



## Full Length Article

# Ultrasonic effect on etching tunnel morphology and distribution of aluminum foil



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## ABSTRACT

Etching aluminum foil was prepared by electrochemical DC etching under ultrasonic superimposition. Specifically, the relationship of electrochemical behavior, interface behavior and mass transfer enhancement from ultrasound was investigated intensively by chronopotentiometry, potentiodynamic polarization, cyclic voltammetry and electrochemical impedance spectra. Meanwhile, the etching specimens were characterized by SEM, N<sub>2</sub> adsorption and XRD patterns measurements. The results showed that ultrasonic agitation inhibited the growth of aluminum oxide film and facilitated pit initiation effectively via increasing the Cl<sup>-</sup> adsorption on electrolyte/aluminum oxide film interface, and strengthened the inward/outward migration of Cl<sup>-</sup> and AlCl<sub>3</sub> within tunnels by thinning the thickness of diffusion layer and decreasing the electrolyte resistance. Moreover, the double layer capacitance C<sub>dl</sub>, pit density, average pit size/tunnel length and its homogeneity are all enhanced under ultrasonic superimposition.

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## 1. Introduction

Capacitor, one of the three passive components (resistor, capacitor and inductor), is mainly used in electrical and electronic equipment. Therein, aluminum electrolytic capacitor is widely employed in the communications market, electrical applications and industrial field for its superior performance, low price and reliable quality.

Capacitance is a key evaluation parameter for capacitor quality. The capacitance formula of plate capacitor is  $C = (\epsilon\epsilon_0 S)/d$ , where the vacuum permittivity  $\epsilon_0$  is equal to  $8.85 \times 10^{-12} \text{ F m}^{-1}$ ,  $S$  denotes the specific surface area of the electrode pad,  $d$  is the thickness of oxide film. As for aluminum electrolytic capacitors, whether Al<sub>2</sub>O<sub>3</sub> is amorphous or crystalline, its relative dielectric constant is fixed about 8–10. Thus, it is essential to increase  $S$  (the specific surface area) to obtain high capacitance.

In aggressive ion-containing solution, such as Cl<sup>-</sup>, the  $S$  can be enlarged via electrochemical etching [1–6]. It is much affected by relevant pit parameters such as density, diameter and depth. Therefore, it is necessary to study the behaviors of pit initiation and its

propagation. The Cl<sup>-</sup> adsorption on oxide-coated aluminum has been adequately clarified [7]. Interaction of substantial adsorbed Cl<sup>-</sup> at electrolyte/aluminum oxide film interface with active sites induced pit initiation [2,8–11]. Then, Cl<sup>-</sup> led to the beginning of local dissolution and sufficiently thinning of the passive layer by intensely attacking defects within the passive film [12]. Simultaneously, Cl<sup>-</sup> penetrated to the aluminum/aluminum oxide film interface, where it caused further specific action with metallic aluminum of high reactivity, thus to ensure pit propagation [8], as illustrated in Fig. 1(a). Hence, with regard to electrochemical etching, the importance of Cl<sup>-</sup> is apparent.

Studies have demonstrated that the pit commences when the applied potential exceeds a critical value  $E_{\text{pit}}$  [13–15].  $E_{\text{pit}}$  can be expressed by Eq. (1) [13]:

$$E_{\text{pit}} = a - b \log[\text{Cl}^-] \quad (1)$$

Where  $a$  and  $b$  are both constants. So, the relationship between  $E_{\text{pit}}$  and pit initiation is: a lower  $E_{\text{pit}}$  denotes an easier pit initiation and vice versa. However, as illustrated in the left part of Fig. 1(b), the thickness of the laminar layer  $\delta_D$  is the rate-determining step of Cl<sup>-</sup> diffusion, affecting the adsorbed Cl<sup>-</sup> concentration  $C_i$  (not the concentration of bulk solution,  $C_o$ ) and subsequent pit initiation. However, in fact, from a consideration of the known heterogeneity of aluminum surface, the Cl<sup>-</sup> adsorption on oxide film is

