

Effect of citric acid on microstructure and electrochemical characteristics of high voltage anodized alumina film formed on etched Al Foils

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Abstract: Aluminum capacitor foils with a tunnel etch structure were reacted with boiling water and then anodized at 530 V in boric acid solution or boric acid+citric acid mixed solution. The microstructure and crystallinity of the resulting anodized film were examined by TEM and XRD. The special capacitance, resistance and withstanding voltage of the film were explored with electrochemical impedance spectroscopy (EIS), LCR meter and small-current charging. The results show that the high voltage anodized oxide film consists of an inner layer with high crystallinity and an outer layer with low crystallinity. However, the crystallinity of the film formed in boric acid+citric acid mixed solution is higher than that of the film formed in only boric acid solution, leading to an increase in film's field strength and special capacitance. Meanwhile, there are more defects from phase transformation in the out layer of the film formed in boric acid+citric acid mixed solution than in that of film formed in only boric acid solution, leading to a decrease in film's resistance and withstanding voltage.

Key words: citric acid; anodized oxide film; Al foil; Al electrolytic capacitor; electrochemical performance

1 Introduction

Aluminum electrolytic capacitor is one of the key components in electric appliances and is widely used in energy storage and conversion, liquid crystal display fabrication, integrated circuit process, etc[1]. As working dielectric medium of Al electrolytic capacitor, barrier anodic alumina film is formed on Al foil in weak acid solutions and its microstructure and special capacitance determine the capacitor's volume and performance[2–3]. Depending on anodizing conditions, either amorphous or crystalline barrier aluminum oxide can be formed. The crystalline form is always γ' -Al₂O₃, similar to γ -Al₂O₃ but with more disorder on the cation lattice. Because the crystalline oxide can sustain a higher voltage, has a higher relative dielectric constant, and possesses a lower ionic conductivity than the amorphous one, work on developing an anodized film with a high degree of crystallinity is of continuous interest to researchers. CHANG et al[4] reported that heat-treatment of Al foil at 500 °C before and after anodization could induce the formation of crystalline γ' -Al₂O₃ in the outer layer of

anodized oxide. ONO and ALWITT et al found that the hydration treatment of Al foil using hot water before anodization not only could save much electrical power for the formation of anodized oxide, but also could improve the anodized oxide's crystallinity[5]. In modern industry, one popular way to make anodic alumina film for high voltage Al electrolytic capacitor is to electrochemically etch smooth Al foil with direct current and then to react the etched foil with boiling water to deposit a hydrous oxide (e.g. pseudoboehmite), followed by anodization in boric acid solution[6–9]. Because of the difficulty in making thin cross section of the etched and high voltage anodized foil for TEM observation, there are little reports about the microstructure and electrochemical performance of the high voltage anodized film on etched Al foil. Meanwhile, citric acid is one of the common working electrolytes for high voltage Al electrolytic capacitor[10–14]. However, the microstructure and its correlation with the electrochemical performance of the high voltage anodic oxide film formed in boric acid+citric acid mixed solution on etched Al foil have been less frequently explored. Therefore, in this investigation, the microstructure and

crystallinity of the 530V anodized oxide film formed in boric acid solution or boric acid+citric acid mixed solution on etched foil are analyzed with TEM and XRD. The cross section of the film is prepared by using focused ion beam for TEM examination. The film's special capacitance, resistance and withstanding voltage are measured with EIS, LCR meter and small-current charging. The effects of citric acid on the microstructure and electrochemical performance of high voltage anodized aluminum oxide films formed on tunnel-etched Al foils are discussed and analyzed.

2 Experimental

2.1 Specimen

A commercial tunnel-etched aluminum foil for high voltage usage with high purity (>99.99%) and cubic texture (>95%) was used as specimen. For this foil, 95% of the area was orientated with the (100) plane parallel to the surface. The tunnels followed a $\langle 100 \rangle$ direction, and the metal texture caused the tunnels to be mostly aligned normal to the surface. The average diameter and length of tunnels were 1–2 μm and 25–30 μm , respectively.

