Effects of Electrolyte Species and Their Combination on Film Structures and Dielectric Properties of Crystalline Anodic Alumina Films Formed by Two-Step Anodization*1

Yoshiteru Sato*2, Hidetaka Asoh and Sachiko Ono*3

Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, Tokyo 192-0015, Japan

The effects of electrolyte species and their combination during the two-step anodization of anodic oxide films formed in various ammonium salts solutions on aluminum in terms of the crystallinity and dielectric properties for use as an electrolytic capacitor were investigated. The aluminum substrates were pretreated by dipping in boiling water to form a hydrated layer. Anodic films were annealed at 500°C after the first anodization. The CV (capacitance C multiplied by withstand voltage V) of the films formed with a second anodization in ammonium borate was higher than that of the films formed using the same electrolyte for the first and second anodizations. The increase in CV due to the improved crystallinity when using borate for the second anodization and the following electrolytes for the first anodization increased in the order salicylate < succinate < tartrate < phosphate < citrate < adipate < borate. When phosphate or organic electrolytes were used in the second anodization, considerable spike noise was observed. However, the spike noise was significantly suppressed when borate was used in the second anodization. [doi:10.2320/matertrans.L-M2013826]

(Received December 23, 2012; Accepted July 25, 2013; Published September 13, 2013)

Keywords: aluminum, anodic oxide film, electrolytic capacitor, dielectric property, crystallinity

1. Introduction

In recent years, it has become necessary to increase the capacity and lifetime of aluminum electrolytic capacitors for medium- and high-voltage applications owing to the increased use of large industrial inverters and hybrid vehicles. In general, crystalline alumina films are used as the dielectric films of medium- and high-voltage aluminum electrolytic capacitors. These films are formed by a two-step anodization process involving hydration of the aluminum substrate, followed by a first anodization, heat treatment and a second anodization. A high-concentration aqueous solution of borate is generally used as the electrolyte. Although the thickness of the crystalline anodic film per unit voltage (the anodizing ratio) depends on the concentration and electrolysis conditions, the anodizing ratio is approximately 1 nm V⁻¹. In other words, the film has a lower thickness per unit voltage and a higher withstand voltage than a noncrystalline film with a higher anodizing ratio (1.4–1.6 nm V⁻¹). In addition, it has been reported that the dielectric properties of such a film, such as the capacitance and leakage current, are strongly affected by the anions incorporated into the film. However, the effects of the anion species and distribution on the dielectric properties of a crystalline alumina film have not been elucidated.

We previously examined the effects of electrolytic anion species on the dielectric properties of crystalline anodic alumina films formed by two-step anodization combined with heat treatment. When an anodic film was formed by two-step anodization employing the two electrolytes mainly used industrially, i.e., high-concentration boric acid/sodium borate and ammonium adipate, the incorporation of boron into the film was suppressed. In addition, the film exhibited higher capacitance than a film formed in only boric acid/sodium borate. We also investigated the effects of various ammonium salts on the dielectric properties of crystalline anodic alumina films. When the same electrolyte was used in both the first and second anodizations, the crystallinity of the anodic films increased in the following order: adipate < succinate < tartrate < phosphate < citrate < borate. While the films formed in phosphate and citrate (whose crystallinity was high) exhibited a high capacity, their leakage currents also tended to be higher. Although the film formed using ammonium borate (hereinafter referred to as borate) through multistep anodization had a high capacity and the highest crystallinity, its leakage current was low compared with those of the films formed in the other electrolytes. Thus, the film formed in borate exhibited superior dielectric properties. These results suggested that using borate improved the dielectric properties of the anodic film. Therefore, the aims of this study were to examine the effects of electrolyte combinations on film crystallinity and dielectric properties and to find strategies for improving the dielectric properties of films. In this study, we used various ammonium salts for the first anodization and the same salts or borate for the second anodization.

