimen, and this value is much higher than that of the electrolyte resistance. We also found the resistance of the sealed porous layer increased with its thickness, as shown in Fig. 5. This implies similar sealing of the porous layer in depth direction. The extrapolation of the linear line to the film thickness of $0 \mu\text{m}$ indicates the resistance of $\sim 80 \text{ kW cm}$, which is probably owing to the presence of outer flaky surface of the hydrated layer.

In anodizing the specimens with the boiling water treatment in tungstate electrolyte, the barrier layer thickens with anodizing voltage. An example of the scanning electron micrograph of a cross-section of the SA26-BW specimen anodized to 1100 V in tungstate electrolyte is shown in Fig. 6a. The barrier layer of $1.2 \mu\text{m}$ is rather uniform in thickness, and the metal/film interface is also rather flat, confirming the uniform growth of the barrier layer up to 1100 V. Only microvoids-like feature appears in the middle part of the barrier layer, being probably formed as a consequence of dehydration of the hydrated alumina under the high electric field in the growing barrier layer. Figure 6b shows transmission electron micrograph of a FIB cross-section of the SA4.8-BW specimen anodized to 890 V. Again, it is evident that a uniform barrier layer of $1.1 \mu\text{m}$ thickness is formed on aluminum under the presence of sealed porous layer. The high magnification image of the barrier layer (Fig. 6c) reveals diffraction contrast, suggesting the presence of a crystalline phase, in the similar region where the microvoids-like feature is found in the scanning electron micrograph (Fig. 6a). It is known that a crystalline γ' -alumina is formed by anodizing an aluminum specimen with boiling water treatment [2]. It is believed that hydrated alumina (pseudo-boehmite) acts as a nucleation site of the crystalline γ' -alumina. Microvoids, as shown in Fig. 6a, are also incorporated in the crystalline region.

Figure 6d shows the change in the thickness of the barrier layer with anodizing potential. There is a linear correlation between the thickness of the barrier layer and the anodizing potential with a slope of 1.08 nmV^{-1} .

When electropolished aluminum is anodized at 50 Am^{-2} , the barrier film thickens generally at 1.2 nmV^{-1} [33]. The reduced formation ratio from 1.2 nm^{-1} to 1.08 nmV^{-1} is associated with the presence of crystalline alumina, which can sustain higher electric field [2]. It is also worth mentioning that this linear correlation suggests the negligible contribution of the resistance of sealed porous layer to the anodizing potential because the linear line crosses the origin. This means that the potential was applied mainly in the barrier layer during anodizing in tungstate electrolyte and not in the sealed porous layer. However, the EIS data (Figs. 4 and 5) show the high resistance of the sealed porous layer. This discrepancy is still unclear and the subject of further study.

Elemental in-depth distribution of anodized specimens was examined using GDOES depth profile analysis. Figure 7 shows the GDOES elemental depth profiles of the SA4.8 and SA4.8-BW specimens anodized to 500 V in the tungstate electrolyte. Since the porous anodic film was formed in sulfuric acid electrolyte, it is obvious that sulfur species distribute uniformly in the anodic oxide films for both the specimens. Since sulfate is mobile inwards [34], both sulfur and oxygen species distribute similarly to the metal/film interface at the available resolution. Tungsten species are also present in the anodic film of the SA4.8 specimen without boiling water treatment (Fig. 7a). The higher intensity of tungsten near the metal/film interface is due to the incorporation of tungsten species in the barrier layer grown in the tungstate electrolyte. In a growing barrier-type alumina film, tungsten species migrate toward the electrolyte at a rate of 0.3 that of Al^{3+} ions [35, 36]. Thus, the tungsten-free inner barrier layer is formed after anodizing to 500 V in tungstate electrolyte, but the tungsten-free layer cannot be resolved in this depth profile because of the presence of a thick porous layer relative to the barrier layer between the outer porous layer and the metal substrate. Tungstate anion is also adsorbed on the pore wall of the porous layer, showing a slightly higher intensity of tungsten compared with that in the aluminum substrate (background level). The distribution of tungsten species changes in the anodic film of the SA-4.8-BW specimen (Fig. 7b). In this case, the intensity of tungsten is in the background level except for the outermost surface, indicating the absence of tungsten species in the barrier layer as well as the hydrated porous alumina layer.

The highly increased E_B is probably related to the negligible incorporation of tungsten species through the sealed porous layer. The E_B was reported to increase linearly with the logarithm of electrolyte resistance [11, 12]. The E_B of anodic alumina increases with the logarithm of the electrolyte at a slope of 266 V. In this study, if the

resistance of a porous layer is responsible for the increased E_B , the resistance of the porous layer must increase more than one order of magnitude with thickening of the porous layer because the E_B increases largely with the thickness of the sealed porous layer (Fig. 3). However, the resistance of the porous layer, estimated from the EIS measurements (Fig. 5), increases only twice when thickening the sealed porous layer from 4.8 to 26 μm . The GDOES depth profiles (Fig. 7) show negligible incorporation of tungsten species in the barrier layer beneath the sealed porous layer. Recently, it was reported that a hydrated alumina film formed by a sol-gel process could be utilized as a solid electrolyte for anodizing aluminum under high electric field [37]. The hydrated amorphous alumina film was assumed to supply the O^{2-} and/or OH^- anions to grow a dielectric alumina layer by anodizing in Pt/hydrated amorphous alumina/Al system. In the present study, it is also likely that the sealed porous alumina layer is utilized mainly as a solid electrolyte layer with highly reduced penetration of tungstate solution to grow the dielectric alumina barrier layer. Under such a situation, the incorporation of tungsten species in the barrier layer must be highly suppressed, leading to the highly enhanced E_B to >1500 V.