2.2 Formation of anodized alumina films

Foil coupons with 10 cm^2 area were hydrated in the boiling deionized water for 10 min and then subjected to formation process which was composed of primary anodization, stress relaxation at 500 $^{\circ}\text{C}$ for 2 min and reanodization. The primary anodization was conducted in 1.29 mol/L H_3BO_4 solution or 1.29 mol/L H_3BO_4 +0.021 mol/L $\text{C}_6\text{H}_8\text{O}_7$ solution at 95 $^{\circ}\text{C}$ with a nominal constant current density of $J_a=25 \text{ mA/cm}^2$ until the specimens were anodized to 530 V cell voltage and then held at this voltage for time up to 20 min. After the primary anodization, the specimens were heat-treated in air at 500 $^{\circ}\text{C}$ for 2 min followed by reanodization in the same solution except with a shorter holding time of 5 min under the controlled-potential condition. Table 1 summarized the formation conditions, such as rated cell voltage (V_{re}), solution pH and conductivity (σ), cell IR drop (V_{ic}) at the beginning of primary anodization, final nominal current density (J_f) and formation voltage (V_f) that the films really sustained at the end of reanodization.

2.3 TEM examination

The anodized foils were thinned with focused beam of Ar ions radiating parallel to the plane of specimen face to a proper thickness, and the cross sections of the foils were examined under a transmission electron microscope (Hitachi H-800H) operating at 175 kV. A camera length of 80 cm was adopted as the nanobeam electron diffraction was performed.

2.4 X-ray diffraction

The crystallinity of the anodized aluminum oxide film was determined by using a high power X-ray diffractometer (MAC Science Company Ltd M21X). The incident radiation was obtained from a high power ceramic tube with copper (Cu) anode operating at 40 kV and 200 mA. The samples were measured in a continuous mode with 0.02 $^{\circ}$ step size in a 2θ range of 10 $^{\circ}$ to 90 $^{\circ}$ and a scanning speed of 10 ($^{\circ}$)/min.

2.5 Electrochemical impedance spectroscopy

The electrochemical characteristics of the film were investigated by electrochemical impedance spectroscopy (EIS) in 80 g/L $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ solution at 30 $^{\circ}\text{C}$. The test cell was a three-electrode system consisting of the anodized foil, a platinum sheet and a saturated calomel electrode (SCE) assembled as working electrode, counter electrode and reference electrode, respectively. The reference electrode employed a salt bridge with a probe adjacent to the working electrode. And an EG&G model 273A potentiostat which was connected to a Schlumberger 1255 frequency response analyzer (FRA) was used to make electrochemical measurements. The input voltage signal had a root mean square amplitude of 10 mV at the open circuit potential and was typically scanned from 100 kHz to 5 mHz.

2.6 Capacitance and withstanding voltage

The special capacitance of the films was measured using a typical LCR meter in 80 g/L $\text{NH}_4\text{B}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ solution at 30 $^{\circ}\text{C}$. A pure aluminum sheet with a very large area was used as the counter electrode. The formed foils were charged with a nominal constant current density of $J_a=0.2 \text{ mA/cm}^2$ for 70 s in 0.9 mol/L H_3BO_4 solution at 80 $^{\circ}\text{C}$, during which the change in the cell voltage with time (E_c vs t) was monitored by a digital

Table 1 Formation conditions of anodized alumina films

Electrolyte	Rated cell voltage, V_{re}/V	pH value	Conductivity, $\sigma/(\mu\text{S}\cdot\text{cm}^{-1})$	Cell IR drop, V_{ic}/V	Final nominal current density, $J_f/(\text{mA}\cdot\text{cm}^{-2})$	Formation voltage, V_f/V
1.29 mol/L H_3BO_4 solution	530	3.0	180	75	0.38	528.9
1.29 mol/L H_3BO_4 +0.021 mol/L $\text{C}_6\text{H}_8\text{O}_7$ solution	530	2.5	1730	45	0.55	529.0

multi-meter connected to a PC system and the final E_c was regarded as the withstanding voltage.

