

# 鋁箔電蝕時蝕孔衍生與腐蝕膜結構

吳恩育、林招松、李春穎

E-mail: 9224280@mail.dyu.edu.tw

## 摘要

本研究以電解模擬器，藉由精密訊號產生器與功率放大器輸出25Hz電流密度60A/dm<sup>2</sup>正弦波的交流電源，於鹽酸電解液中對鋁質電解電容器用鋁箔進行電化學腐蝕，同時量測電壓-電流關係。利用掃描式電子顯微鏡(scanning electron microscopy, SEM)觀察去除腐蝕膜前後之蝕孔表面形貌，並以橫截面穿透式電子顯微鏡(transmission electron microscopy, TEM)觀察蝕孔結構和腐蝕膜形貌與結構，並量測腐蝕膜重量和鋁箔溶蝕量。結果顯示當鹽酸濃度增加時，鋁箔表面發孔面積會減少，未受侵蝕區域面積因而增加，同時腐蝕膜重量與鋁溶蝕量減少。橫截面TEM觀察發現蝕孔形貌逐漸由扁方轉變成直方，即蝕孔衍生擴展方式由側向擴展轉為垂直深入鋁底材，同時覆蓋在鋁箔表面腐蝕膜厚度亦減少。電壓-電流曲線發現，隨著鹽酸濃度增加，孔蝕電位下降，而同時每個週期蝕孔溶蝕時間遞減，蝕孔誘發時間遞增。在較高鹽酸濃度下觀察的較長蝕孔誘發時間與較短溶蝕時間說明鋁箔表面有較多未受侵蝕面積與較小的鋁溶蝕量。電量曲線顯示，隨著鹽酸濃度增加，所得到的單一電量和累積電量會降低。在鹽酸中添加硫酸鈉後，發現硫酸根會抑制侵蝕初期的蝕孔產生，隨著硫酸根增加，直方形蝕孔的比例遞增。同時在0.8M鹽酸中添加硫酸鈉時，隨著硫酸根濃度增加，孔蝕電位升高，溶解時間減少，誘導時間增加。相反地，在3.2M鹽酸中添加硫酸鈉後，孔蝕電位、溶解時間與誘導時間的變化必不明顯。硫酸鈉濃度的增加，會促進每一個週期所得到的單一週期電量及累積電量增加。在0.8M鹽酸中添加2.4M氯化鈉電解液中鋁箔發孔型態和0.8M鹽酸中較為接近。同時腐蝕膜重量和鋁溶蝕量介於0.8M鹽酸和3.2M鹽酸中的結果。又孔蝕電位、溶蝕時間及誘導時間的結果與0.8M鹽酸中的結果較為接近。添加了氯化鈉會提升每個週期所得到的總電量。