2. Experimental

An aluminum sheet (area 10 cm²) with 99.99% purity was used as the specimen. As pretreatment, the specimen was dipped in 5 mass% aqueous solution of sodium hydroxide (at 65°C) for 20 s, then dipped in 30 vol% nitric acid (at room temperature) for 60 s. A hydrated oxide layer was formed on the aluminum by dipping in boiling pure water for 10 min. After that, constant-current anodization was performed at a constant current density of 0.5 mA cm⁻² up to a predefined voltage at 85°C in the various electrolytes shown in Table 1 (ammonium tetraborate, ammonium phosphate, ammonium...
adipate, ammonium tartrate, ammonium citrate, ammonium succinate, ammonium salicylate) at a concentration of 0.01 mol dm$^{-3}$. When the formation voltage reached 300 V, constant-voltage anodization was performed for 45 min (first anodization). After the first anodization, heat treatment was performed for 5 min in air at 500°C, and then a second anodization was performed under the same electrolysis conditions as the first anodization in 0.01 mol dm$^{-3}$ borate. As a reference, two-step anodization was also performed using the same electrolyte species for the first and second anodizations. Specimens were washed with ion-exchange water after each step.

The dielectric properties of the anodic films were evaluated on the basis of the capacitance, withstand voltage and leakage current. The capacitance of each anodic film was measured at a frequency of 120 Hz with an LCR meter (NF Corporation ZM2353), using a large-area platinum plate as the counter electrode, in a 150 g dm$^{-3}$ ammonium adipate solution. The withstand voltage was measured by reanodizing the specimen at a very low current of 0.1 mA cm$^{-2}$ in 1.6 mol dm$^{-3}$ borate –0.008 mol dm$^{-3}$ sodium tetraborate at 85°C. In the voltage-time ($V$-$t$) curve obtained during reanodization, the part with high linearity after the voltage jump (anodization time of 1–5 min) was extrapolated to the $V$-axis, and the voltage at the intercept with the $V$-axis was taken to be the withstand voltage. The withstand voltage has been suggested to be proportional to the film thickness if the oxide properties are constant. Here, the relative difference in film thickness was evaluated by the difference in the withstand voltage. The leakage current was measured using the constant-voltage application method, where a voltage of 225 V (75% of the formation voltage) was applied in 0.5 mol dm$^{-3}$ boric acid –0.05 mol dm$^{-3}$ sodium tetraborate at 20°C. The current measured 15 min after applying a voltage of 225 V was taken to be the leakage current. The capacitance, withstand voltage and leakage current were each measured at least five times. Then, the average values were found, and the maximum and minimum measured values are indicated with error bars in the figures.

Field-emission scanning electron microscopy (FESEM; JEOL, JSM-6701F) was used to observe the film structure. The crystallinity was measured using thin-film X-ray diffraction (TFXRD; MAC Science, MXP-18AHF22) at an X-ray incidence angle of 0.3°. The depth profiles of constituent elements in the films were measured by glow discharge optical emission spectroscopy (GDOES; Jobin-Yvon, JY5000RF).

**Table 1** Chemical formula and pH of anodizing electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Chemical formula</th>
<th>pH</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium tetraborate</td>
<td>$(\text{NH}_4)_3\text{B}_2\text{O}_7$</td>
<td>9.0</td>
<td>Borate</td>
</tr>
<tr>
<td>Ammonium phosphate</td>
<td>$(\text{NH}_4)_2\text{HPO}_4$</td>
<td>8.0</td>
<td>Phosphate</td>
</tr>
<tr>
<td>Ammonium citrate</td>
<td>$(\text{NH}_4)_2\text{C}_6\text{H}_5\text{O}_7$</td>
<td>7.3</td>
<td>Citrate</td>
</tr>
<tr>
<td>Ammonium succinate</td>
<td>$(\text{NH}_4)_2\text{C}_4\text{H}_6\text{O}_7$</td>
<td>7.0</td>
<td>Succinate</td>
</tr>
<tr>
<td>Ammonium adipate</td>
<td>$(\text{NH}_4)\text{OCO(CH}_2\text{)}_2\text{COONH}_4$</td>
<td>6.9</td>
<td>Adipate</td>
</tr>
<tr>
<td>Ammonium tartrate</td>
<td>$(\text{NH}_4)\text{OCOCH(OH)}\text{CH(OH)}\text{COONH}_4$</td>
<td>6.5</td>
<td>Tartrate</td>
</tr>
<tr>
<td>Ammonium salicylate</td>
<td>$\text{HOC}_6\text{H}_4\text{COONH}_4$</td>
<td>6.0</td>
<td>Salicylate</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Film structure observation using FESEM

