Effect of electrolyte composition on hydration resistance of anodized aluminum oxide

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Abstract

The hydration reactions (in boiling water) of aluminum oxide films, which are used in electrolytic capacitor applications, are investigated. The films formed by a two-step anodization process in various electrolytes at 100 V are investigated. The anodization solutions are ammonium adipate, phosphoric acid, ammonium dihydrogen phosphate, and their mixtures. The cross-section morphologies and crystal structure of the oxides are examined by transmission electron microscopy. The hydration resistance of the anodized film, judging by its variation in film capacitance and retention (tolerance) voltage after immersion in boiling water for 15 min, is explored. After the hydration test, an outer fibrous hydrated layer was observed for each film primarily anodized in ammonium adipate (regardless of the electrolyte used in the re-anodization process). The hydrated layer is a composite with many fine γ'-Al_2O_3 grains dispersed in the pseudoboehmite matrix. Re-anodization in phosphorous-containing electrolytes can cause an increase in hydration resistance by retarding the formation of fibrous hydrated oxide. Phosphorus is found to be incorporated in the oxides for those formed in phosphorous-containing primary anodization electrolytes. The presence of phosphorus in the oxides can significantly improve their stability against hydration. The formation of fibrous hydrated layer results in an increase in capacitance and a decrease of retention voltage.
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Keywords: Electrolytic capacitor; Aluminum oxide; Anodization; Hydration; TEM analysis

1. Introduction

Barrier aluminum oxide films have found many applications [1], e.g., integrated circuit (IC) processes [2], thin-film-transistor liquid crystal display (TFT/LCD) fabrication [3], MIM cathodes for electron beam lithography [4], and electrolytic capacitors [5,6]. When used in electrolytic capacitors, one of the most critical issues is the loss of dielectric performance that results from contact of the film with the aqueous electrolyte. Previous investigations [7–9] have suggested that the conversion of anhydrous aluminum oxide to a hydrous counterpart is responsible for deterioration of the dielectric material. Nevertheless, the change in microstructure due to hydration has not been well elucidated. Furthermore, the modification of aluminum oxide, in terms of changes in microstructure and composition, to enhance its resistance to hydration should be of practical interest.

Katoh [10] has indicated that the composition of electrolyte greatly affects the anodizing efficiency and the properties of the aluminum oxide formed. It was found that ammonium adipate electrolyte gave an extreme high current efficiency (99.4%) in forming aluminum oxide. The resulting oxide exhibited a low leakage current, good durability against acid, and superior transient behaviour (stability). On the other hand, its reliability against hydration was poor. By contrast, the film anodized in ammonium dihydrogen phosphate electrolyte had excellent hydration resistance. Konno et al. [11] also showed that the phosphate ions adsorbed on the oxide surface would hinder the penetration of water

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Table 1
Composition and concentration of various anodization electrolytes employed

Electrolyte	Composition	Concentration
A	Ammonium adipate solution	$150\,g/1000\,g\ H_2O$
B	Phosphoric acid solution	$2\,cm^3/1000\,g\ H_2O$
C	Ammonium dihydrogen phosphate solution	$2\,g/1000\,g\ H_2O$
D	Ammonium adipate and phosphoric acid mixed solution	$150\,g + 2\,cm^3/1000\,g\ H_2O$
E	Ammonium adipate and ammonium dihydrogen phosphate mixed solution	$150\,g + 2\,g/1000\,g\ H_2O$

molecules into the anodized film. Based on this information, it is thus reasonable to assume that an anodized aluminum oxide with optimum characteristics may be formed by modifying the ammonium adipate electrolyte with the addition of phosphorous-containing species.

In the preparation of aluminum oxide for electrolytic capacitor applications, a two-stage process, namely re-anodization following the primary anodization treatment, is usually used in the industry. In this investigation, the effect of the electrolyte composition, either for primary or re-anodization treatment, on the hydration resistance of aluminum oxide is examined. Transmission electron microscopy (TEM) is employed for crystallinity, phase identification and composition analyses. The hydration resistance of each anodized oxide film is also evaluated by means of measuring the variation in capacitance (C) and retention (tolerance) voltage after immersion in boiling water for 15 min.