關鍵詞：電解電容器，電蝕鋁箔，腐蝕膜，孔蝕電位，溶蝕時間

## 目錄

第一章 導論 .....	1 1.1前言 .....	1 1.2研究動機 .....
.....2 第二章 文獻回顧 .....	3 2.1鋁電解電容器之基本結構與原理 .....	
.....3 2.2增加電解電容器靜電容量之方法 .....	4 2.3鋁電解電容器中陰、陽極箔 .....	
.....4 2.3.1 陰極箔 .....	4 2.3.2 陽極箔 .....	
.....5 2.4.1 物理方法 .....	5 2.4.2 化學方法 .....	
.....6 2.4.3 電解腐蝕 .....	6 2.5 前處理對鋁箔電	
.....7 2.5.1 鹼洗 .....	7 2.5.2 酸洗 .....	
.....8 2.6 電蝕行為探討 .....	8 2.7 電化學方程式 .....	
.....9 2.8 鋁箔電蝕之進行機構 .....	9 2.9 交流電蝕之原理與機構 .....	
.....12 2.9.1 影響交流電蝕之因素 .....	12 2.10 直流電蝕之原理與機構 .....	
.....14 2.10.1 影響直流電蝕之因素 .....	15 2.11 鋁箔在含有氯離子溶液中的腐蝕型態 .....	
.....16 2.11.1 氯離子在鋁箔電蝕過程中的影響 .....	17 2.11.2 硫酸根離子在鋁箔電蝕過程中的影 響 .....	
.....18 第三章 實驗方法 .....	19 3.1 鋁底材的種類 .....	
.....19 3.2 電化學腐蝕設備 .....	19 3.2.1 電流-電壓-時間量測 .....	
.....21 3.3 電蝕操作條件與程序 .....	26 3.3.1 實驗製程規劃 .....	
.....26 3.3.2 電化學腐蝕操作程序 .....	30 3.4 微觀試片製備與觀察 .....	
.....32 3.4.1 掃描式電子顯微鏡試片製作與觀察 .....	32 3.4.1.1 鋁箔橫截面的觀察 .....	
.....32 3.4.2 穿透式電子顯微鏡試片製作與觀察 .....	32 3.5 重量變化量測 .....	
.....36 3.6 電流-電壓-時間量測 .....	36 第四章 結果與討論 .....	
.....37 4.1 鹽酸濃度的影響 .....	37 4.1.1 含腐蝕膜之鋁箔表面形貌 .....	
.....37 4.1.2 去腐蝕膜之表面形貌 .....	37 4.1.3 蝕孔橫截面TEM觀察 .....	
.....38 4.1.4 鋁箔溶蝕量與腐蝕膜重量 .....	39 4.1.5 動態電流電壓實驗 .....	
.....39 4.2 於鹽酸中添加硫酸鈉的影響 .....	41 4.2.1 含腐蝕膜之鋁箔表面形貌 .....	
.....41 4.2.2 去腐蝕膜之表面形貌 .....	41 4.2.3 蝏孔橫截面TEM觀察 .....	
.....42 4.2.4 動態電流電壓實驗 .....	42 4.3 純鹽酸中添加氯化鈉交流電蝕的 影響 .....	
.....45 4.3.1 含腐蝕膜之鋁箔表面形貌 .....	45 4.3.2 去腐蝕膜之表面形貌 .....	

.....46 4.3.3 蝕孔橫截面TEM觀察 .....	.....46 4.3.4 鋁箔溶蝕量與腐蝕膜重量
.....46 4.3.5 動態電流電壓實驗 .....	.....47 第五章 結論
.....115 第六章 展望.....	.....118 參考文獻
	.....119