3 Results and discussion

3.1 Effect of citric acid on microstructure of anodic oxide film

Figure 1 shows TEM cross section images and electron diffraction patterns of the anodized alumina films formed in different solutions. From Figs.1(a) and (b), either the film formed in boric acid solution or formed in the boric acid+citric acid mixed solution consists of an inner layer with high crystallinity, where the crystallites aggregate, are large in size and rich in number, and an outer layer with low crystallinity, where the crystallites disperse, are small in size and poor in number. However, the out layer of the film formed in the mixed-acids solution is more crystallized, thinner in thickness and with larger crystallites than that of the film formed in only boric acid. As demonstrated by electron diffraction patterns in Figs.1(a) and (b), the outer layer of the former is polycrystalline and the outer layer of the latter is rather amorphous. The out layer of the film comes from the transformation of pseudoboehmite to either γ' - Al_2O_3 or amorphous Al_2O_3 under electric field during anodization[5, 15]. It is obvious that the addition

of citric acid to boric acid solution can facilitate the transformation of pseudoboehmite to γ' - Al_2O_3 . Figs.1(c) and (d) further indicate that there are more numerous occluded voids and slits in the outer layer of the film formed in mixed-acids solution than the film formed in only boric acid solution, because the transformation of pseudoboehmite to γ' - Al_2O_3 leads to more internal stress and volume shrinkage than that of the transformation of pseudoboehmite to amorphous Al_2O_3 . From Fig.1, the thickness of the film formed in only boric acid solution is 550 nm, but that of the film formed in the mixed-acids solution is only 500 nm. According to the equation $E = V_f/d$, where V_f is the formation voltage and d is the thickness of film, the field strength of the films formed in boric acid solution and formed in the mixed-acids solution can be obtained as 0.96 V/nm and 1.06 V/nm, respectively. Obviously, the addition of citric acid to boric acid solution can contribute to the formation of a more crystallized film, leading to an increase in the field strength.

3.2 Effect of citric acid on crystallinity of anodic oxide film

Figure 2 shows high power X-ray diffraction patterns of the anode foils formed in different solutions. The strongest peak is corresponded to Al(200) from