2. Experimental

2.1. Formation and hydration of anodized aluminum oxide films

Specimens with $10\,cm^2$ in area were cut from $90\,\mu m$ thick, O-temper, 99.99% aluminum foil that contained 0.0035 Fe, 0.0041 Si, and 0.0010 wt.% Cu. All specimens were washed in $HNO_3 + Na_2SO_4$ solution at $80\,^\circ C$ for 2 min to remove the oxide on the sample surface, then rinsed thoroughly in deionized water, and finally dried in a warm air stream. The specimens were then subjected to a two-stage anodization process. The first stage (primary) anodization was conducted in ammonium adipate electrolyte (group I), ammonium adipate/phosphoric acid mixed electrolyte (group II), or ammonium adipate/ammonium dihydrogen phosphate mixed electrolyte (group III) at $85\,^\circ C$. A 304 stainless-steel (SS) plate was used as the counter electrode. A constant current density of $25\,mA\,cm^{-2}$ was passed through the cell between the aluminum foil and the counter electrode until the potential difference reached 100 V. Then, the voltage was held at this potential for 10 min and the current was allowed to decay. After the primary anodization, the specimens were heat-treated in air at $500\,^\circ C$ for 2 min. In the second (re-anodization) stage, the anodization process was repeated except with a shorter holding time of 2 min under the controlled-potential condition. The composition, concentration, and pH values of the electrolytes used in the primary and re-anodization processes

are given in Table 1. The specific conditions for specimen preparation are listed in Table 2.

The hydration test for each anodized aluminum oxide was conducted in boiling water for 15 min. The microstructure, composition, and capacitive behaviour of the anodized oxide films, before and after hydration, were evaluated.

2.2. TEM examination

An ultrathin sectioning technique [12,13] was employed to prepare cross-section samples of the anodized aluminum foils for TEM analysis. Anodized specimens were first cut into strips with the dimension about $0.09\,mm \times 0.1\,mm \times 20\,mm$. These strips were then placed vertically in gelatin capsules that contained Spurr's epoxy resin mix. The capsules were kept under reduced pressure by means of an aspirator. This allowed the resin to penetrate fully the surface of each specimen. The samples were then kept at $60\,^\circ C$ over 24 h for complete polymerization. The blocks of resin were trimmed initially with a knife and then sectioned with a diamond cutter of an ultramicrotome. The cutting direction was parallel to the metal–film interface, and the section thickness was generally 40–60 nm. The sections were mounted on copper grids and examined by means of TEM at 200 kV. Auxiliary EDS

Table 2
Conditions for anodization treatments

Group	Condition	Primary-anodization solution	Heat treatment	Re-anodization solution
I	I1	A	$500\,^\circ C$, 2 min	A
	I2	A	$500\,^\circ C$, 2 min	B
	I3	A	$500\,^\circ C$, 2 min	C
	I4	A	$500\,^\circ C$, 2 min	D
	I5	A	$500\,^\circ C$, 2 min	E
II	II1	D	$500\,^\circ C$, 2 min	A
	II2	D	$500\,^\circ C$, 2 min	B
	II3	D	$500\,^\circ C$, 2 min	C
	II4	D	$500\,^\circ C$, 2 min	D
	II5	D	$500\,^\circ C$, 2 min	E
III	III1	E	$500\,^\circ C$, 2 min	A
	III2	E	$500\,^\circ C$, 2 min	B
	III3	E	$500\,^\circ C$, 2 min	C
	III4	E	$500\,^\circ C$, 2 min	D
	III5	E	$500\,^\circ C$, 2 min	E

Group I: primarily anodized in ammonium adipate solution; group II: primarily anodized in ammonium adipate/phosphoric acid mixed solution; group III: primarily anodized in ammonium adipate/ammonium dihydrogen phosphate mixed solution.

(X-ray energy dispersive spectroscopy) was conducted to elucidate the chemical composition of the anodized oxide film. A camera length of 100 cm was adopted as the nano-beam electron diffraction was performed.

2.3. Capacitance measurement

The capacitance of each anodized oxide film was measured using a typical LCR meter in 25 °C aqueous ammonium adipate electrolyte (150 g/1000 g H_2O). A pure aluminum sheet with a very large area was used as the counter electrode. The perturbation was 1.2 V_{rms} at 120 Hz. After immersion in boiling water for 15 min, the capacitance (C_{15}) of each oxide film was also recorded.

2.4. Retention voltage measurement

A Keithley 2400 instrument was used to determine the retention voltages ((V_R) or tolerance voltages) of the various aluminum oxides. The measurements were performed in 25 °C aqueous ammonium adipate electrolyte (150 g/1000 g H_2O). A 304 stainless-steel plate was used as the counter electrode. A constant current density of 10 μA cm^{-2} was applied to the anodized aluminum specimen and the response voltage was recorded. As soon as the current was applied, the voltage increased immediately and then gradually reached a saturated value. After 1 min, the voltage was recorded as the retention voltage of the anodized aluminum oxide film. It was considered as a parameter to evaluate the reliability of the oxide film [11].