## 參考文獻

- 楊邦朝,余忠,"低壓鋁箔交流腐蝕研究",電子元件與材料, Feb.1998, pp.9-12.
- 歐炳隆,朱俊悌,"電容器用電蝕鋁箔陰極箔研究",中國鋼鐵公司與國立中央大學建教合作期末報告,1997.
- 工業技術研究院技術簡介,固態/晶片型電容器製程,1998年6月
- 肖占文, "電容器鋁箔交流腐蝕擴面機理研究",電子科技大學,July 1999
- 涂肇嘉, "鋁箔電蝕反應之基礎研究及製程改進",行政院國家科學委員會專題研究計劃成果報告,1996.
- 黃志龍, "鋁電解電容器用低壓陽極箔電解腐蝕舉動之研究",中央大學機械工程研究所碩士論文,2000年6月
- 曾美貴, "鋁電解電容器用高壓陽極鋁箔電解腐蝕舉動之研究",中央大學機械工程研究所碩士論文,2000年6月
- C. S. Lin, C. C. Chang and S.H. Hsieh, "Pit Growth of 1050 Aluminum Plates Electrograined in A Nitric Acid ", J. Electrochem. Soc., Vol. 147, No. 10,pp.3647-3653.
- C. S. Lin, C. C. Chang and H. M. Fu, "A-C Electrograining of Aluminum Plates in A Hydrochloric Acid ", Materials chemistry and physics, Vol. 68, No. 1-3, pp. 217-224.
- C. S. Lin and H. M. Fu, "Etch Film and Pit Structure of AA1050 Aluminum Plates Electrograined in Nitric and Hydrochloric Acids", Journal of The Electrochemical Society , Vol. 148, No. 3, in press.
- C. S. Lin and H. M. Fu, 2001, "Effect of AC Current Waveform on the Electrograining of Aluminum Plates I: Etch Film and Pit Morphology; II: Pit Growth and Surface Properties" submitted to Journal of The Electrochemical Society.
- C. K. Dyer and R. S. Alwitt, "Surface Changes during A. C. Etching of Aluminum," J. Electrochem. Soc., Vol.128, No.2,1981, pp. 300-315.
- H. Matsubara , H. Ucki and A. Jamada, "Observation of Chemical Etching Morphology of Aluminum Foil,"表面技術, Vol.45, 1994 , pp. 114-115.
- E. Suganuma and Y. Tanno, "Duplex Structure of Surface Films Formed on Aluminum during AC Etching in Hydrochloric Acid Solution," 表面技術, Vol.41, 1990 , pp. 702-703.
- E. Suganuma , Y. Tanno , T. Ito , A. Funakoshi and K. Matsuki, "Surface Films Formed on Aluminum during AC Etching in Hydrochloric Acid Solution,"表面技術, Vol.41, 1990 , pp. 1049-1053.
- Y. Tanno and E. Suganuma , "TEM Observation of Surface Films Formed on Aluminum under AC Etching in Hydrochloric Acid," 金屬表面技術, Vol.38, 1987 , pp. 492-493.
- K. Fukuoka and M. Kurahashi, "Effect of Indium on the Etching Phenomena for High Purity Aluminum Foil , "住友輕金屬技報, Vol.34, 1993 , pp. 205-212.
- K. Fukuoka and M. Kurahashi, "Effect of Si -Precipitate on the Capacitor Cathode Foil , " 住友輕金屬技報, Vol.31, 1990 , pp. 238-245.
- H. Zhong and T. Oki, "The Effect of Hydrochloric Acid Concentration and Solution Temperature on the Characteristics of Al Foil during AC Etching under Potential Control," 表面技術, Vol.46, 1995 , pp. 270-275.
- E. Suganuma , Y. Tanno , I. Umetsu , A. Funakoshi and K. Matsuki , "Factors Affecting the Formation of a porous Layer during AC Etching of Aluminum in HCL solution,"表面技術, Vol.42, 1991, pp. 928-932.
- 鄭陽助,陳秉琨,游建財,鄭智和, "電解電容器用之鋁箔交流電蝕之研究," 大同學報, 15期, 1985年, pp.109-113.
- K. Vu Quang ,F. Brindel , G. Laslaz and R. Buttoudin, "Pitting Mechanism of Aluminum in Hydrochloric Acid under Alternating Current," J. Electrochem. Soc., Vol. 130, 1983 , pp.1248-1305.
- H. Zhong ,R. Ichins, M. Okids and T. Oki, "The Effect of Frequency on the Characteristics of Al Foil during AC Etching under Potential Control," 表面技術, Vol.46, 1995 , pp. 739-744.
- R. S. Alwitt , T. R. Beck and K. Hebert, "Electrochemical Tunnel Growth in Aluminum,"NACE-9 Advances in Localized Corrosion, 1987 ,pp. 145-152.
- W. Lin, G. C. Tu, C. F. Lin and Y. M. Peng, "The Effect of Lead Impurity on the DC-Etching Behavior of Aluminum Foil for Electrolytic Capacitor Usage," Corrosion, Vol.38, 1996, pp.889-907.
- W. Lin, G. C. Tu, C. F. Lin and Y. M. Peng, "The Effect of Indium Impurity on the DC-Etching Behavior of Aluminum Foil for Electrolytic Capacitor Usage," Corrosion, Vol.39, 1997, pp.1531-1543.
- N. Osawa, K. Fukuoka and Z. Tanobe, "Mechanism of Pit Nucleation of Aluminum Foil for Electrolytic Capacitors during Etching Stage of D.C. Etching," 住友輕金屬技報, Vol.33, 1992 , pp. 166-172.
- A. Hibino, T. Oki, "Etching Behavior of Aluminum Foil in Hydrochloric Acid under Potentiostatic Conduction," 住友輕金屬技報, Vol.34, 1993 , pp. 199-204.
- J. Flis and L. Kowalczyk, "Effect of Sulphate Anions on Tunnel Etching of Aluminum,"Journal of Applied Electrochemistry, Vol.25,1995,pp.501-507.
- A. Hibino, M. Tamaki, Y. Watanabe and T. Oki, "The Effect Sulfuric Acid on Tunnel Etching of Aluminum in Hydrochloric Acid," 輕金屬, Vol.42, 1992 , pp. 440-445.
- E. Makino, K. Takeda, T. Sato, E. Suganuma, T. Ito and Y. Tanno, "Direct Current Etching of Aluminum in NaCl/NaNO<sub>3</sub> Mixed Electrolytes," 金屬表面技術, Vol.37, 1986 , pp. 163-168.
- N. Osawa, K. Fukuoka and Z. Tanobe, "The Etching Behavior of Pit Initiation and Tunnel Growth of Aluminum Foil for Electrolytic Capacitors during Early Stage of D.C. Etching,"住友輕金屬技報, Vol.32, 1991 , pp. 124-131.
- H. Terryn, and J. Vereecken and G. E. Thompson, "AC Electrograining of Aluminum", Trans. IMF, Vol.66,1988, pp. 116-121.
- P.Laevers, H.Terryn, J. Vereecken and G. E. Thompson, "A Study of The Mechanism of A.C. Electrolytic Graining of Aluminum in Hydrochloric and Nitric Acid," Corrosion Science,Vol.35, Nos.1-4, 1993, pp. 231-238.
- H. Terryn, J. Vereecken and G. E. Thompson, "The Electrograining of Aluminum in Hydrochloric Acid-I. Morphological Appearance," Corrosion Science, Vol.32, No.11, 1991, pp. 1159-1172.
- Laevers, H. Terryn, and J. Vereecken, "Comparison of the A.C. Electrograining of Aluminum in Hydrochloric and Nitric Acid," Trans. IMF, Vol.70, No.3, 1992, pp. 105-110.
- G. E. Thompson and G. C. Wood, "The Effect of Alternating Voltage on Aluminum Electrodes in Hydrochloric Acid," Corrosion Science, Vol. 18, 1978, pp. 721-746.
- C. K. Dyer and R. S. Alwitt, "Surface Changes during A.C. Etching of Aluminum," J. Electrochem. Soc., Vol.128, No.2, 1981, pp.300-305.
- 鋁質電解電容器產業專題,詹文雄,李克誠.
- 吳昆祐, "鋁電解電容器用1000系陰極鋁箔之研究", 中央大學機械工程研究所碩士論文,2000年6月.
- 永田伊佐也,鋁箔乾式電解電容器.東京:川竹????????株式會社,1986.
- 王守緒,胡濤,楊邦朝等.低壓鋁箔腐蝕的齡喜工藝.電子元件與材料,1997,16(6),50.
- 世利修美, 田