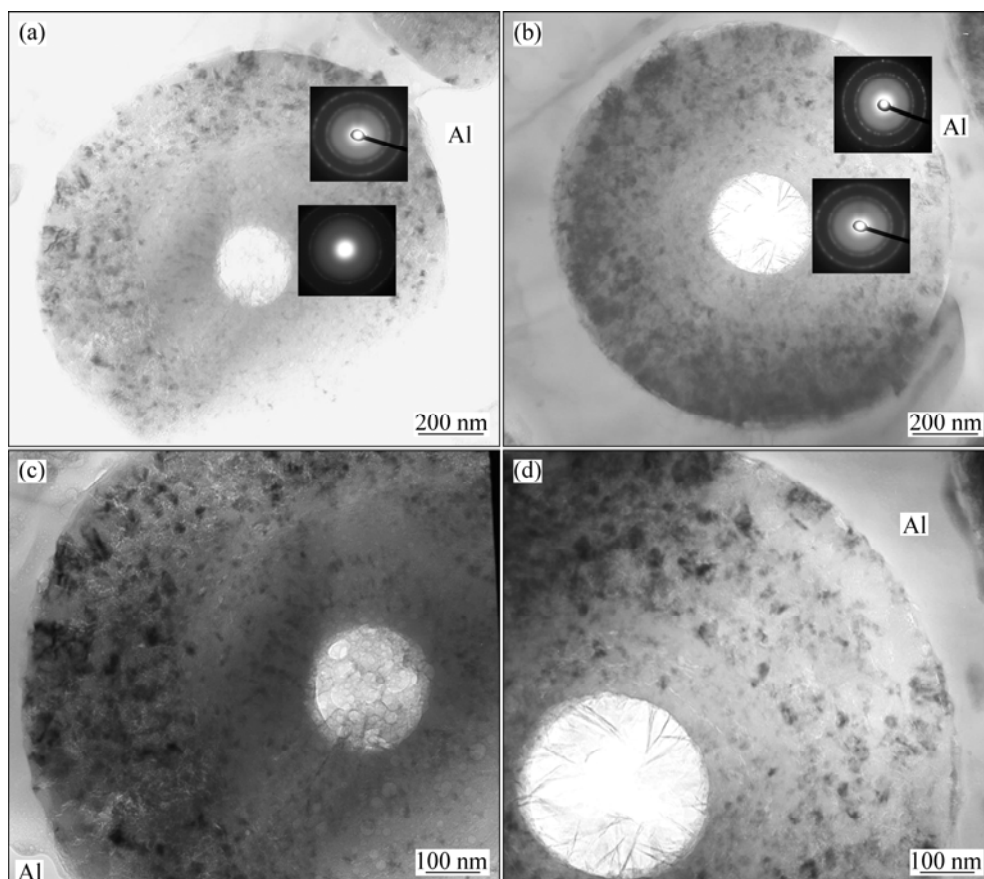


Fig.1 TEM images of cross section and electron diffraction patterns of anodized alumina films formed in different solutions: (a), (c) 1.29 mol/L H_3BO_4 ; (b), (d) 1.29 mol/L H_3BO_4 + 0.021 mol/L $\text{C}_6\text{H}_8\text{O}_7$

substrate and the second peak is $\gamma\text{-Al}_2\text{O}_3$ (400) coming from crystalline oxide in the anodic alumina film on Al substrate, but overwhelmed by Al(200). The third peak is the film's $\gamma\text{-Al}_2\text{O}_3$ (440), further magnified by the insert picture, where scan is slowly performed on a 2θ range of 64° to 70° . The crystallite size of the films was calculated by the Scherrer formula: $d=k\lambda/(B\cdot\cos\theta)$ from the $\gamma\text{-Al}_2\text{O}_3$ (440) peaks, where B is half height width; k is a form factor (shape factor), $k=0.89$ for spheres particles; λ is the wavelength of the radiation used, $\lambda_{\text{Cu},\text{K}\alpha 1}=1.540\ 56\text{\AA}$. The average crystallite size of the film formed in mixed-acids solution is 27 nm, while that of the film formed in only boric acid solution is 22 nm, coinciding with the TEM observation shown in Fig.1. It is well known that the ionization constants of citric acid and boric acid are 7.4×10^{-4} and 5.8×10^{-10} at 25°C , respectively. When a little amount of citric acid is added to the boric acid solution, more H^+ will be produced in the electrolyte, which causes some increment in its acidity, as shown by Table 1. During the formation of film, it is probably easier for citric acid to dissolve amorphous Al_2O_3 in the film than to dissolve $\gamma\text{-Al}_2\text{O}_3$ in the film. As a result, the film formed in mixed-acids solution is more crystallized than the one formed in only boric acid solution.