The electric properties of the anodic films formed by anodizing several potentials were examined by EIS measurements. Figure 8 shows Bode plots of the SA4.8-BW specimens anodized to several potentials in tungstate electrolyte. The impedance modulus and phase shift in the low-frequency region below 1 kHz change with the anodizing potential, reflecting the change in the thickness of the barrier layer. In contrast, both the impedance modulus and phase shift in the high-frequency region above 1 kHz are little changed with the anodizing potential. Thus, the impedance in the high-frequency region is mainly related to the sealed porous layer. Using the equivalent circuit shown in Fig. 4c, the capacitance of the barrier layer, C_b , was calculated, and the reciprocal of C_b is plotted in Fig. 9 as a function of anodizing potential. The reciprocal capacitance increases linearly with anodizing potential, as a consequence of the linear increase of the barrier layer thickness with anodizing potential. The capacitance of the SA4.8 specimen is almost similar to that of the SA26 specimen at any anodizing potential. The specimens with the boiling water treatment (SA4.8-BW and SA26-BW) showed an increased capacitance compared with the specimens without the boiling water treatment. As discussed above, the formation ratio for the specimens with the boiling water treatment (1.08 nm V^{-1}) is smaller than that without the boiling water treatment (1.2 nm V^{-1}). Thus, a thinner barrier layer is developed for the boiling-water-treated

specimens at the same anodizing potential. The capacitance, C , is inversely proportional to the thickness of the barrier layer, d , as shown in the following equation,

$$C = \frac{\epsilon_o \epsilon_{ox} S}{d} \quad (5)$$

where ϵ_o is the permittivity of vacuum, ϵ_{ox} is the relative permittivity of oxide, and S is the surface area. Thus, the thinning of the barrier layer by the boiling water treatment contributes to the enhanced capacitance. The relative permittivity of the barrier layer was also calculated from equation (5) and found to be 9-10. The value is typical of anodic alumina.

Conclusions

The present study demonstrates the markedly increased electric breakdown potential of barrier-type anodic films to >1500 V on aluminum under the presence of a preformed porous alumina layer with pore sealing. The pores of alumina films formed in sulfuric acid electrolyte are filled with hydrated alumina (pseudo-boehmite) after the boiling water treatment, and the sealed porous alumina layer shows an increased electric resistance. In the growth of a barrier-type alumina growth, the electrolyte anion species are usually incorporated into the anodic alumina film, but their incorporation becomes negligible under the presence of a sealed porous alumina layer. The introduction of a highly resistive porous film that also impedes the anion incorporation is an effective way to enhance the potential of electric breakdown of anodic alumina films on aluminum.

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Figure captions

Fig. 1 Scanning electron micrographs of (a, c) surface and (b, d) cross-section of aluminum anodized at 25 V in 0.3 mol dm⁻³ sulfuric acid at 288 K for 30 min (c, d) and (a, b) without boiling water treatment for 10 min.

Fig. 2 The potential-time curves of three aluminum specimens, as-polished and with 4.8 µm-thick porous layer before (SA4.8) and after (SA4.8-BW) pore sealing, during anodizing at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium tungstate electrolyte.

Fig. 3 The potential-time curves of aluminum specimens with 4.8 µm (SA4.8), 11 µm (SA11) and 26 µm (SA26)-thick porous layers (a) before and (b) after pore sealing (BW) during anodizing at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium tungstate electrolyte.

Fig. 4 (a) Bode diagrams of the as-polished, SA4.8 and SA4.8-BW aluminum specimens and equivalent circuits used for **(b)** the as-polished and SA4.8 specimens and **(c)** SA4.8-BW specimen.

Fig. 5 Change in the resistance of the sealed porous layer with the thickness of the porous layer.

Fig 6 (a) Scanning electron micrograph of a fractured cross-section, **(b, c)** transmission electron micrographs of a FIB-cross-section of the SA4.8-BW specimen after anodizing to 1100 V at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium tungstate electrolyte and **(d)** the change in the thickness of the barrier layer with anodizing potential.

Fig. 7 GDOES elemental depth profiles of the SA4.8 and SA4.8-BW specimens after anodizing to 500 V at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium tungstate electrolyte.

Fig. 8 Bode plots of the SA4.8-BW specimens anodized to several potentials at 5 mA cm⁻² in 0.1 mol dm⁻³ sodium tungstate electrolyte.

Fig. 9 Change in the reciprocal capacitance of the barrier layer with anodizing potential.