Figure 1 shows cross-sectional SEM images of specimens (a) after hydration by dipping aluminum in boiling water, and (b) after two-step anodization in 0.01 mol dm$^{-3}$ ammonium borate at 85°C up to 300 V.

Fig. 1 Cross-sectional SEM images of specimens (a) after dipping in boiling water (hydration) and (b) after two-step anodization in 0.01 mol dm$^{-3}$ ammonium borate at 85°C up to 300 V.

The crystallinity was measured using thin-film X-ray diffraction (TFXRD; MAC Science, MXP-18AHF22) at an X-ray incidence angle of 0.3°. The depth profiles of constituent elements in the films were measured by glow discharge optical emission spectroscopy (GDOES; Jobin-Yvon, JY5000RF).
owing to the dehydration of the hydrated oxide under a high electric field. It is also known that the entire film crystallizes when the electrolyte temperature is 85°C or higher.1) Among the films formed using various electrolytes for the first anodization and borate for the second anodization, the hydrated oxide layer grown on the film surface partially dissolved when phosphate was used for the first anodization. However, the structures of all the films were generally similar, and no major differences in film structure were evident under SEM observation.

### 3.2 Structural evaluation of films using reanodization

Figure 2(a) shows the V-t curves for the initial 15 s when reanodization was performed on the films formed using various ammonium salts at 0.01 mol dm−3 for the first anodization and borate at 0.01 mol dm−3 for the second anodization. This technique enables the semiquantitative evaluation of the minute defects present in the film via the delay in the increase of the V-t curve when reanodization is performed at a very low current of 0.1 mA cm−2.6,7,11) The growth of a barrier film proceeds owing to the growth of oxides at the film/solution interface caused by the migration of Al3+ and the growth at the film/substrate interface due to the migration of O2−. The growth rate of the latter is the same for all films during reanodization. With regard to the growth of the former film, on the other hand, if there are defects in the original oxide layer, the growing film fills these defects. Therefore, because differences appear in the V-t curve, the defect structure of the film can be evaluated.

In all the V-t curves obtained during reanodization, the voltage initially jumped to the 50–150 V range, then inflected, gradually increased and increased again near approximately 220 V. After exceeding 300 V, the voltage became almost constant with a rate of increase of about 0.025 V s−1. The time required until the voltage became almost constant near 300 V depended on the electrolyte species used for the first anodization and increased in the following order: borate < phosphate < tartrate < citrate < salicylate < succinate < adipate. The delay in the increase in voltage is due to the repair of defects present in the film, and thus it is conjectured that the delay is longer when there are more defects in the film.6,7,11) However, the amount of defects in the case that the increase in voltage is delayed by 10 s corresponds to about 0.25% of the amount of defects in the film.11) In the results of FESEM observation, it was difficult to confirm a difference in the crystalline oxide structure depending on the electrolyte species or a difference in the defect distribution in the film depth direction. On the other hand, the amount of defects present in the film depth direction can be inferred by the reanodization method, as indicated in the schematic diagram in Fig. 2(b). That is, it is considered that the crystalline film has a three-layer structure whose layers have different amounts of defects. In region ①, which is in contact with the metal substrate, the voltage rapidly increases in the initial period of reanodization, and thus this is a compact layer with few defects. In region ②, the increase in voltage is the most gentle, and thus this layer has the most defects in the film. In region ③, the voltage increases more slowly than in ① but more rapidly than in ②, and thus the amounts of defects contained in the three layers are thought to be ordered as follows: ① < ③ < ②.

