



Research Article

Effects of temperature on electrochemical dissolution behavior of aluminum foil

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Abstract

Electrochemical dissolution behavior of aluminum foil in acid etchants was clearly investigated with different temperatures. Due to the electrochemical activation of temperature, the surface dissolution of aluminum foil in H_2SO_4 etchant slightly increased with the temperature. Even if NaCl was contained in the H_2SO_4 solution, the dissolution of aluminum surface and the value of E_{pit} were dependent on the temperature. The rising temperature decreased the resistance of pitting on aluminum foil surface, which enhancing the density and uniformity of the tunnel pits. The surface dissolution and tunnel etching behavior of aluminum foil was discussed by a schematic diagram.

Keywords Aluminum · SEM · Polarisation · Pitting corrosion

1 Introduction

Direct current (DC) tunnel pitting of (100)-oriented aluminum foil in chloride ion-containing solution has been usually used for enlargement of the specific surface area of aluminum foil used in high-voltage electrolytic capacitors [1–4]. A high density of tunnel pits can be generated on aluminum surface by using the DC etching [5–9]. Because the capacitance of the etched aluminum foil is primarily decided by the specific surface area, the distribution and size of the tunnel pits on etched aluminum surface must be generated uniformly to enhance the specific surface area [10–18]. The effects of concentration, components, and temperature on the etched tunnel pits have been well investigated [12, 19–23].

Electrochemical etching at temperature of 70–95 °C is currently carried out in chloride ion-containing solutions, such as NaCl and HCl [24]. The investigation of temperature on etched tunnel growth on aluminum foil surface has been studied significantly. Osawa and Fukuoka [3] investigated the effects of temperature on the tunnel shape

growth, and indicated that the time for etched tunnels to initiate decreased as temperature increases. At 70 °C, etched tunnels were first seen at about 250 ms. Alwitt et al. indicated that the steady state tunnel growth occurred at constant rate with activation energy of 15 kcal mol^{-1} , from 97 to 50 °C [19, 25]. Makino et al. also investigated the steady state tunnel growth at temperatures below 60 °C [12, 26]. However, the surface dissolution of aluminum foil in various etchant at different temperature was few investigated. Currently, the surface dissolution is synchronously occurred on aluminum surface and into the etched tunnels.

In this paper, DC etching of aluminum foil was carried out in etchants, and the evaluation of temperature on the electrochemical dissolution of etched aluminum foil was studied clearly.

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2 Experimental

In this work, aluminium foil (JOINWORLD,China) used was 99.99 wt% pure and 120 μm thickness. The foil was fully annealed so that the {100} cubicity texture fraction was above 95%. The aluminum foil was firstly handled in a solution of 1.5 M NaOH at 50 $^{\circ}\text{C}$ for 40 s. An electrochemical tank of three electrodes was used for the electrochemical testing of the as-received aluminum foil in 3.5 M H_2SO_4 solutions with or without NaCl at different temperature. The testing area of the as-received aluminum foil was 1 cm^2 by coating epoxy resin and transferred into etchant for etching. The working electrode (WE), counter electrode (CE) and reference electrode (RE) were performed by the aluminum foil, a Pt foil and a saturated calomel electrode (SCE), respectively [7]. A scanning rate of 15 mV s^{-1} was used to test the potentiodynamic polarization curve. And a current density of 200 mA cm^{-2} was used to test the initial potential transient. Electrochemical impedance spectroscopy (EIS) was tested in the various frequency.

The surface morphologies were observed by scanning electron microscope (SEM, JSM-6610A). To observe the etched tunnels easily, the etched specimens were electropolished using voltage of 18 V in solutions of 15 vol% HClO_4 and 85 vol% ethanol at 0 $^{\circ}\text{C}$ for 25 s. The density, size and uniformity of the tunnels on aluminum surface were analyzed clearly based on the images.