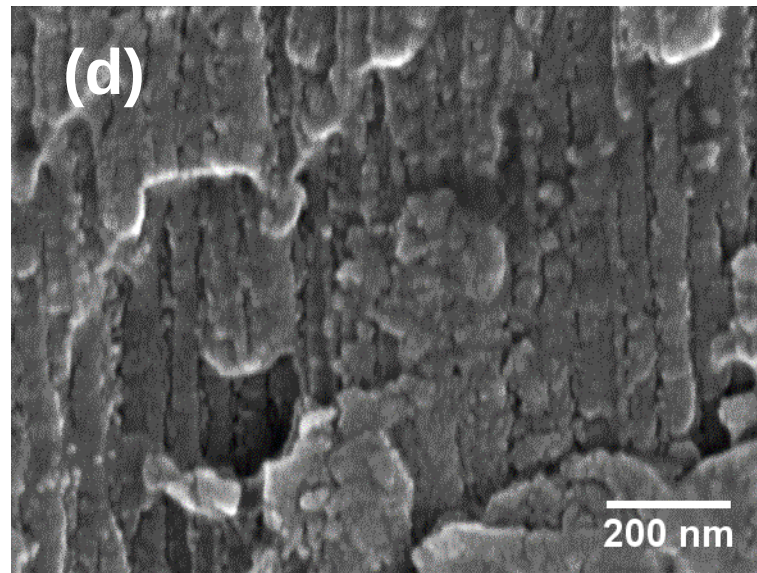
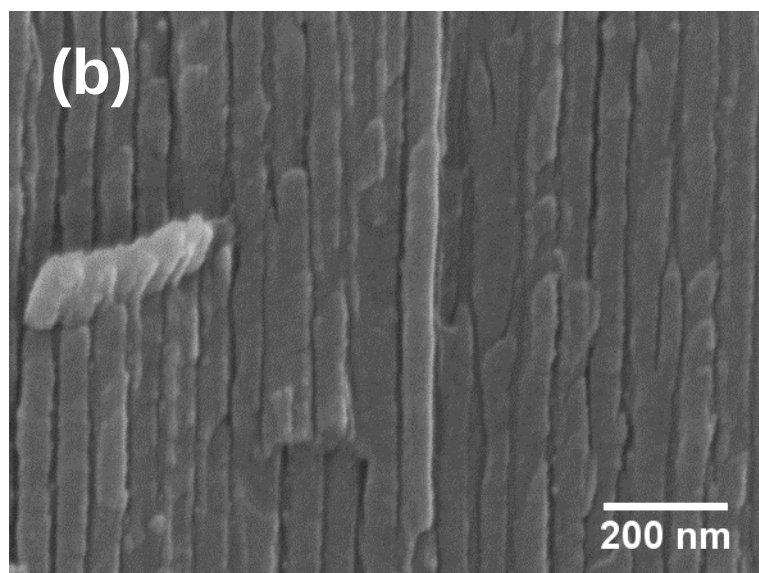
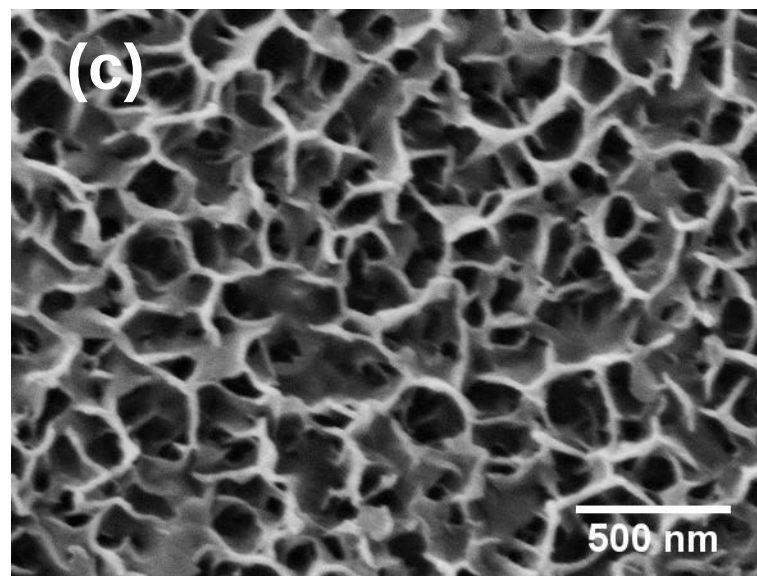
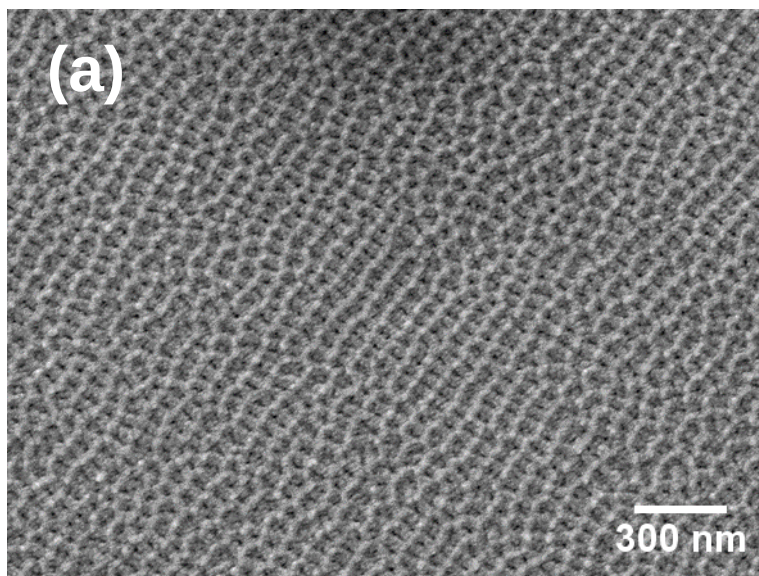