When aluminum specimens subjected to hydration are anodized in a high-temperature electrolyte, the inner layer of hydrated amorphous oxide crystallizes owing to the effect of the high electric field. On the other hand, the outer layer of hydrated amorphous oxide crystallizes owing to the dehydration of the hydrated oxide. Therefore, the voids and cracks formed during the crystallization of the film are concentrated at the boundary between the inner and outer layers.12) Thus, it is considered that region ② in the center of the film is where defects such as voids and cracks are concentrated owing to film crystallization.

According to the results shown in Fig. 2(a), the slowest increase in voltage was observed for the film formed using adipate for the first anodization. Therefore, region ② of this film is considered to have the largest amount of defects. That is, it is suggested that crystallization is greatly promoted in films formed in adipate. It can be inferred, on the other hand, that the films formed in phosphate and borate have a comparatively small amount of defects.
3.3 Withstand voltage and capacitance of crystalline films formed by two-step anodization

Figures 3(a)–3(c) show the withstand voltage, capacitance and \( CV \) of films formed with each electrolyte species used in two-step anodization, respectively. When borate was used in the second anodization, the withstand voltage of the film depended on the type of electrolyte used for the first anodization. Moreover, the use of inorganic salts such as borate and phosphate resulted in a higher withstand voltage than those obtained using organic salts such as adipate. This is consistent with the fact that the amount of defects was small, as revealed by the reanodization method and shown in Fig. 2. The withstand voltages of the anodic films increased in the following order: adipate < tartrate < salicylate < succinate < citrate < phosphate < borate. The withstand voltage of the films was almost independent of the electrolyte species used in the second anodization. This result indicates that the withstand voltage of anodic films is strongly dependent on the electrolyte species used in the first anodization.

When borate was used for the second anodization, the capacitance of the film increased in the following order of electrolytes used in the first anodization: salicylate < borate < phosphate < succinate < tartrate < citrate < adipate (Fig. 3(b)). These capacitances were higher than those of the films formed using the other electrolyte species for the second anodization. In particular, the capacitance was highest (approx. 320 \( \mu \text{F m}^{-2} \)) when adipate and borate were used in the first and second anodizations, respectively. The withstand voltage was almost independent of the electrolyte species used in the second anodization. Thus, if the film thickness (\( d \)) is assumed to be constant, an increase in capacitance (\( C \)) due to the use of borate for the second anodization should lead to an increase in film permittivity (\( \varepsilon \)) in accordance with

\[
C = \varepsilon S/d,
\]

where \( S \) is the surface area. The \( CV \) values shown in Fig. 3(c) were higher for films subjected to the second anodization with borate, similarly to the capacitance. The \( CV \) of the films formed using borate for the second anodization increased in the following order of electrolytes used for the first anodization: salicylate < succinate < tartrate < phosphate < citrate < adipate < borate. Among these films, the film formed using borate for both the first and second anodizations exhibited the highest \( CV \) value (103 mF V m\(^{-2}\)).