3. Results and discussion

3.1. Microstructure and crystalline characteristics of anodized oxide films

The bright-field cross-section morphology of a specimen primarily anodized at 100 V in 85 °C ammonium adipate electrolyte and re-anodized in the same electrolyte (condition I1)

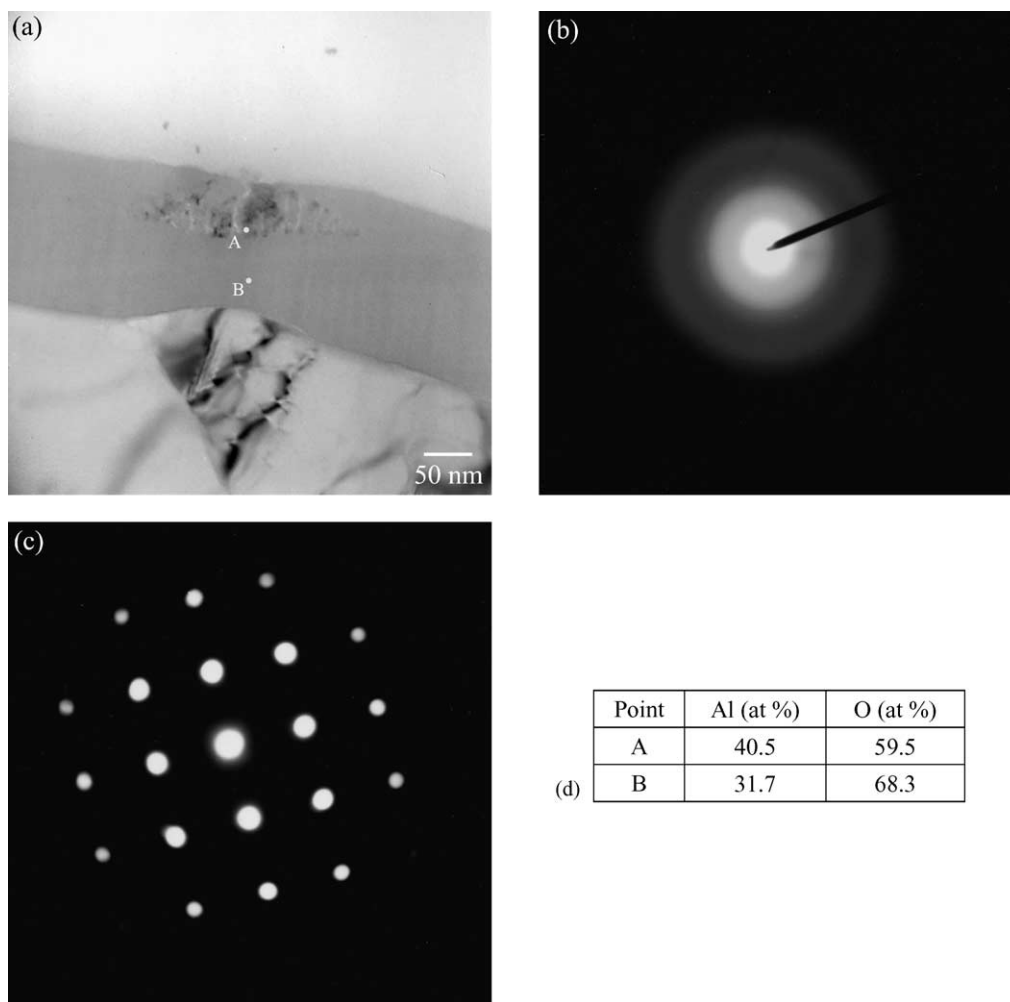| Point	Al (at %)	O (at %)
A	40.5	59.5
B	31.7	68.3

Fig. 1. (a) TEM cross-section image of aluminum foil primarily anodized in ammonium adipate electrolyte and re-anodized in same electrolyte (condition I1); (b) electron diffraction pattern taken from inner oxide layer; (c) electron diffraction patterns taken from (0 0 1) pole of crystalline region in outer oxide layer; (d) chemical composition taken at various positions by EDS.

is shown in Fig. 1(a). The barrier oxide, observed on top of the aluminum substrate, consists of an inner featureless layer and an outer layer with some regions of high contrast. A nano-beam electron diffraction pattern taken from the inner layer, as presented in Fig. 1(b), indicates that the oxide is amorphous. A diffraction pattern of the outer crystalline region with a $(0\,0\,1)$ pole is given in Fig. 1(c). The results confirmed that this is γ'-Al_2O_3 [14] with a face centre cubic (FCC) structure. The chemical composition of the anodized oxide was examined by EDS. The experimental data, given in Fig. 1(d), indicate that the atomic ratio of Al:O for the crystalline oxide (point A) is close to the stoichiometric ratio of Al_2O_3 (i.e., 2:3). By contrast, the Al:O atomic ratio for the amorphous oxide is lower than that of the Al_2O_3. The thickness of the inner amorphous layer and that of the outer crystal-containing layer is about 105 and 75 nm, respectively. Similar morphology, crystallinity, and chemical composition are also observed for the group I oxides.