Fig. 1

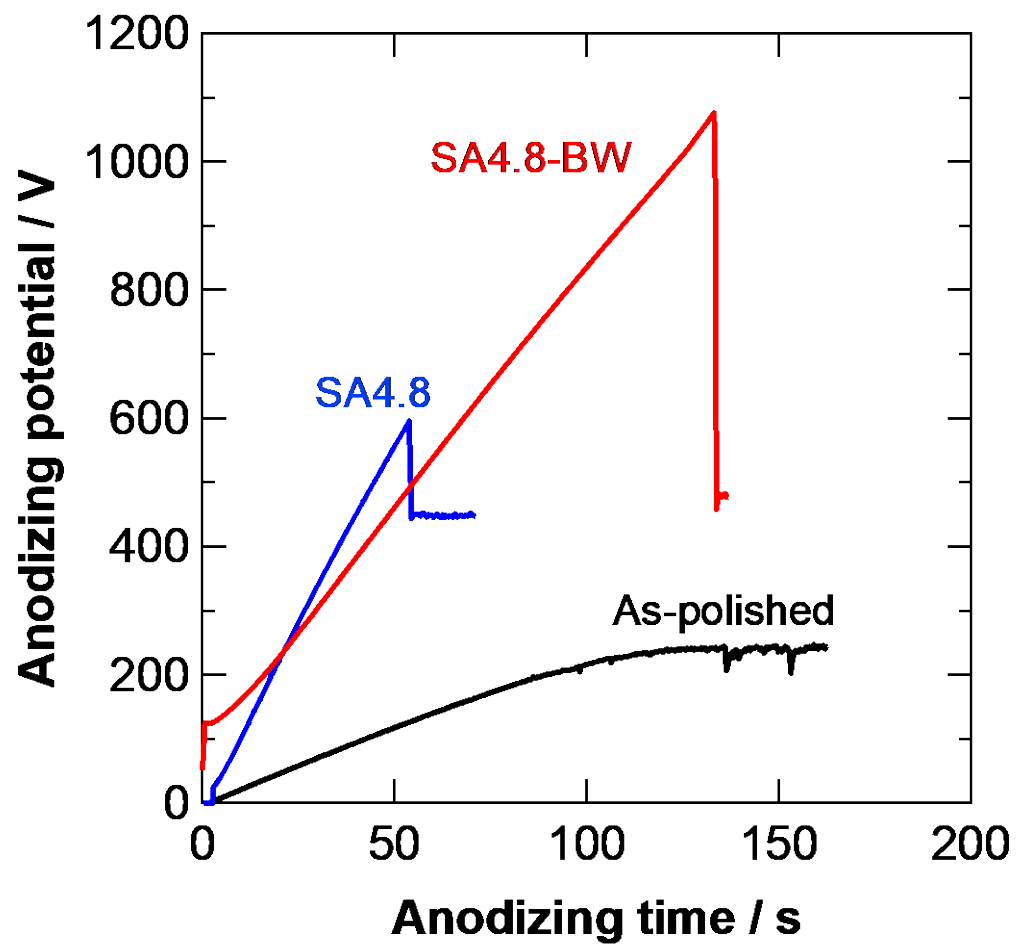


Fig. 2

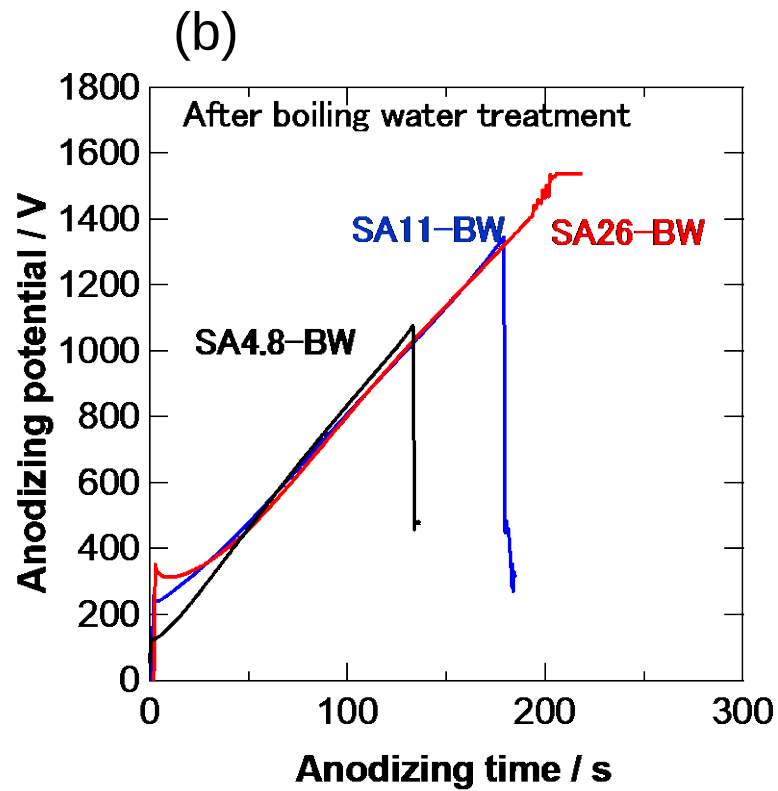
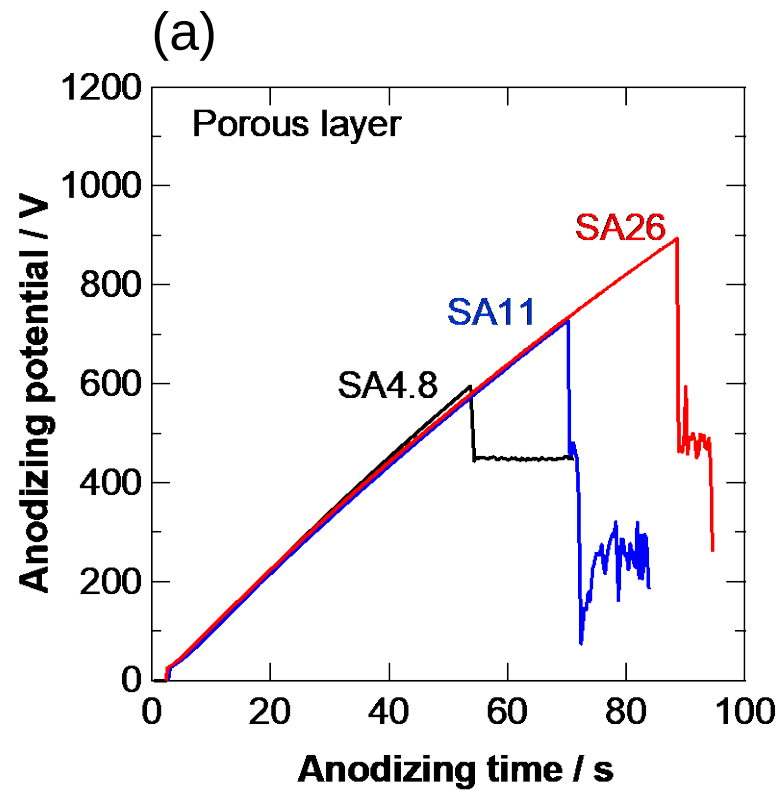