3.4 Distribution of elements in the film depth direction determined by GDOES

Figure 4 shows the distributions of phosphorus and boron in the depth direction of the film, measured using GDOES. Figure 4(a) shows that the depth of incorporated phosphorus (P) was about 30% of the film thickness when only a first anodization was conducted in phosphate. Although there was no change in the incorporation depth of P when a second anodization was also conducted using the same electrolyte, there was a significant increase in the amount of P incorporated. When the second anodization was conducted in borate, there was no change in the incorporation depth of P, but there was a significant decrease in the amount incorporated. The incorporation depth of boron (B) in this case was about 20% of the film thickness, as indicated in Fig. 4(b). In the film formed using borate for both the first and second anodizations, B was incorporated to a depth of about 50% of the thickness (Fig. 4(b)). On the other hand, in the film formed using organic salts or phosphate for the first anodization and borate for the second anodization, the incorporation depth of B was markedly suppressed to about 20% of the film thickness. Moreover, the amount of B incorporated was estimated by integration of the profile curve. The amount of B was only about one-fifth of that in the film formed in borate for both the first and second anodizations.

On the basis of these results, the \( CV \) value of the film formed using borate instead of the same electrolyte for the second anodization was considered to be higher because it
was possible to avoid an increase in the amount of anion incorporation, and the amount of B incorporated was low. Thus, it was found that the amount of electrolyte anions incorporated in the film during the first anodization is significantly suppressed when the second anodization is conducted in a different electrolyte. It is presumed that this contributed to the increase in the $CV$ value of the films formed in the second anodization using borate.

### 3.5 Evaluation of crystallinity of anodic films using XRD

The crystallinity of a film has a major impact on its dielectric properties, and thus XRD was conducted on the crystalline films subjected to two-step anodization. Figure 5 shows the results. The peaks at $2\theta = 46$ and $67^\circ$ in the XRD spectra are both attributable to $\gamma$-Al$_2$O$_3$. The intensity of the $\gamma$-Al$_2$O$_3$ peaks from the films formed in the same electrolyte for the first and second anodizations depended on the electrolyte species and was greatest for the film formed in borate. The peak intensity indicates that the film crystallinity increased in the following order: salicylate $\leq$ adipate $\leq$ succinate $< $ tartrate $< $ phosphate $< $ citrate $< $ borate. In addition, the order of crystallinity of the films almost matched that of the $CV$ values shown in Fig. 3(c). That is, films with higher crystallinity have higher permittivity, and thus exhibit a higher $CV$ value.

On the other hand, the peak intensities of $\gamma$-Al$_2$O$_3$ from the films subjected to the second anodization using borate were almost independent of the electrolyte in the first anodization, except for phosphate, which exhibited a lower intensity (Fig. 5(b)). When these intensities, excluding that for phosphate, are compared with the peak intensities shown in Fig. 5(a), it is evident that the use of borate for the second anodization improves the film crystallinity to the same level in all cases. In other words, the electrolyte species used for the first anodization has little effect on crystallinity.

It is known that the electrolyte anion species has a major impact on film crystallinity during anodization. When anions incorporated in the film migrate to the metal substrate side, as in the case of phosphate, crystallinity is markedly suppressed compared with the case where the incorporated anions do not migrate, as in the case of borate.2 In the results of this study, there was considerable variation in the crystallinity of the films depending on the combination of electrolytes used for multistep anodization. Even when organic salts, which suppress crystallization, were used for the first anodization, it is considered that the film crystallinity was improved by using borate for the second anodization, which promotes film crystallization, instead of using an organic salt (Fig. 5(b)). However, in the case of the film formed using phosphate for the first anodization and borate for the second anodization, there was no change in the intensity of the $\gamma$-Al$_2$O$_3$ peaks after the second anodization. This result indicates that crystallization was not promoted when this combination of electrolytes was used for multistep anodization. It is not clear why the film crystallinity did not increase even though the $CV$ value increased. However, when borate is used for the second anodization, the amount of P incorporated decreases (Fig. 4(a)), and thus it is possible that the reduction in the amount of P incorporated contributes to the increase in the $CV$ value.