A TEM cross-section micrograph of an anodized specimen after immersion in boiling water for 15 min is shown in Fig. 2. The specimen was initially anodized in ammonium adipate electrolyte and then re-anodized in the same electrolyte (condition I1). As can be seen, the film is damaged after immersion in boiling water. A fibrous hydrated layer is clearly detected at the outer part of the film. It is converted from the barrier aluminum oxide by the hydration reaction. This micrograph reveals that only the most inner oxide layer remains unchanged. The fibrous hydrated layer revealed in Fig. 2 is similar to that formed on the aluminum metal surface; it reacts with boiling water and is identified as pseudoboehmite, as reported by Bernard and Randall [7] and others [15,16]. Some discrete pores are observed between the oxide and the alu-
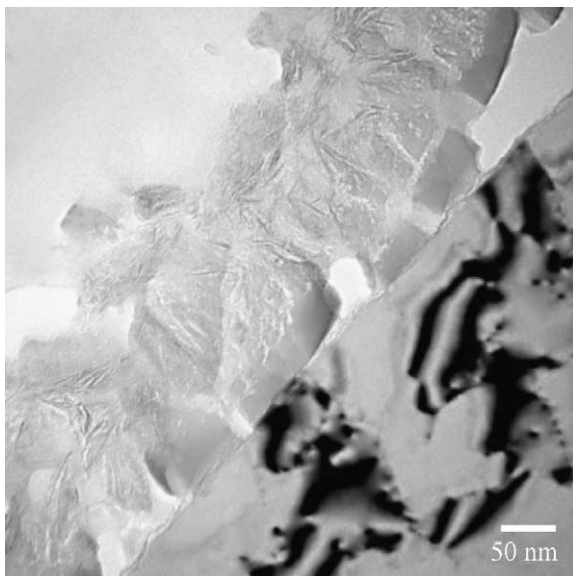
minum substrate, which indicates a loss of adhesion after hydration.

An electron diffraction pattern of the fibrous hydrated film is shown in Fig. 3(a). The ring pattern reveals the existence of a polycrystalline structure. The diffraction rings are attributed to γ'-Al_2O_3. Since pseudoboehmite is a poorly crystallized form of boehmite (γ-AlOOH) that contains excess water [17], it is difficult to identify from the electron diffraction pattern. A dark-field image of the same specimen is given in Fig. 3(b). This shows that fine crystalline γ'-Al_2O_3 grains are dispersed within the fibrous pseudoboehmite layer.

The TEM cross-section micrograph of a hydrated specimen that was first anodized in ammonium adipate electrolyte
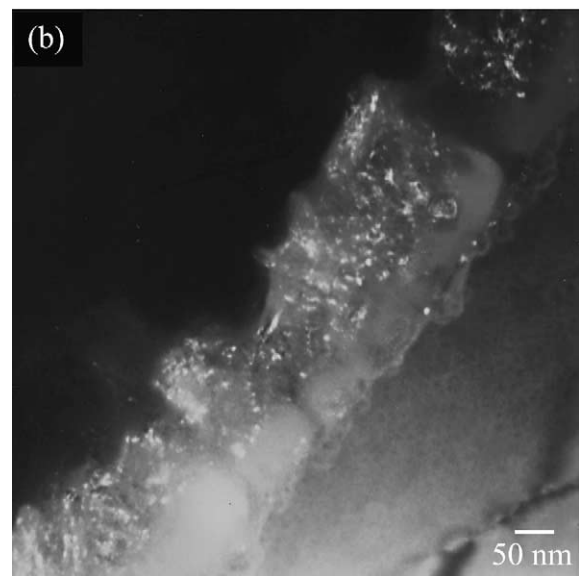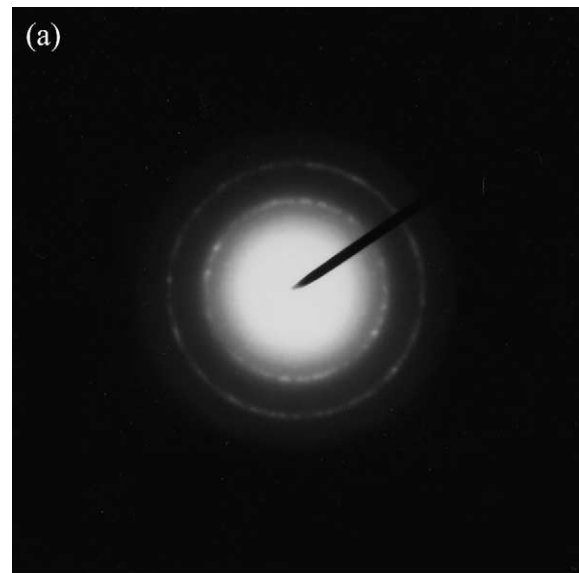

Fig. 2. TEM cross-section image of aluminum foil primarily anodized in ammonium adipate electrolyte and re-anodized in same electrolyte (condition I1) after immersion in boiling water for 15 min.