Fig. 3

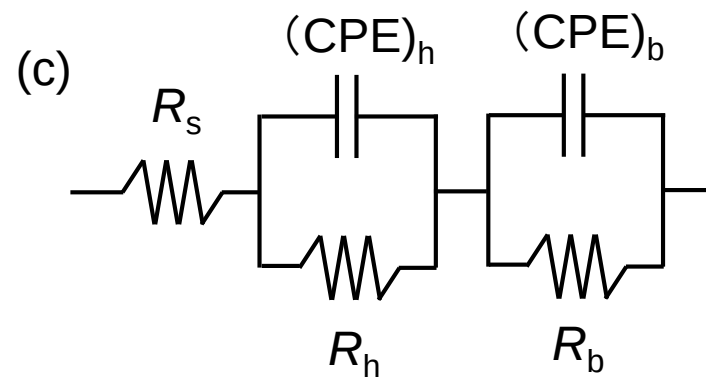
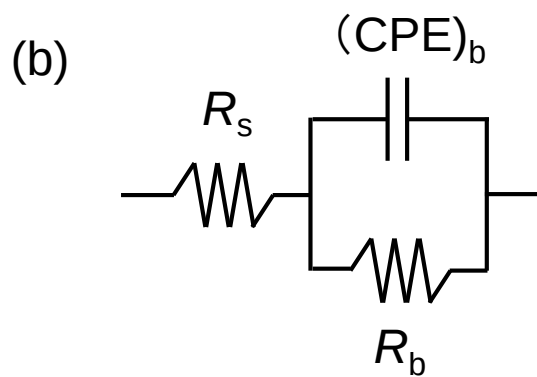
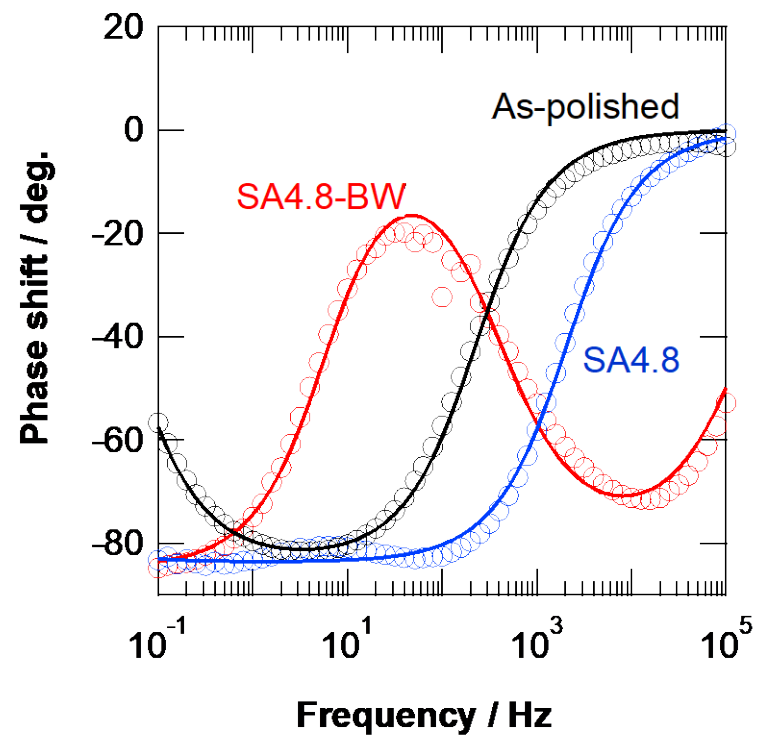
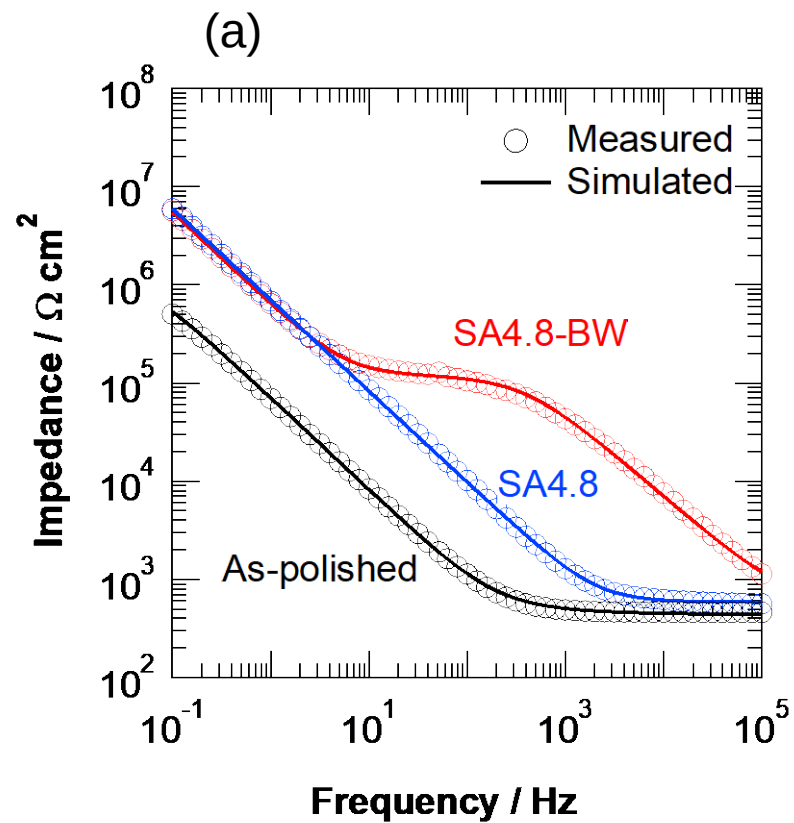