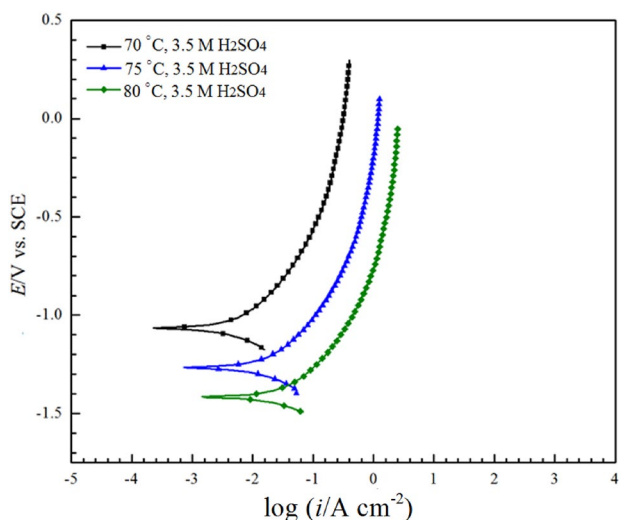


Fig. 1 Potentiodynamic polarization curves of aluminum foil etched in 3.5 M H_2SO_4 solution at different temperature

3 Results and discussion

3.1 Etching solution without NaCl

The potentiodynamic polarization of aluminum foil etched in 3.5 M H_2SO_4 solution at different temperature is shown in Fig. 1. In the positive region of potential, the current density slightly increased with the increasing solution temperature. Figure 2 shows the Nyquist plots of aluminum foil etched in the same condition. With the increasing solution temperature, the capacitance loop in Fig. 2 gradually becomes smaller. In order to evaluate the corrosion resistance of the etched aluminum foil, the impedance curves were studied using the fitting equivalent circuit, which is appeared in the inset of Fig. 2. It composed of the electrolyte resistance (R_s), the resistance of surface corrosion (R_{ct}) as well as a double layer capacitance (C_{dl}). The evaluated parameters based on the equivalent circuit model are given in Table 1. It can be expected from the parameters

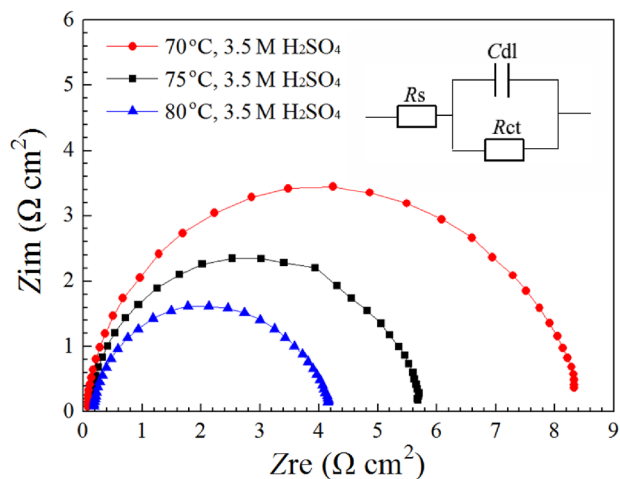


Fig. 2 Impedance spectra on Nyquist plot of aluminum foil etched in 3.5 M H_2SO_4 solution at different temperature. The inset shows the equivalent circuit

Table 1 Evaluated impedance parameters of the equivalent circuit model in Fig. 2

Specimen	R_s ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F cm}^{-2}$)	R_{ct} ($\Omega \text{ cm}^2$)
a	0.853 ± 0.012	430 ± 19	7.61 ± 0.05
b	0.658 ± 0.013	441 ± 16	5.45 ± 0.08
c	0.425 ± 0.009	455 ± 15	2.96 ± 0.03

Mean value and the standard deviation are listed in detail

a, b and c represent the specimens of aluminum foils etched in 3.5 M H_2SO_4 solutions at 70, 75 and 80 $^{\circ}\text{C}$

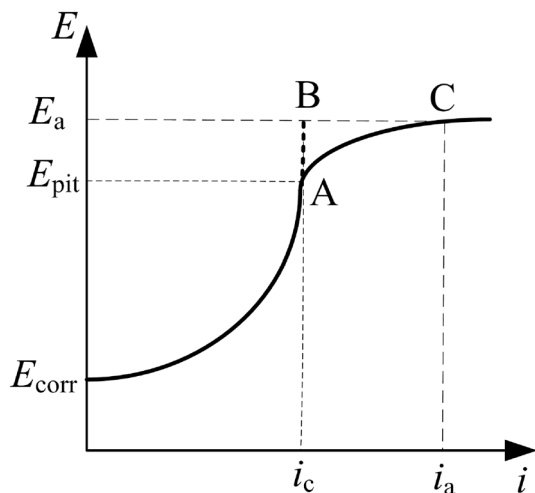


Fig. 3 The essential polarization curve of aluminum foil etched in Cl^- containing solution