Fig. 3. (a) Electron diffraction pattern taken from outer fibrous hydrated layer of condition I1 film after immersion in boiling water for 15 min; (b)TEM dark-field image of condition I1 specimen after hydration.

and then re-anodized in phosphoric acid electrolyte (condition I2) is shown in Fig. 4. The fibrous hydrated layer, with similar crystallinity to that of the oxide formed according to the I1 condition (as shown in Fig. 3), has also been examined. The inner oxide with a thickness of about 35 nm is apparently immune to hydration, as shown in Fig. 4.

For the oxide formed according to condition I3, namely anodized initially in ammonium adipate electrolyte and then re-anodized in ammonium dihydrogen phosphate electrolyte, an improved hydration resistance is clearly observed, as demonstrated by the TEM micrograph presented in Fig. 5. The formation of a fibrous hydrated layer is suppressed, and a rather thick (about 95 nm) immune layer is formed after immersing in boiling water for 15 min. This indicates that the hydration resistance of the anodized aluminum oxide depends on the re-anodization electrolyte that is used. A previous investigation has shown [18] that re-anodization in phosphorous-containing electrolytes results in the formation of $AlPO_4 \cdot xH_2O$ on the oxide surface [18]. It has been reported [19] that the formation of an insoluble phosphate compound on the oxide surface would hinder its hydration reaction with water. The improvement of hydration resistance of the oxide anodized in the phosphorous-containing electrolytes can thus be explained. The superior hydration resistance for a specimen re-anodized in ammonium dihydrogen phosphate electrolyte (I3), as compared with that in phosphoric acid electrolyte (I2), is due to the higher amount of $AlPO_4 \cdot xH_2O$ that is formed on the oxide surface. The through-film-thickness cracks shown in Fig. 5 are artifacts formed during ultramicrotomy for TEM sample preparation.

Mixed electrolytes were also used for re-anodization. TEM micrographs are given in Fig. 6 and these provide a comparison of the hydration resistance of two oxides pre-

Fig. 5. TEM cross-section image of aluminum foil primarily anodized in ammonium adipate electrolyte and re-anodized in ammonium dihydrogen phosphate electrolyte (condition I3) after immersion in boiling water for 15 min.
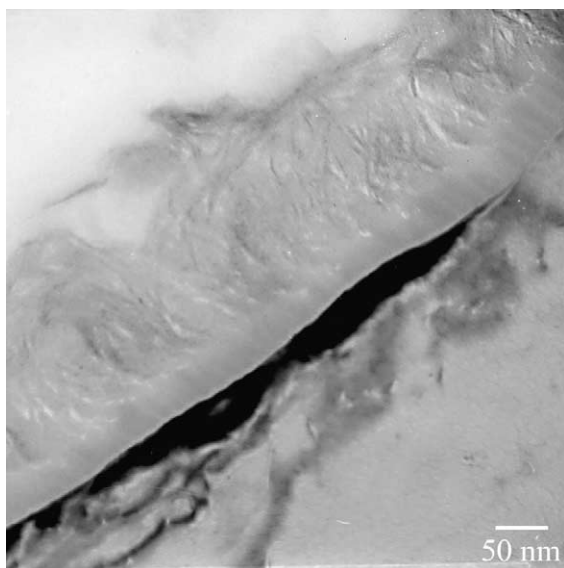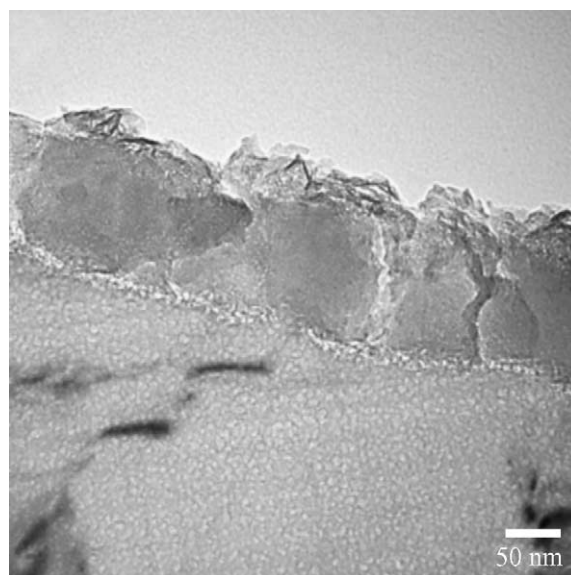