Fig. 4

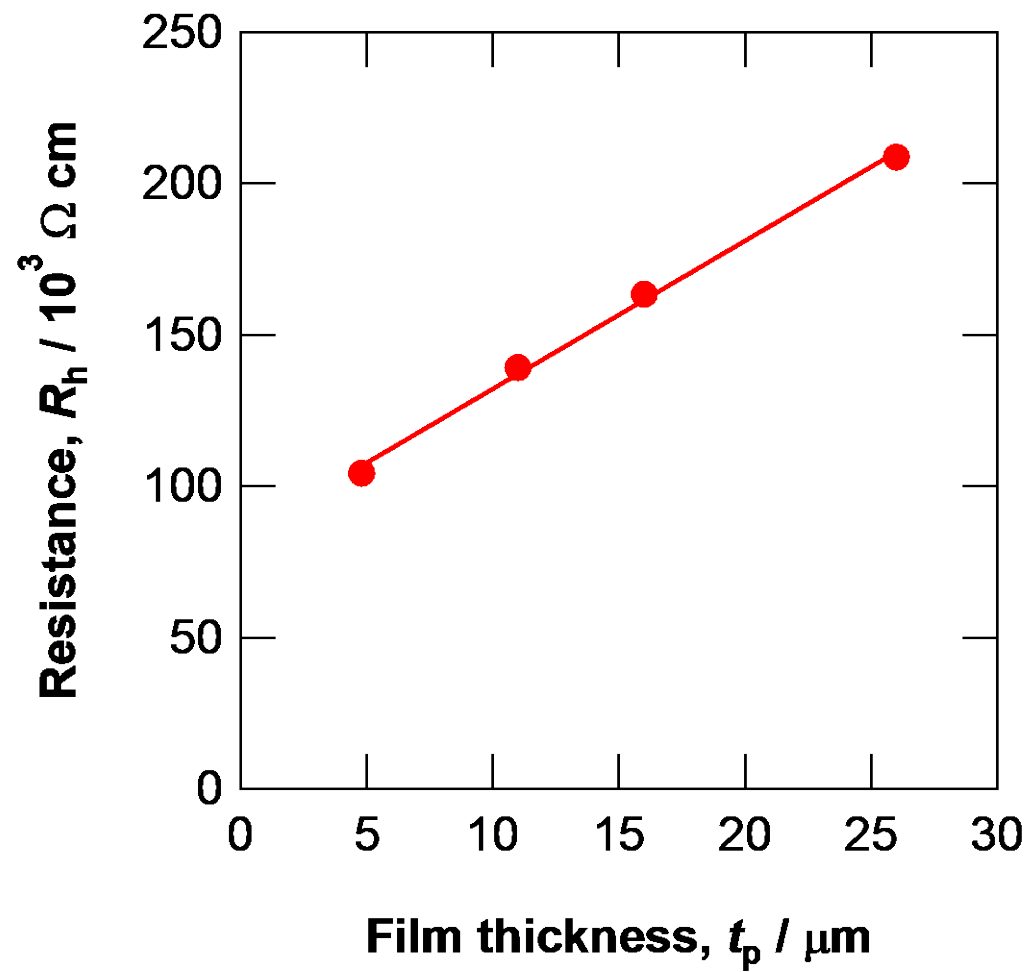


Fig. 5

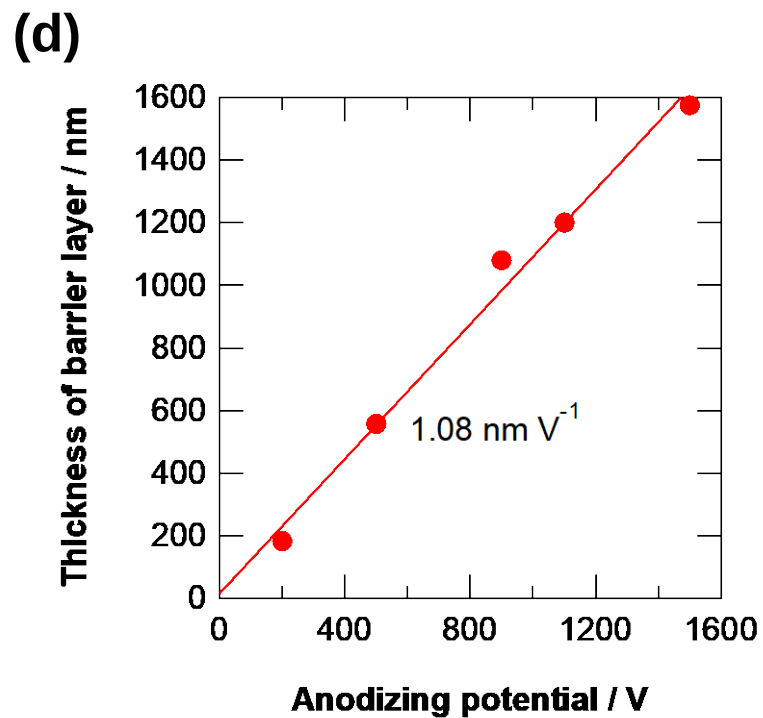
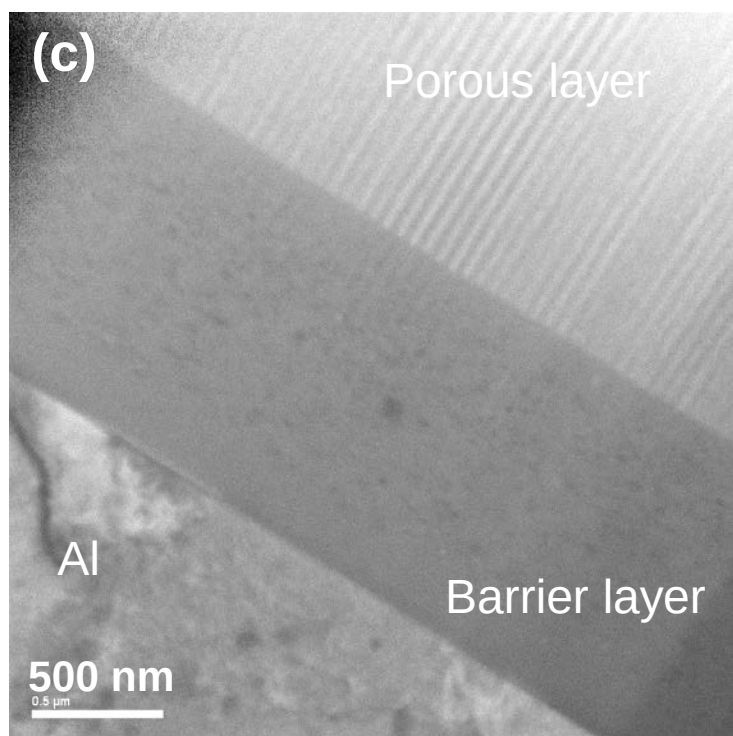
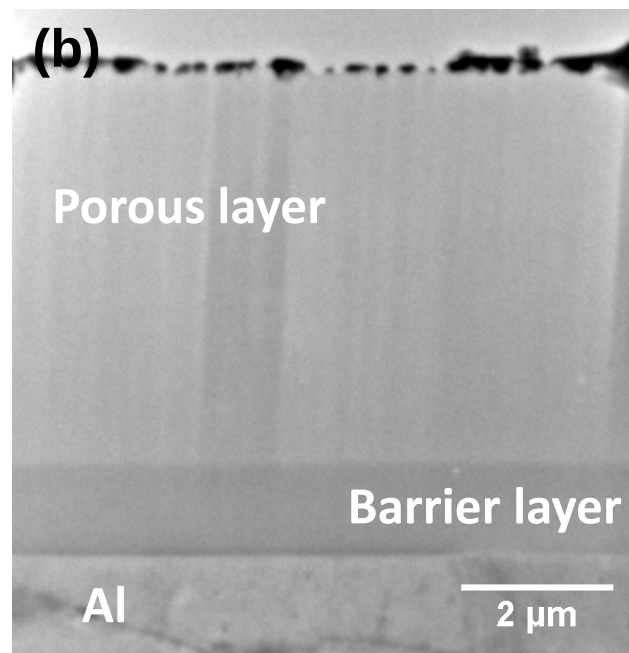
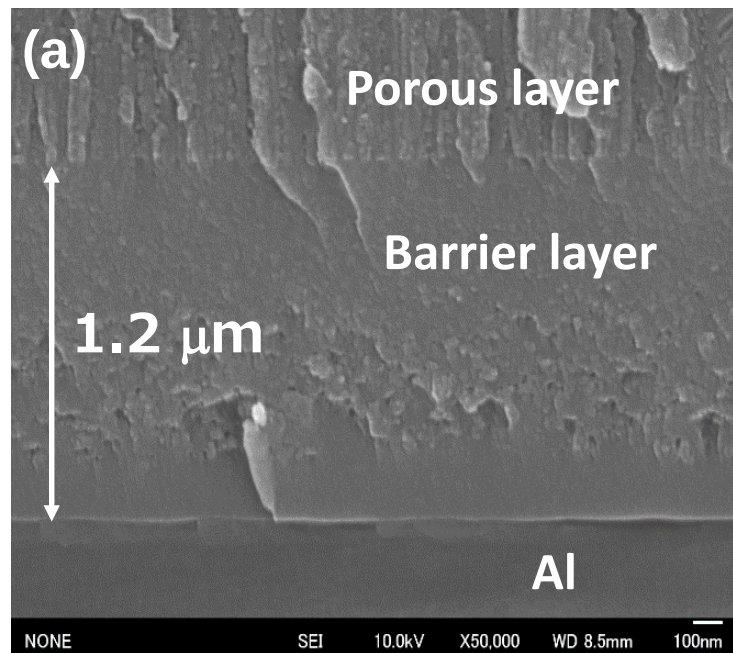