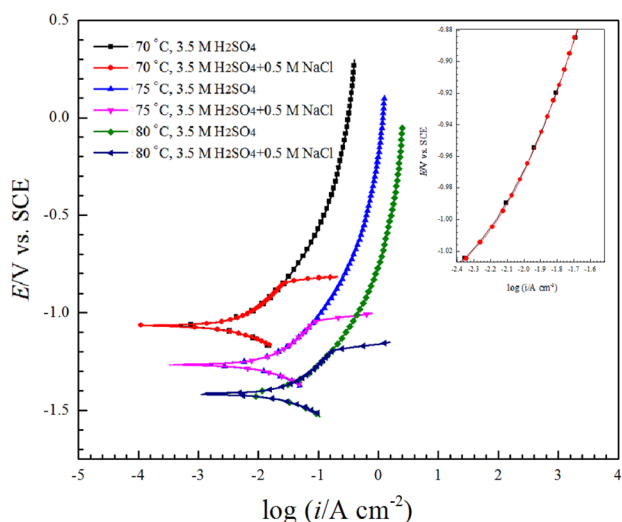


Fig. 4 Polarization curves of aluminum foil etched in 3.5 M H_2SO_4 solutions with or without 0.5 M NaCl at different temperature

that the value of R_{ct} slowly reduced with increasing solution temperature. It indicates that the increasing solution temperature enhance the uniform dissolution of the native oxide film.

3.2 Etching solution with NaCl

The essential polarization of etched aluminum foil in solutions of H_2SO_4 and NaCl is shown in Fig. 3. Tunnel pits of the aluminum surface were initiated as the potential gradually raised to the critical pitting potential (E_{pit}). Under E_{pit} , the maximum value of the current density (i_c) is decided by lengthening the curve to B point. The current density increased rapidly when pitting was initiated.

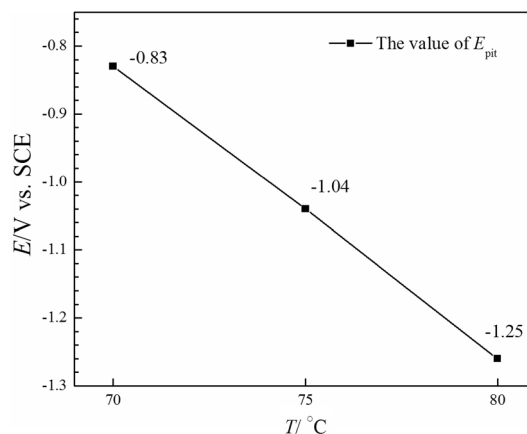


Fig. 5 Effect of solution temperature on the value of E_{pit}

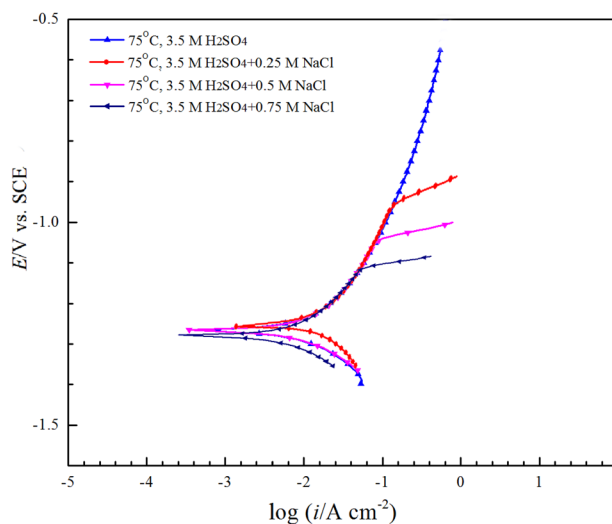


Fig. 6 Polarization curves of aluminum foil etched in 3.5 M $\text{H}_2\text{SO}_4 + n$ M NaCl ($n=0, 0.25, 0.5$ and 0.75) solutions at 75°C

In various solutions, the polarization curves of aluminum foil etched at different temperature is shown in Fig. 4. When the scanning potential is lower than the value of E_{pit} , the polarization curves tested in the solutions of 3.5 M $\text{H}_2\text{SO}_4 + 0.5$ M NaCl at different temperature were almost coincided with those tested in the H_2SO_4 solution without NaCl. This novel result implies that the surface dissolution was independent on the solution temperature even if etching were carried out in solutions contained NaCl. The added NaCl hardly affected the surface dissolution of etched aluminum foil. Besides, the increasing temperature made the value of E_{pit} gradually decreased, which indicates that the initiation of etched pits become easier. The evaluation of E_{pit} at different temperature was depicted in Fig. 5. The value of E_{pit} is reduced linearly with increased temperature. It indicates that the value of E_{pit} is

directly determined by the extent of surface dissolution of aluminum foil.