Fig. 4. TEM cross-section image of aluminum foil primarily anodized in ammonium adipate electrolyte and re-anodized in phosphoric acid electrolyte (condition I2) after immersion in boiling water for 15 min.

pared according to conditions I4 (Fig. 6(a)) and I5 (Fig. 6(b)). These two oxides were both primarily anodized in ammonium adipate electrolyte, followed by re-anodization in mixed ammonium adipate/phosphoric acid and mixed ammonium adipate/ammonium dihydrogen phosphate electrolytes, respectively. Similar to those observed for specimens I2 and I3, a two-layer microstructure of the oxide film, namely an inner immune layer and an outer hydrated layer, is also observed for either the I4 or the I5 specimen. In both specimens, the thicknesses of the immune layers were about 65 and 80 nm, respectively. The results further indicate that ammonium dihydrogen phosphate in the re-anodization electrolyte has a greater effect (than phosphoric acid) on improving the hydration resistance of the anodized aluminum oxide.

The use of a mixed electrolyte which contains phosphoric acid or ammonium dihydrogen phosphate in the primary anodization process exerts an even more significant effect on the microstructure of the oxide before and after the hydration test. A TEM cross-section micrograph of the as-anodized specimen prepared according to condition II1 is shown in Fig. 7(a). The addition of phosphoric acid to the ammonium adipate electrolyte used as the primary anodization electrolyte causes the formation of fully amorphous aluminum oxide. The absence of a crystalline phase is also found in the as-anodized aluminum oxide prepared according to condition III1 (with ammonium dihydrogen phosphate addition in the primary anodization electrolyte). In fact, the presence of phosphorous-containing species in the primary anodization electrolyte gives rise to the exclusive formation of a single layer of amorphous oxide. EDS analysis (Fig. 7(b)) reveals that phosphorus is incorporated in the oxide. It appears that retardation of the formation of crystalline γ'-Al_2O_3
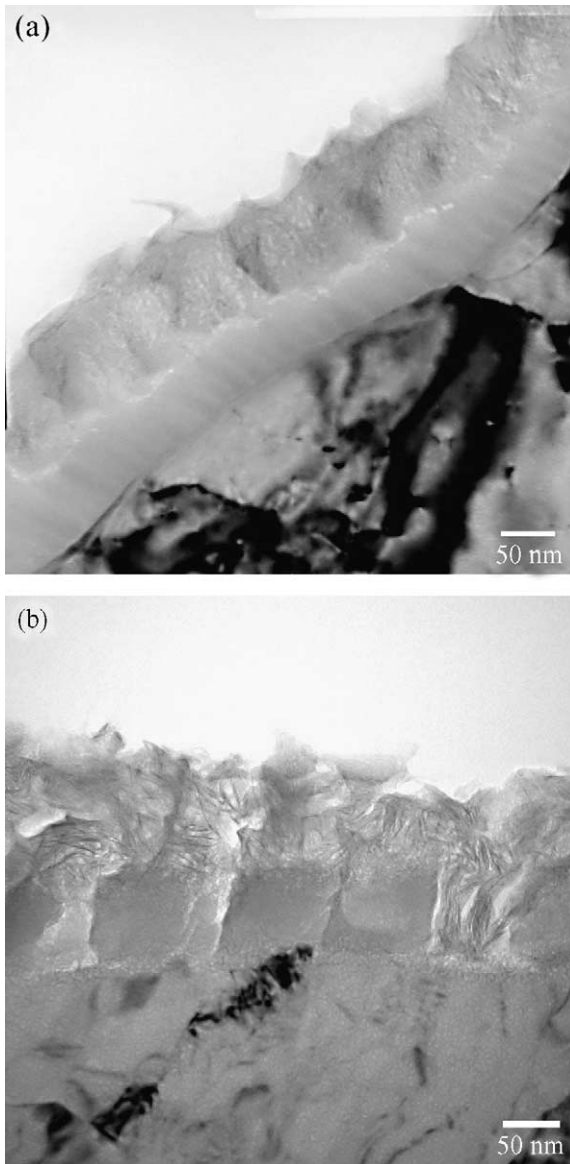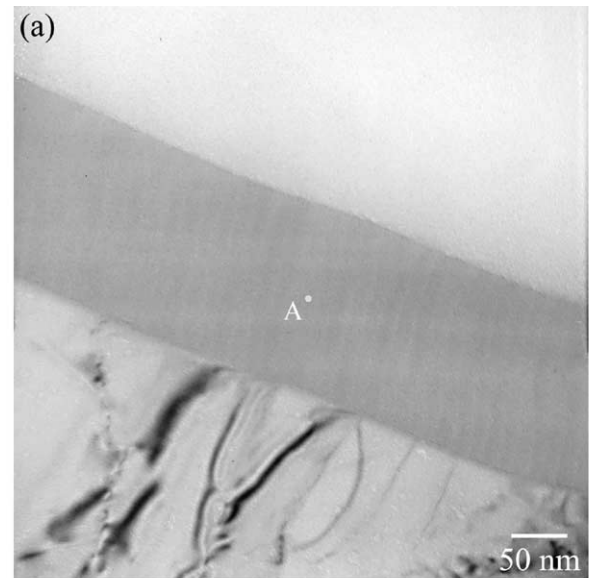
Fig. 6. TEM cross-section image of aluminum foil primarily anodized in ammonium adipate electrolyte and re-anodized in: (a) ammonium adipate/phosphoric acid mixed electrolyte; (b) ammonium adipate/ammonium dihydrogen phosphate mixed electrolyte after immersion in boiling water for 15 min.