實孝介. ???????????前處理???NaOH洗滌??\_?處理?檢討.金屬表面技術,1988,39(12),803. 44. 松木健三, 船越明, 管沼榮一, et al. 鹽酸溶液中??????????交流??????????前處理?影響. 金屬表面技術, 1986, 37(11), 655. 45. 火田知克. 電解????用陽極箔?製造方法. 特開平6-346260. 46. Wu X, Hebert K, et al. Development of surface impurity segregation during dissolution of aluminum. J Electrochem Soc, 1996,143(1),83. 47. Wu X, Asoka-kumar P, Lynn K G, et al. Detection of corrosion related defects in Aluminum using positron annihilation spectroscopy. J Electrochem Soc, 1994, 141(12), 3361. 48. 永田伊佐也, ?????乾式電解電容器, 日本蓄電器工業株式會社刊, chap.4, 171, (1985). 49. P. Laevers, H. Terryn, . Vereecken, B. Kernig and B. Grzemba, "The Influence of Manganese on The AC Electrolytic Graining of Aluminum,"Corrosion Science, Vol.38, No.3, 1996, pp.413-429. 50. H. Terryn, J. Vereecken and G. E. Thompson, "The Electrograining of Aluminum in Hydrochloric Acid-II. Formation of Eath Products,"Corrosion Science, Vol.32, No.11, 1991, pp. 1173-1188. 51. 日比野淳, 玉置充宏, 渡邊吉章, et al . ?????箔??????????及???硫酸影響. 輕金屬, 1992, 42(8), 440. 52. Wu T I, Wu J K. Effect of sulfate ions on corrosion inhibition of AA 7075 aluminum alloy in sodium chloride solution. Corrosion, 1995, 51(3), 185. 53. Flis J, Kowalczyk L. Effect of sulphate anions on tunnel etching of aluminum. J Appl Electrochem, 1995, 25(5),501. 54. M. S. Hunter, J. Electrochem. Soc. 117(1970)1215. 55. C. G. Dunn, R. B. Bolon, A. S. Alwan and A. W. Stirling, ibid. 118(1971)381. 56. C. E. Welch, Jr., US. Patent 3316164(1967). 57. M. T. Kosmyrina and K. P. Bartashov, Zhur. Prikl. Khimii 6(1975)1476. 58. N. A. Hampson, N. Jackson and B. N. Stirrup, Surf. Techol. 5(1977)277. 59. H. Leckie and H. Uhlig, J. Electrochem. Soc., V.113, 1262(1966).