At 75 °C, the polarization curves of aluminum foil etched at different concentration of NaCl is shown in Fig. 6. Under the values of E_{pit} , the polarization curves

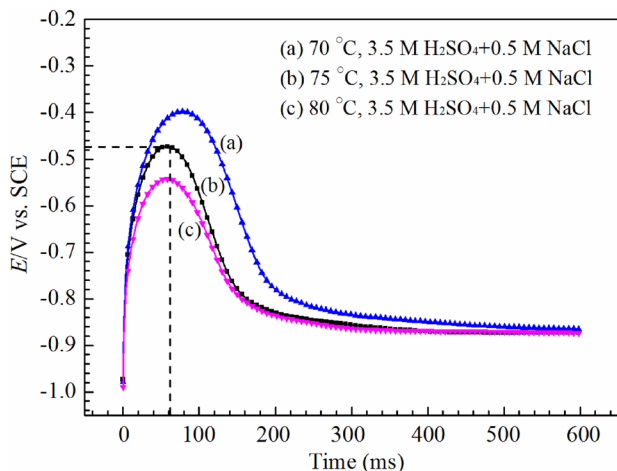


Fig. 7 Initial potential transients of aluminum foil etched in solutions of 3.5 M H₂SO₄ + 0.5 M NaCl at different temperature with an anodic current density of 210 mA cm⁻²

tested in the solutions of 3.5 M H₂SO₄ + n M NaCl (n = 0.25, 0.5 and 0.75) at 75 °C were also coincided with the curve tested in the 3.5 M H₂SO₄ solution without NaCl at 75 °C. This result implies that the surface dissolution was independent on the NaCl concentration. The added NaCl hardly affected the surface dissolution of etched aluminum foil. However, it is well known that the increased NaCl concentration can reduce the the value of E_{pit} .

The initial potential transient of etched aluminum foil in 3.5 M H₂SO₄ + 0.5 M NaCl solution at different temperature is shown in Fig. 7. The potential, induced by the ohmic drop and the electric double layer, rapidly increased from the initial potential. Then, due to the appearance of the film, the potential slightly rased to the maximum value (E_m). The duration of potential increase (τ_a) gradually decreased with increasing solution temperature. The breakdown potential of the native oxide film can be estimated by the maximum potential E_m [27, 28]. It can be seen that E_m and τ_a slowly reduced with increased solution temperature, which indicated that the native oxide film dissolved more intensively with temperature. The gradually decreased oxide film can expose more and more aluminum surface to pitting initiation.