Fig. 6

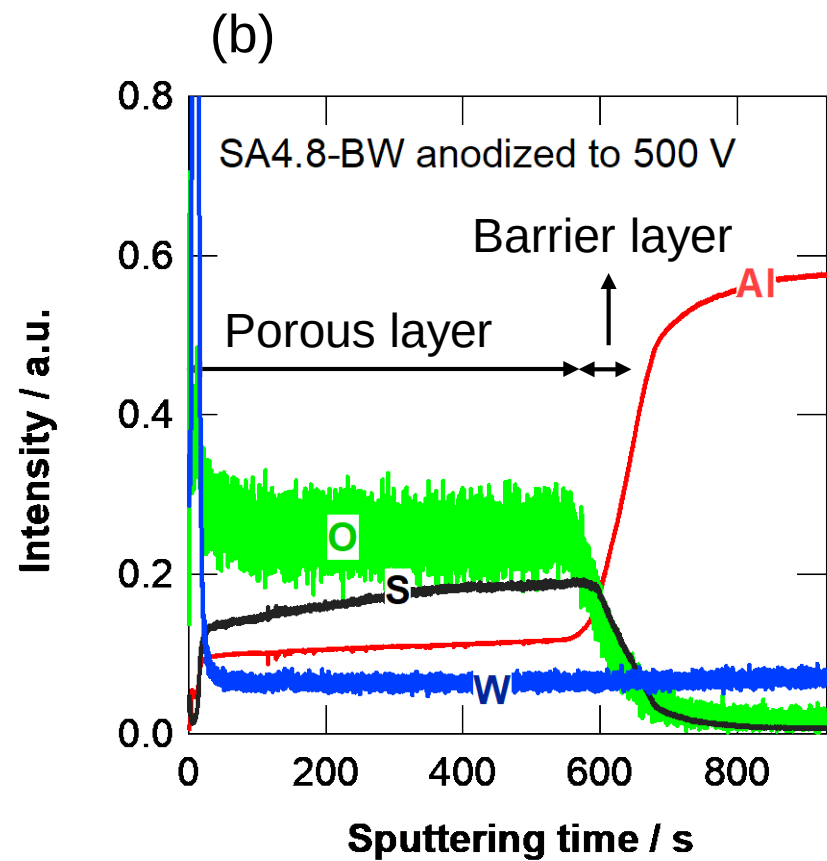
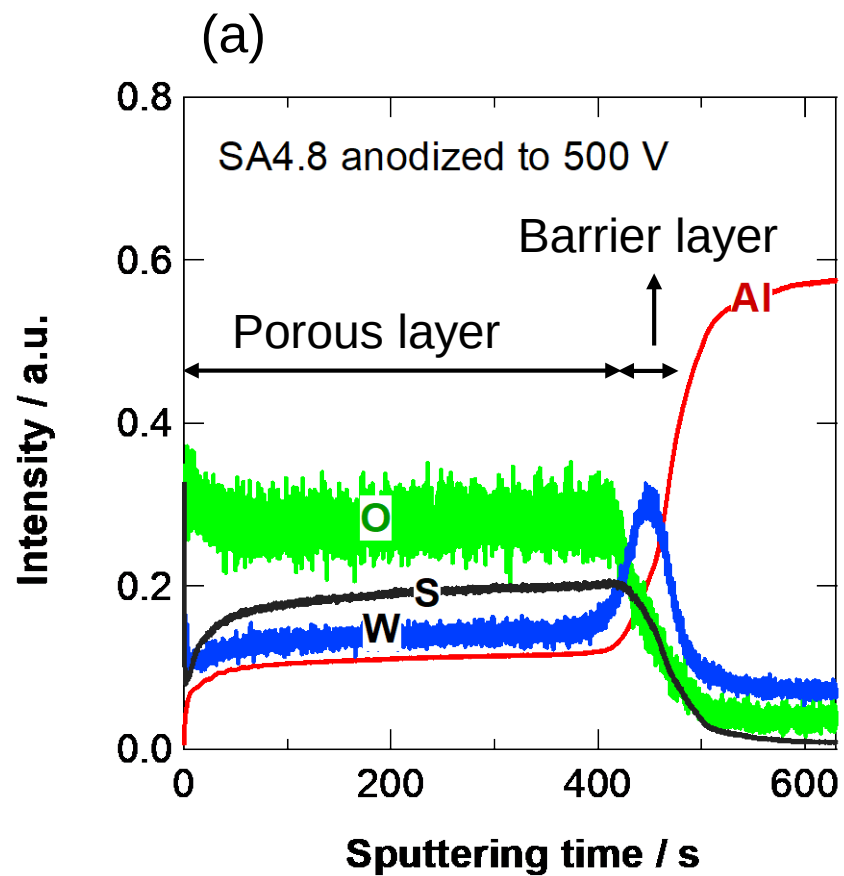