### 3.6 Effectiveness of combining electrolytes in suppressing leakage current of crystalline film

Figure 6 shows the $I$-$t$ curves obtained during leakage current measurement for the crystalline films formed by two-
step anodization. In the case of the films formed using the same electrolyte for the first and second anodizations, spike noise was observed during the measurement of leakage current for the phosphate and organic salts (except for adipate) as shown in Fig. 6(a). On the other hand, as shown in Fig. 6(b), when the films were formed using borate for the second anodization, spike noise was markedly suppressed regardless of the electrolyte used for the first anodization.

The cause of the spike noise is unclear, but in the case of the films formed by two-step anodization, two tendencies were observed: (i) more spike noise tended to appear when electrolyte anions migrated to the inside of the film after being incorporated into the film during the second anodization, such as for the phosphate and organic salts, and (ii) spike noise tended to be suppressed when electrolyte anions did not migrate after being incorporated into the film, such as for borate.13)

The relation between the electrolyte type and the leakage current after 15 min for the crystalline films formed by two-step anodization is summarized in Fig. 7. When borate was used for the second anodization, the film formed using salicylate for the first anodization had the lowest leakage current ($5 \times 10^{-6}$ mA cm$^{-2}$). Among the films formed using the same electrolyte for the first and second anodizations, the films with high crystallinity tended to have a high $CV$ value but also a high leakage current. In the case of the films formed using borate for the second anodization, although the crystallinity of the films tended to increase regardless of the electrolyte species used for the first anodization, there was no marked increase in the leakage current of the films. However, when the second anodization was conducted in borate, the leakage current increased or was suppressed, depending on the combination of electrolytes, compared with that of the case of the film formed using the same electrolyte species for the first and second anodizations. That is, the leakage current increased when the first anodization was conducted in adipate, citrate, or salicylate and the second anodization was performed in borate. On the other hand, spike noise was suppressed for all combinations when the second anodization was performed in borate, as is clear from Fig. 6(b). Therefore, the second anodization in borate has the effect of suppressing the leakage current, as shown by the reduction in spike noise.

![Fig. 6 Effect of electrolyte combination on suppression of leakage current of crystalline anodic alumina. The second anodization was conducted in (a) the same electrolyte as that used for the first anodization and (b) borate.](image)

![Fig. 7 Relation between leakage current and electrolyte type. Leakage current was measured for 15 min while applying 75% of the formation voltage, i.e., 225 V, as shown in Fig. 6. •: Second anodization conducted in borate. ◇: Second anodization conducted in the same electrolyte as that used for the first anodization.](image)

4. Conclusions

To evaluate the suitability of anodic alumina films as a dielectric oxide films for electrolytic capacitors, we examined the effect of various combinations of electrolytes on the dielectric properties of crystalline anodic alumina films formed through a combination of two-step anodization and heat treatment. The following conclusions were obtained as a result.

1. The films obtained after the second anodization had a two-layer structure comprising a flaky hydrated oxide and a granular crystalline oxide. In addition, the $V$-$C$ curve measured by reanodization showed that the anodic films had defects, the amount of which varied in the depth direction and a three-layer structure comprising a compact inner layer on the substrate side, an intermediate layer with the most defects and an outer layer with few defects.

2. When borate was used for the second anodization, the film capacitance and $CV$ value were higher than those of films formed using the same electrolyte species for the first
and second anodizations. At the same time, the crystallinity of the films was generally improved.

(3) The depth and amount of boron incorporated in the films formed using organic salts or phosphate for the first anodization and borate for the second anodization were suppressed compared with the case when borate was used for both steps. During the second anodization, the incorporation of electrolytic anions from the first anodization was also suppressed.

(4) When borate was used for the second anodization, the crystallinity of the films was improved, resulting in a higher CV. In addition, the amount of spike noise was markedly reduced.

Acknowledgments

This work was partially financially supported by a Grant-in-Aid for Scientific Research (A) No. 20241026 from the Japan Society for the Promotion of Science. We also acknowledge the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) — Supported Program for the Strategic Research Foundation at Private Universities, 2011–2015.

REFERENCES