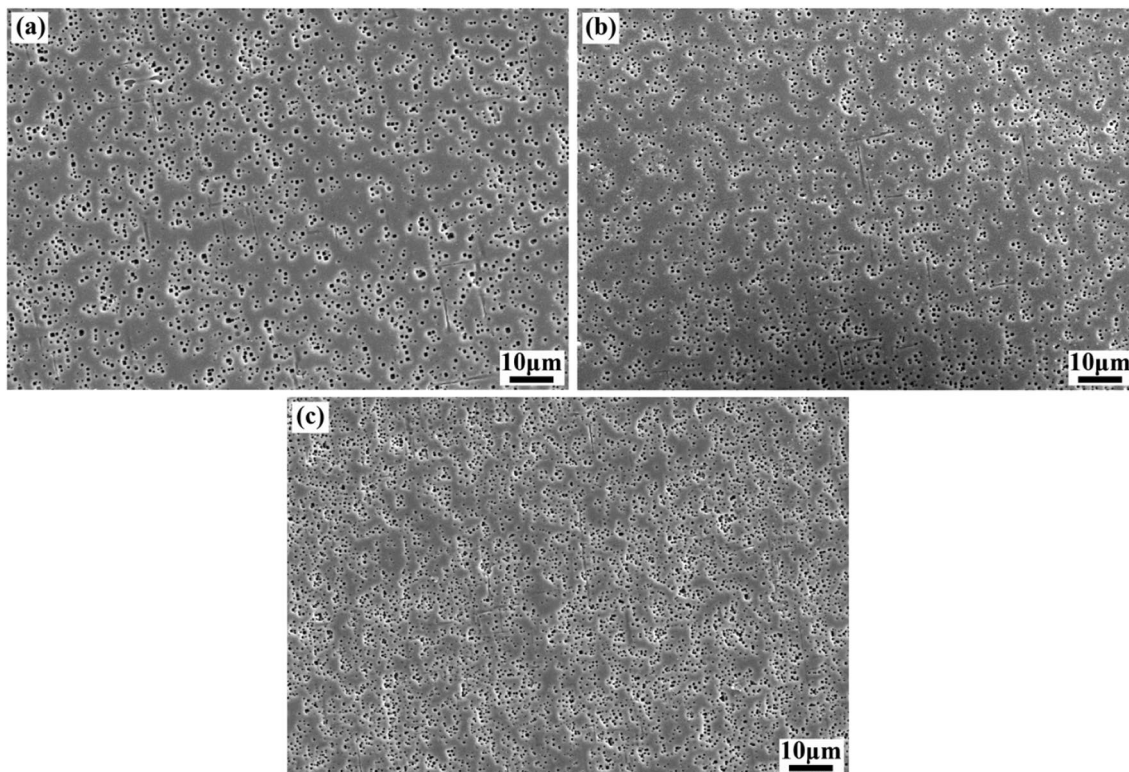


Fig. 8 SEM surface images of aluminum foil etched in 3.5 M H₂SO₄ + 0.5 M NaCl solution at different temperatures for 95 s: **a** 70 °C, **b** 75 °C and **c** 80 °C

3.3 Morphologies of etched aluminum foil

Figure 8 shows the scanning electron micrographs of etched aluminum surface in solutions of 3.5 M $H_2SO_4 + 0.5$ M NaCl at different temperature for 95 s. With the increasing solution temperature, the density of the etched tunnels gradually increased and the distribution of the etched tunnels slowly uniform. In order to evaluate the surface morphologies clearly, the statistics of etched tunnels were shown in Fig. 9. A normal distribution of the sizes of etched tunnels can be seen in Fig. 9. The average size and density of etched tunnels is 0.44 μm and $2.08 \times 10^7 \text{ cm}^{-2}$ for 70 $^\circ\text{C}$, and 0.41 μm and $2.61 \times 10^7 \text{ cm}^{-2}$ for 75 $^\circ\text{C}$, and 0.33 μm and $4.3 \times 10^8 \text{ cm}^{-2}$ for 80 $^\circ\text{C}$, respectively. The evaluated data for the etched aluminum foil at different temperature are listed in Table 2, where ρ_s is the corroded area per unit surface area. The above results imply that with the increasing solution temperature, the distribution and density of the etched tunnels will be

Table 2 Size distribution of the etch tunnels based on the statistical analysis of etch tunnels in Fig. 8

Sample	Average tunnel diameter ($d/\mu\text{m}$)	Average tunnel area ($s/\mu\text{m}^2$)	Tunnel density ($\rho/\times 10^7 \text{ cm}^{-2}$)	$\rho_s (\text{cm}^2 \text{ cm}^{-2})$
a	0.44 ± 0.01	0.19 ± 0.03	2.08 ± 0.1	0.39 ± 0.05
b	0.41 ± 0.02	0.17 ± 0.04	2.61 ± 0.3	0.45 ± 0.04
c	0.33 ± 0.04	0.11 ± 0.03	43.1 ± 0.9	0.48 ± 0.02

All the analysis was conducted by the Image-Pro Plus software. Mean value and the standard deviation are listed in detail

a, b and c represent the specimens of aluminum foils etched in 3.5 M $H_2SO_4 + 0.5$ M NaCl solutions at 70, 75 and 80 $^\circ\text{C}$, respectively

improved largely. Besides, the corroded area per unit surface area (ρ_s) is improved with increased solution temperature, implies that the enhanced specific capacitance.