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## Nomenclature

$C$	the capacitance of plate capacitor, $\mu\text{F}$
$\varepsilon_0$	the vacuum permittivity, $8.85 \times 10^{-12} \text{ F m}^{-1}$
$\varepsilon$	Relative dielectric constant, $\text{F m}^{-1}$
$S$	the specific surface area, $\text{m}^2$
$d$	the thickness of oxide film, $\mu\text{m}$
$E_{\text{pit}}$	Pitting potential, V
$\delta_{\text{D}}$	the thickness of the laminar layer, $\mu\text{m}$
$C_i$	the adsorbed $\text{Cl}^-$ concentration on electrolyte/oxide interface, $\text{mol L}^{-1}$
$C_0$	the concentration of bulk solution, $\text{mol L}^{-1}$
$E_s$	Steady-state potential, V
$\tau_b$	the time corresponding to pitting potential, s
$\tau_s$	the time corresponding to steady-state potential, s
$b_a$	Anodic tafel slope, $\text{V dec}^{-1}$
$-b_c$	Cathodic tafel slope, $\text{V dec}^{-1}$
$E_{\text{corr}}$	Free corrosion potential, V
$i_{\text{corr}}$	Free corrosion current density, $\text{A cm}^{-2}$
$i_{\text{lim}}$	the limiting current densities, $\text{A cm}^{-2}$
$N$	the number of electrons
$F$	the faraday constant, $96485.33 \text{ C mol}^{-1}$
$D$	the diffusion coefficient
$C_b$	Bulk concentration of the electroactive compound, $\text{mol L}^{-1}$
$R_s$	the solution resistance, $\Omega \text{ cm}^2$
$R_{\text{ct}}$	the charge transfer resistance, $\Omega \text{ cm}^2$
$C_{\text{dl}}$	the double layer capacitance, $\mu\text{F cm}^{-2}$
$n$	the deviation from the ideal behavior
$S_{\text{BET}}$	the BET specific surface areas, $\text{m}^2 \text{ g}^{-1}$

inhomogeneous. Namely, the  $\text{Cl}^-$  concentration at defects is different [15]. When the  $\text{Cl}^-$  concentration at certain defects goes below the critical value, corresponding to  $E_{\text{pit}}$ , as demonstrated in the left part of Fig. 1(c), the critical pitting potential would be higher than the applied potential. In this case, there is no onset of pit corrosion locally, which eventually leads to uneven pit distribution and low porosity as for whole surface.

As is generally accepted, the accumulation of corrosion product  $\text{AlCl}_3$  at pit bottom is a stabilizing factor for pit growth [16,17]. Existence of  $\text{AlCl}_3$  is the result of a high dissolution rate within the pit and the consequent acidification [16]. Mass transfer resistance increases with pit depth, making the ions in and out of pits difficult. The shortage of  $\text{Cl}^-$  results in less aggressive environment and lower concentration of  $\text{AlCl}_3$  at pit bottom. In this case,  $\text{H}_2\text{O}$  molecules can pass through the  $\text{AlCl}_3$  salt film quickly, and cause the reaction:  $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-}$ . The presence of  $\text{O}^{2-}$  competes with  $\text{Cl}^-$ , and reacts with the Al atom to form passivation film  $\text{Al}_2\text{O}_3$  at tunnel tip, making tunnel stop growing and reach to its limiting length [18–20], as illustrated in the left part of Fig. 1(d). In addition, when  $\text{AlCl}_3$  transfers from the bottom to mouth of pit, mass transfer resistance causes passivation film formation on pit mouth, leading to the decrease of effective pit size. Consequently, diffusion-limited  $\text{Cl}^-$  restrains pit propagation as well as the homogeneity of pit depth.