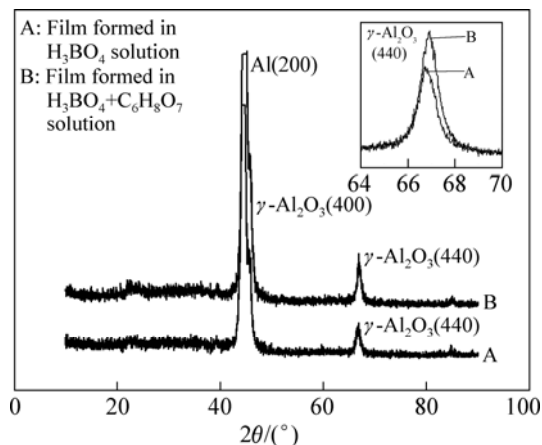


Fig.2 XRD patterns of anode foils formed in different solutions

3.3 Effect of citric acid on electrochemical performance of anodic oxide film

The results of EIS measurements for anode foils formed in both solutions are shown in Fig.3. A single time-constant capacitance behavior is predominant over the frequency range in this investigation. The equivalent circuit of EIS should consist of a parallel combination of the film resistance (R_{ox}) and its capacitance (C_{ox}), connected in series to a solution resistance (R_s). With this equivalent circuit and the impedance data obtained, the values of R_{ox} and C_{ox} of film could be evaluated (R_{ox} and C_{ox} are nominal values without considering the effect of the etched foils area), as demonstrated in Table 2. The

film's withstanding voltage (U_w) measured with small-current charging and special capacitance (C_s) measured with LCR meter were also listed in Table 2. The film's C_{ox} measured with EIS is almost identical to its C_s measured with LCR. When a little amount citric acid was added to boric acid solution, the film's C_{ox} could be increased from $0.47\ \mu\text{F}/\text{cm}^2$ to $0.58\ \mu\text{F}/\text{cm}^2$. Crystalline barrier aluminum oxide possesses a higher relative dielectric constant (ϵ_r) and a higher field strength (E) than the amorphous one, which allows withstanding identical formation voltage (V_f) with a thinner film. At the same time, reduction in the film's thickness (d) can weaken its trend to block off tiny etch tunnels and is helpful to increasing the film's real area (A). According to $C=\epsilon_0\epsilon_r A/d$, C_{ox} of the film formed in mixed-acids solution is certainly higher than that of the film formed in only boric acid solution, because the former is more crystallized than the latter[16]. However, as shown in Table 2, the R_{ox} and U_w of the film decrease from $9.017\ \text{M}\Omega\cdot\text{cm}^2$ and $532.5\ \text{V}$ to $8.537\ \text{M}\Omega\cdot\text{cm}^2$ and $531.2\ \text{V}$, respectively, when there was a little amount of citric acid in boric acid solution. The more defects in the outer layer of the film formed in mixed-acids solution may cause a decrease in R_{ox} and U_w , as seen in Figs.1(c) and (d). Figure 4 shows E_c-t curves of films during charging

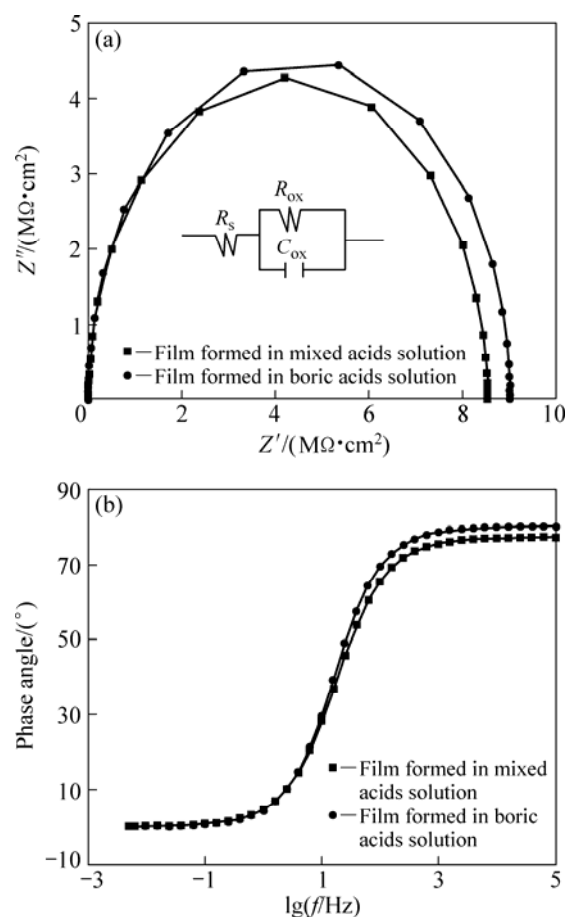
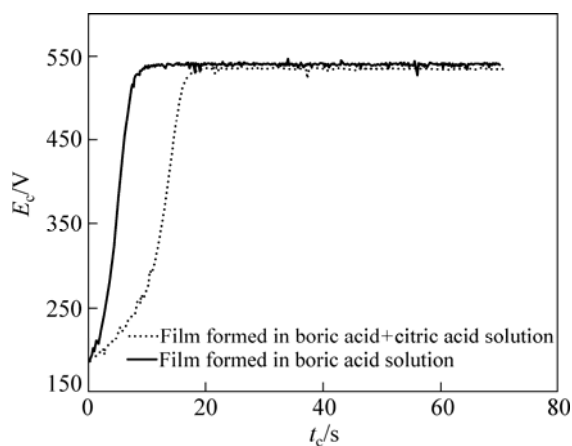