can be attributed to the presence of phosphorus in the oxide layer.

After immersion in boiling water for 15 min, the TEM cross-section micrograph of specimen II1 is given in Fig. 8. This micrograph shows that only the most outer layer of the oxide film is affected by hydration, i.e., most of the oxide remains unchanged. The result indicates that phosphorus-containing anodized aluminum oxide is very resistant to hydration. The hydration resistance can be even more improved if the anodized aluminum oxide is prepared according to condition III1, namely initial anodization in ammonium adipate/ammonium dihydrogen phosphate mixed electrolyte followed by re-anodization in ammonium adipate electrolyte. A

Point	Al (at %)	O (at %)	P (at %)
A	31.0	66.1	2.9

(b)

Fig. 7. (a) TEM cross-section image of aluminum foil primarily anodized in ammonium adipate/phosphoric acid mixed electrolyte and re-anodized in ammonium adipate electrolyte (condition II1); (b) chemical composition taken at point A by EDS.

TEM cross-section micrograph for specimen III1 after immersion in boiling water for 15 min is demonstrated in Fig. 9. Clearly, the addition of either phosphoric acid or ammonium dihydrogen phosphate to ammonium adipate electrolyte for use in the primary anodization stage, rather than in the
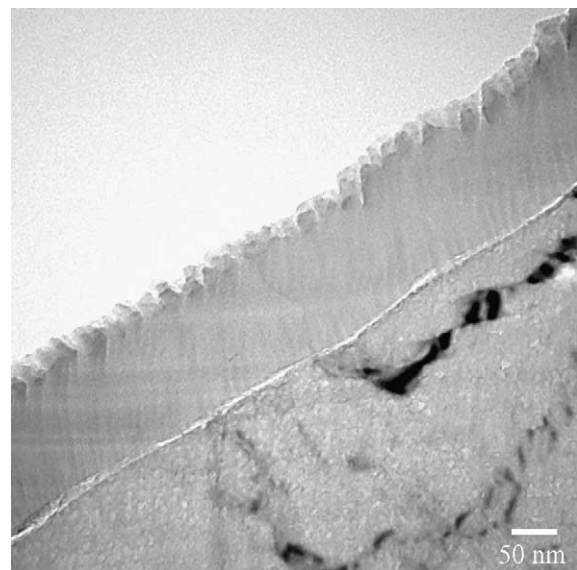

Fig. 8. TEM cross-section image of aluminum foil primarily anodized in ammonium adipate/phosphoric acid mixed electrolyte and re-anodized in ammonium adipate electrolyte (condition II1) after immersion in boiling water for 15 min.
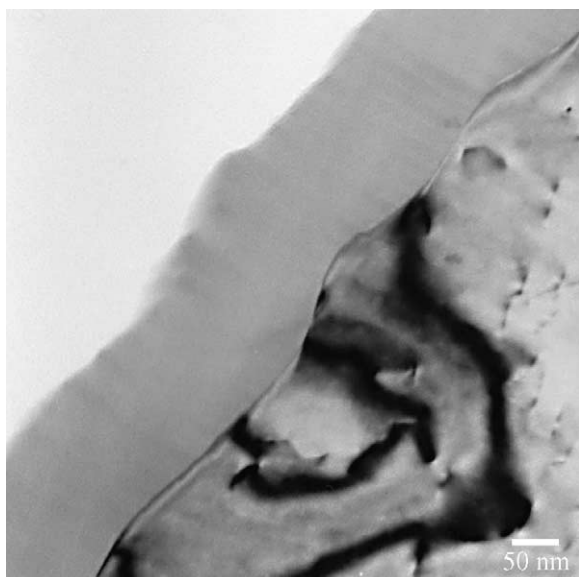
Fig. 9. TEM cross-section image of aluminum foil primarily anodized in ammonium adipate/ammonium dihydrogen phosphate mixed electrolyte and re-anodized in ammonium adipate electrolyte (condition III1) after immersion in boiling water for 15 min.

re-anodization electrolyte, is more advantageous in enhancing the hydration resistance of aluminum oxide. This suggests that incorporation of phosphorus within the anodized film, rather than a surface phosphate compound, is more effective in inhibiting the hydration reaction of the aluminum oxide. Moreover, the addition of ammonium dihydrogen phosphate is more effective than phosphoric acid in maintaining oxide stability in boiling water.