In general, strengthening the transfer of  $\text{Cl}^-$  and  $\text{AlCl}_3$  would effectively improve the porosity and the homogeneity of pit depth and size, thus to improve the specific surface area and capacitance performance of etching aluminum foil. In this work, the ultrasound was introduced in electrochemical DC etching. We aim to strengthen mass transport by ultrasonic agitation [21–24] to:

1) reduce the thickness of the diffusion layer  $\delta_{\text{D}}$ , as illustrated in the right part of Fig. 1(b), increase the  $\text{Cl}^-$  adsorption on

electrolyte/aluminum oxide film interface, and thus to improve the pit initiation;

- 2) increase the homogeneity of  $\text{Cl}^-$  at electrolyte/oxide interface by strengthening the flow disturbance in the vicinity of the aluminum foil, and then enhance the even distribution of pits on the whole foil surface, as demonstrated in the right part of Fig. 1(c);
- 3) reinforce the inward/outward migration of  $\text{Cl}^-$  and  $\text{AlCl}_3$  within tunnels, and then improve tunnel length and its homogeneity, as shown in the right part of Fig. 1(d).

## 2. Experimental

### 2.1. Material and etching specimen preparation

The aluminum foil specimen (Lot number L6031231-06-01, Ruyuan DongYangGuang UAC J Fine Foil Co., LTD, China) was 115  $\mu\text{m}$  thickness, 99.99 wt.% purity, fully annealed and its (100) cubic texture fraction was more than 95%. The main impurities of specimen were 55 ppm copper, 10 ppm silicon, 10 ppm iron and 1.5 ppm lead, where the impurity concentration was given in ppm by weight. The preparation processes of etching samples were as follows: the foils were cleaned by immersion in 1.0 M NaOH solution at 60 °C for 30 s, rinsed, and then pre-treated in boiled distilled water for 60 s, then cut into rectangular shape with a dimension of  $1.0 \times 2.0 \text{ cm}^2$ , subsequently, covered with an insulating tape except for a  $1.0 \times 1.0 \text{ cm}^2$  area left open for single-side etching, lastly transferred to the electrochemical cell, which placed in the ultrasonic bath (KQ-300VDE, power 300W, frequency 28 kHz and 45 kHz). Concretely, electrochemical etching was performed in a mixed solution of 1 M HCl and 3 M  $\text{H}_2\text{SO}_4$  with a constant current density of  $250 \text{ mA cm}^{-2}$  at 70 °C under different ultrasonic frequency for 120 s. Wherein, current density was applied by potentiostat/galvanostat (Instrument model DH1720A-6, Beijing Dahua Radio Instrument Factory, China), aluminum foil and platinum sheet were used as working electrode (WE) and counter electrode (CE) respectively.

### 2.2. Electrochemical test

The electrochemical cell, a mixed solution of 1 M HCl and 3 M  $\text{H}_2\text{SO}_4$  as electrolyte, was placed in the ultrasonic bath at constant 70 °C. A three-electrode system was used for electrochemical measurements. Wherein, as-prepared aluminum foil, platinum sheet and Ag/AgCl electrode were used as working electrode (WE), counter electrode (CE), and reference electrode (RE) respectively. From the CHI 660E electrochemical workstation, the chronopotentiometry was measured by a constant current density of  $250 \text{ mA cm}^{-2}$  for 300 ms, potentiodynamic polarization curve by sweeping the potential with a rate of  $10 \text{ mV s}^{-1}$ , and cyclic voltammetry curve at a scan rate of  $5 \text{ mV s}^{-1}$ . The electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 1.0 to  $10^5 \text{ Hz}$  at its open circuit potential with the Autolab-PGSTAT30. To investigate ultrasonic agitation effect intensively, all electrochemical tests conducted under 0, 28 and 45 kHz ultrasonic frequency respectively.

### 2.3. Samples characterization

The surface and tunnel morphology of etching foils were characterized by S-4800 II field emission scanning electron microscope (FESEM, Hitachi, Japan). To observe clearly, the surface of etching foils was electropolished by a DC voltage of 18 V in a mixed solution of 10 vol.%  $\text{HClO}_4$  and 90 vol.% ethanol at 0 °C for 12 s, where the platinum sheet and the etching foil were used as cathode and anode respectively. Furthermore, as for the sectional structure

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