Fig. 7

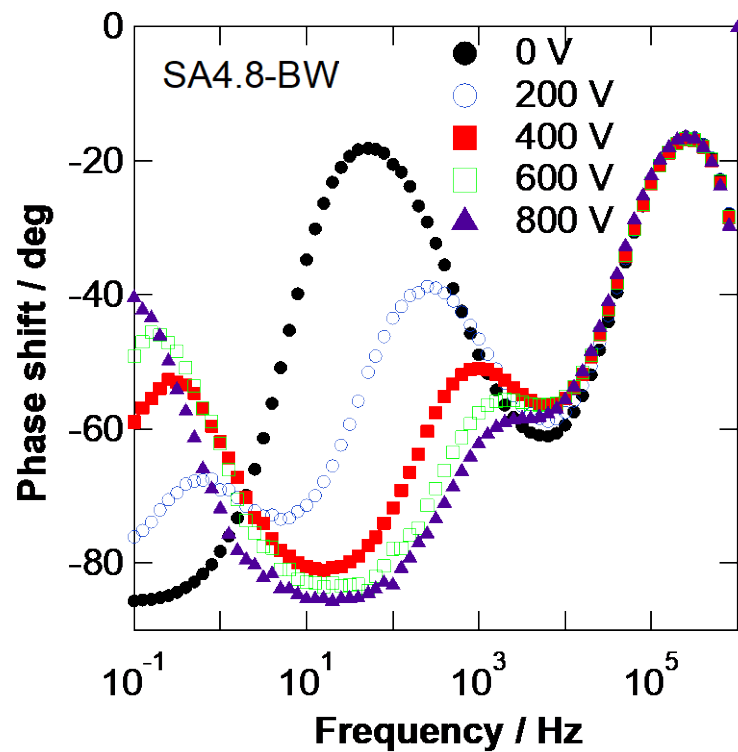
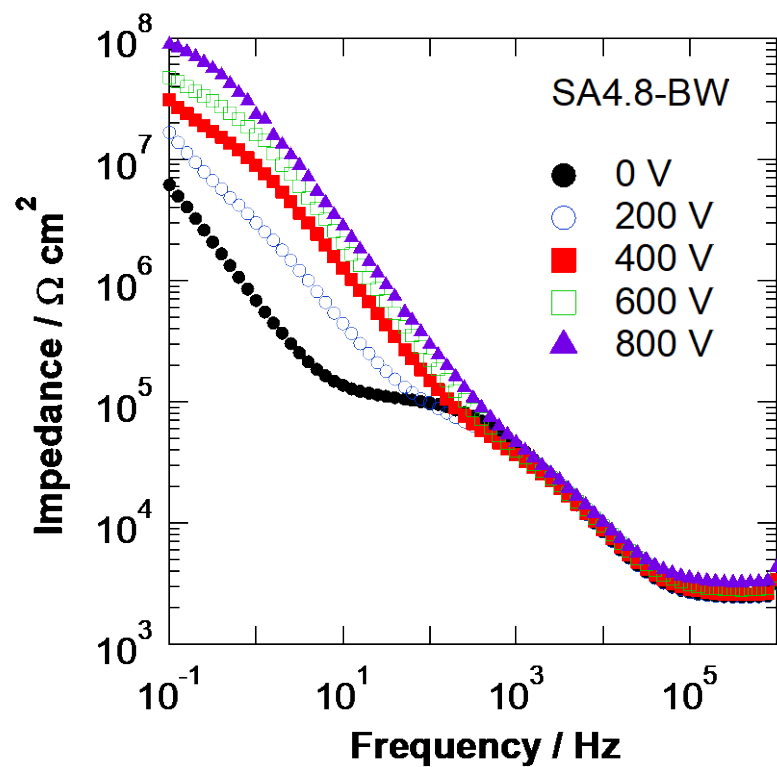


Fig. 8

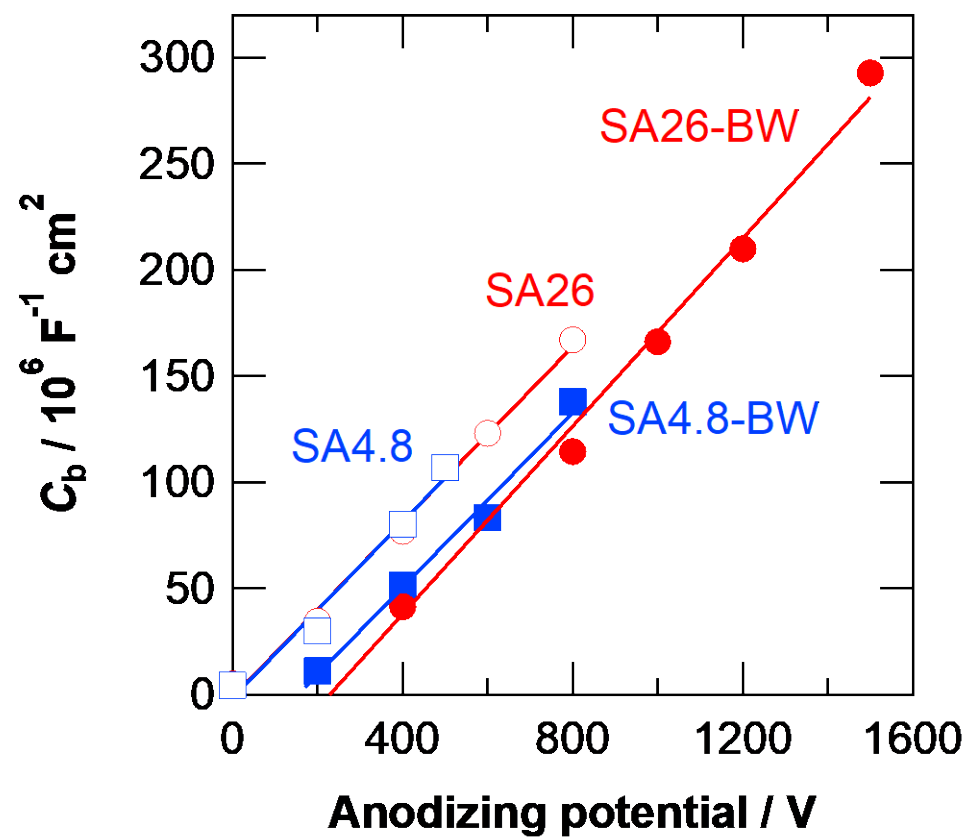


Fig. 9