3.2. Effect of hydration on capacitance and retention voltage

The capacitances of various anodized aluminum oxide films, before and after hydration, are listed in Table 3. The results indicate that the capacitance of the oxide electrode (I2, II2, or III2) before hydration is highest in each group if it is re-anodized in phosphoric acid electrolyte. TEM analyses show that re-anodization in phosphoric acid electrolyte gives rise to the thinnest oxide formation in each group. This is the main reason for the high capacitance. It is also found that the capacitances of the group I oxides are higher than those of groups II and III. This can be attributed to the presence of crystalline γ'-Al_2O_3 (consequently, a higher relative dielectric constant [20,21]) within the aluminum oxide that has been formed in ammonium adipate electrolyte in the primary anodization stage. After immersion in boiling water for 15 min, the capacitance (C_{15}) of each oxide electrode in group I is increased, while that in groups II and III does not change appreciably. The former effect is attributed to the formation of pseudoboehmite accompanied by a decrease in the thickness of the dielectric (barrier) oxide layer. The poor stability of the oxide, however, limits its long-term application. By contrast,

oxides formed using the primary electrolyte containing phosphoric acid or ammonium dihydrogen phosphate are rather stable with capacitances that remain almost unchanged after hydration.

The retention (tolerance) voltages, before and after hydration, of various anodized aluminum oxides are given in Table 4. It is interesting to find that oxides subjected to re-anodization in $2\,cm^3/1000\,g\,H_2O$ phosphoric acid electrolyte have low values of V_R, though they exhibit the highest capacitances in groups I, II, and III. A substantial decrease in retention voltage due to hydration is observed for each oxide electrode in group I. For group II and III oxides, however, the retention voltage does not change appreciably even after immersion in boiling water for 15 min. This indicates that the oxides of these two groups are stable and resistant to hydration. The results of capacitance and retention voltage measurements are consistent with those of TEM analyses.

Table 3
Capacitances, before (C) and after (C_{15}) 15-min hydration, of various anodized aluminum oxide electrodes

Group	Condition	C (nF)	C_{15} (nF)
I	I1	571	1112
	I2	628	954
	I3	575	641
	I4	580	732
	I5	575	694
II	II1	520	537
	II2	587	595
	II3	523	526
	II4	525	537
	II5	524	529
III	III1	520	531
	III2	583	589
	III3	522	524
	III4	524	532
	III5	523	526

Table 4
Retention (tolerance) voltages, before (V_R) and after (V_{R15}) 15-min hydration, of various anodized aluminum oxide electrodes

Group	Condition	V_R (V)	V_{R15} (V)
I	I1	122.1	36.6
	I2	111.6	70.4
	I3	122.9	106.3
	I4	121.8	95.2
	I5	122.5	103.2
II	II1	126.6	120.2
	II2	114.2	108.9
	II3	127.5	122.1
	II4	126.0	120.2
	II5	126.8	120.9
III	III1	129.0	122.8
	III2	116.9	111.5
	III3	129.6	124.2
	III4	128.7	122.7
	III5	129.5	123.7

4. Conclusions

The microstructure and hydration resistance of anodized aluminum oxide depend greatly on the composition of the electrolyte used, especially in the primary anodization process. The use of ammonium adipate electrolyte as the primary anodization electrolyte (regardless of the re-anodization electrolyte) results in the formation of an inner amorphous and an outer γ'-Al_2O_3-containing oxide on the aluminum substrate. An extensive fibrous hydrated layer can be formed at the outer part of the oxide film after immersion in boiling water for 15 min. The hydrated layer is a composite with many fine γ'-Al_2O_3 grains dispersed in the pseudoboehmite matrix. Re-anodization in phosphorous-containing electrolytes retards the formation of fibrous hydrated oxide and increases film stability. The presence of phosphoric acid or ammonium dihydrogen phosphate in the primary anodization electrolyte results in the formation of a single-layer amorphous aluminum oxide with phosphorus incorporated in the film. The hydration resistance of the anodized film can be significantly improved by the formation of a phosphorous-containing aluminum oxide.

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