Fig.3 Electrochemical impedance spectra for anode foils formed in different solutions: (a) Nyquist plot; (b) Bode plot

Table 2 R_{ox} , C_{ox} , C_s and U_w of anodic oxide films formed in different electrolytes

Film	Film resistance, $R_{ox}/(M\Omega \cdot cm^2)$	Film capacitance, $C_{ox}/(\mu F \cdot cm^{-2})$	Solution resistance, $C_s/(\mu F \cdot cm^{-2})$	Film withstanding voltage, U_w/V
Formed in boric acid solution	9.017	0.4757	0.4812	532.5
Formed in mixed-acids solution	8.537	0.5794	0.5729	531.2

**Fig.4** E_c-t curves of films formed in different solutions during charging with small current

with small current. The slope of E_c-t curve for the film formed in only boric acid solution is steeper than that of the film formed in mixed-acids solution and finally reaches a higher plateau voltage. During charging the film with small current, most electric quantity is probably applied to repair its defects such as slits and voids, rather than to form new oxide layer, leading to induction in the E_c-t slope when the film possesses more defects.

4 Conclusions

1) The addition of a little amount of citric acid to the boric acid electrolyte can help to promote crystalline oxide formation and obtain a barrier film with a higher degree of crystallinity so as to reduce its thickness and increase its field strength and special capacitance.

2) The barrier film formed in boric acid+citric acid mixed solution is rich in defects at its outer layer from transformation of pseudoboehmite to γ' - Al_2O_3 , leading to induction in film's withstanding voltage and resistance. Therefore, it is necessary to repair the above defects with multi-anodization to improve the film's all-round performance.

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柠檬酸对腐蚀铝箔高压阳极氧化膜 微观结构与电化学性能的影响

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摘 要: 将高压铝电解电容器用腐蚀铝箔与沸水反应, 然后再在硼酸溶液或硼酸-柠檬酸混合酸溶液中进行 530 V 高压阳极氧化制得耐压薄膜, 应用透射电镜(TEM)、X 射线衍射(XRD)研究不同电解液所形成的高压阳极氧化膜的微观结构与结晶程度, 利用电化学交流阻抗(EIS)、LCR 数字电桥与小电流充电测试阳极氧化膜的电化学性能。结果表明: 高压阳极氧化膜具有明显层状结构, 内层结晶程度较高、外层结晶程度较低; 与单纯硼酸溶液所形成的氧化膜相比, 混合酸液所形成的阳极氧化膜的外层结晶程度与晶粒平均尺寸较大, 抗电场强度与比电容均比较高, 但相变使得氧化膜外层微观缺陷密度增多, 氧化膜比电阻与耐电压值有所降低。

关键词: 柠檬酸; 阳极氧化膜; 铝箔; 铝电解电容器; 电化学性能

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