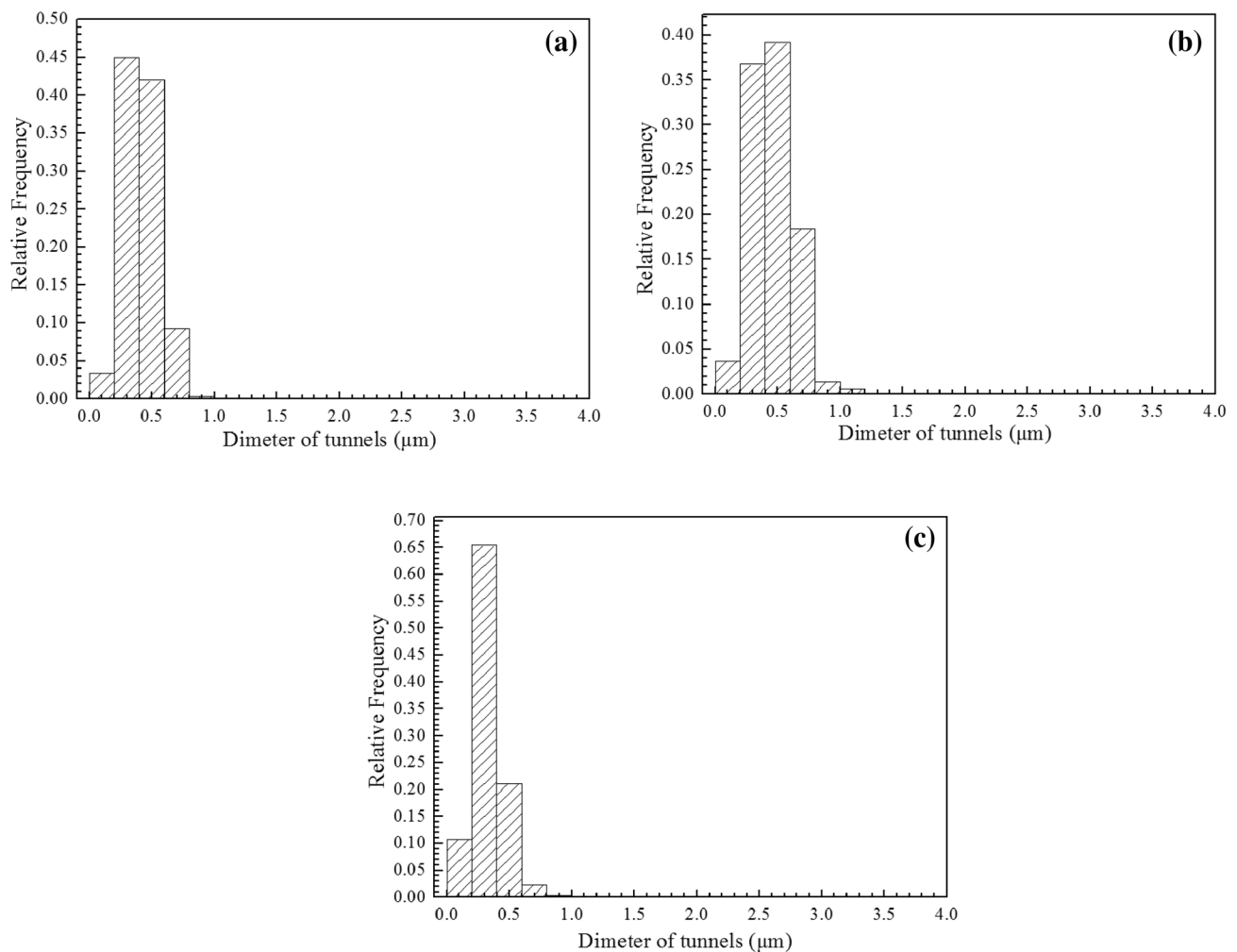


Fig. 9 Size distribution of etched tunnels based on the surface images of Fig. 7: **a** 70 $^\circ\text{C}$, **b** 75 $^\circ\text{C}$ and **c** 80 $^\circ\text{C}$

3.4 Interpretation of the etching processes

As shown in Fig. 10, based on the schematic diagram, the effect of solution temperature on the native oxide film and etched tunnels of aluminum foil were analyzed. To obtain high {100} cube texture which is necessary for tunnel etching of high-voltage aluminum foil, aluminum foil should be annealed at 500 °C for a long time. As shown in Fig. 10(a-1), (b-1), the annealed treatment will inevitably result in the formation of native oxide film on the aluminum foil surface. The surface dissolution etching depended mainly on the solution temperature and was hardly affected by the added NaCl, which has been proved by the polarization curves in Fig. 4. Because the increasing solution temperature promote the activity of ions, the dissolution of the native oxide film generated on aluminum surface is accelerated, which implies that a thinner oxide film is obtained, as shown in Fig. 10(b-2). So at high temperature, Cl⁻ can penetrate lightly to aluminum surface and initiate tunnel pitting. At last, the density and uniformity of the etched tunnels are improved significantly, as shown in Fig. 10(b-3).

4 Conclusions

Electrochemical dissolution of etched aluminum foil was carried out in solutions of 3.5 M H₂SO₄ solution with or without NaCl at different temperature. The effects of solution temperature on the dissolution behavior were studied clearly. The relevant conclusions were described as follows:

- (1) The solution temperature decided the surface dissolution of aluminum surface, and the added NaCl would not affect it. A surface of lower resistance could be generated with increasing temperature to improve the pitting initiation.
- (2) The size and uniformity of the etched tunnels on etched aluminum foil were improved obviously with increased solution temperature, which was helpful for enhancing the specific surface area.
- (3) A schematic diagram was proposed to evaluate the effect of solution temperature on the surface dissolution and dissolution behavior of aluminum foil.

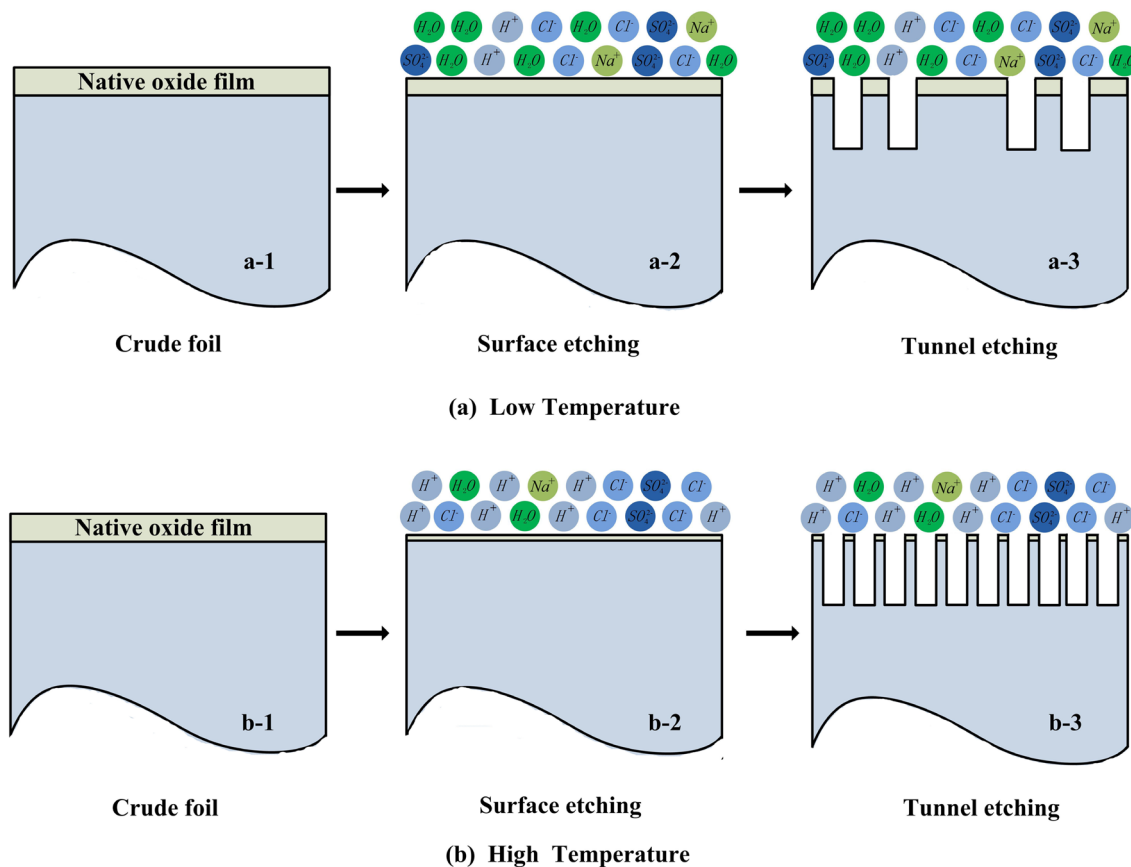


Fig. 10 Schemes of the etching process: **a** at the low temperature and **b** at the high temperature

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Compliance with ethical standards

Conflict of interest We have not any financial/commercial conflicts of interest.

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