



# Research & Reviews On

# Electrochemistry

Full Paper

RREC, 4(4), 2013 [117-120]

## Porous anodic alumina film formation in oxalic and phosphoric acid solutions and their photoluminescence properties

Naveen Kumar\*, Krishan Chander Singh, Hariom, Jitender  
 Department of Chemistry, Maharshi Dayanand University, Rohtak-124001, (INDIA)  
 E-mail : vermanaveen17@gmail.com

### ABSTRACT

The porous anodic alumina (PAA) film has been fabricated in oxalic acid, phosphoric acid solutions and as a sequence in both one after other. The photoluminescence (PL) and morphological properties were studied. The porous films were formed in both oxalic acid and phosphoric acid electrolytes and found to be more ordered array of pores of film formed in oxalic acid. The PL intensity of PAA membrane prepared in oxalic acid is much higher than that in phosphoric acid. The maxima of PL peaks reveal the presence of different luminescent centre in film formed in oxalic acid and phosphoric acid. The PL peaks were attributed to oxalic acid impurities incorporated and  $F^+$  centers in the film formed in oxalic acid. F centers were considered for the origin of PL in film formed in phosphoric acid.

© 2013 Trade Science Inc. - INDIA

### KEYWORDS

AAO membrane;  
 Phosphoric acid;  
 Oxalic acid etc.

### INTRODUCTION

Porous anodic alumina film is a very important and useful material in nanoscopic research<sup>[1-3]</sup>. The self organised regular cylindrical pores make it a good template for the fabrication of nanostructural materials such as carbon nanotubes<sup>[4]</sup>, Ni nanotubes and nanowires arrays<sup>[5-6]</sup>. The light emitting properties become an interest of investigation due to the application in optoelectronics studies<sup>[7-8]</sup>. Anodic oxide membrane can be used in optoelectronic devices such as photonics crystals, organic light emitting diodes<sup>[9-11]</sup>. These studies have importance for both scientific & technological purposes. The photoluminescence properties of AAO membrane help in elucidation of nature of nanosynthesized materials. Anodic oxide film on aluminium is long range hex-

agonal array of cells containing pores which were formed during anodization. The depth of these pores may be up to 90 micrometer with a very high aspect ratio and pore density ( $10^8 - 10^{12}$  pores/cm<sup>2</sup>). It is simple and inexpensive technology for the fabrication of nanomaterials.

In recent years large numbers of investigators have focussed their attention to study the photoluminescence properties of porous oxide film formed in various anodic electrolytes mainly in oxalic, sulphuric acid & phosphoric acid<sup>[12-13]</sup>. Little has been published on the AAO produced in phosphoric acid. Generally there are two opinions about the PL centre in organic acid like oxalic acid. First centre is related to the oxygen in vacancies [ $F$ ,  $F^+$ ,  $F^{++}$ ] formed during the formation of Anodic oxide film & second PL centre is attributed to the incor-

## Full Paper

porated oxalic acid impurities<sup>[14]</sup>. Most of the PL studies concluded that the luminescence centres are carboxyl groups that are embedded in the oxide film and oxygen vacancies formed during the anodization process. In this article we examine the morphological and PL properties of PAA film in oxalic and phosphoric acid solutions.

### EXPERIMENTAL

High purity (99.99%) aluminium foils were first mechanically polished with fine grade (400#, 600#, 1000#, 2000#) emery paper, degreased in acetone and etched in NaOH solution (100gm/litre) at about 60°C for 3 minutes and thoroughly rinsed in double distilled water. The samples were electro polished in mixtures of perchloric acid and ethyl alcohol (1: 4) at 15 V for three minutes. By the electro polishing the sample achieve smooth mirror finish. After the pre-treatment, aluminium foils were anodized under a constant voltage in acidic electrolytes to form AAO films (All samples are labelled). The sample a and b were anodized in oxalic acid (0.3M) and phosphoric acid (0.3M) respectively for 1 hours where the sample c was firstly anodized in oxalic acid (0.3M) for 30 minutes then anodized in phosphoric acid (0.3M) for 30 minutes. Now the anodization sequence was changed and the sample d was firstly anodized phosphoric acid (0.3M) and then in oxalic acid (0.3M) each for 30 minutes. The anodizing voltage was 40V for all samples. The temperature of the bath was maintained at 20°C.

The morphology of anodic alumina samples were characterized with SEM JEOL JSM6300. The PL spectral measurements were carried out on a spectrometer with He – Cd laser (325nm) as the light source. The emitted light was analyzed by HR-4000 cean Optics USB spectrometer optimized for the UV–VIS range. All spectra were recorded at room temperature.

### RESULT & DISCUSSION

The recorded current density characteristic for anodization in oxalic acid (Figure 1) shows that there is rapid drop of current density in the beginning indicates the growth of barrier layer, while the process of step increase in current corresponds to the pore nucleation

and formation and nearly exponential decrease to the pore elongation. In the case of H<sub>3</sub>PO<sub>4</sub> electrolyte (Figure 2), there is small current density in the process of pore nucleation and formation. In the initiation of pore formation and self organization the field assisted dissolution reaction results in spatially irregular tope arrays.

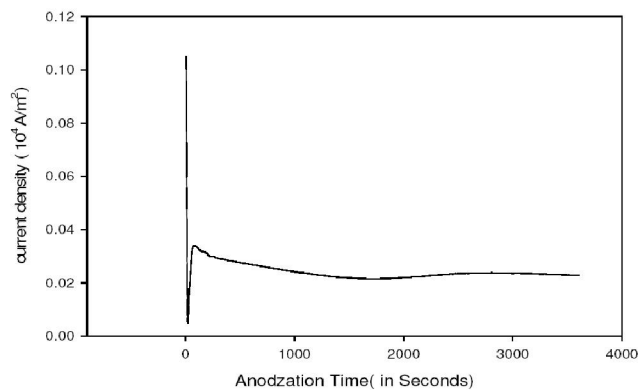


Figure 1 : Current time plot for anodization in oxalic acid

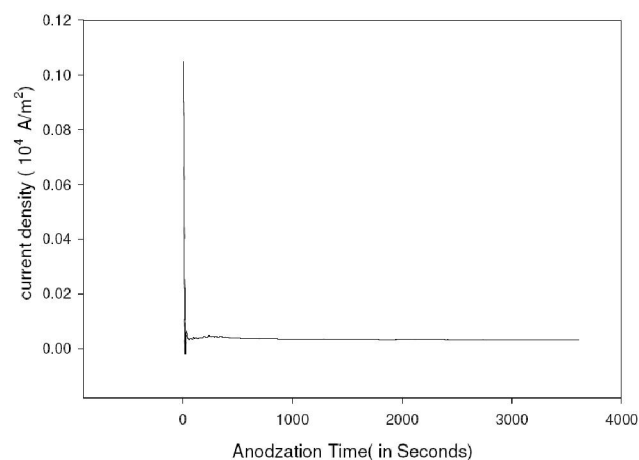
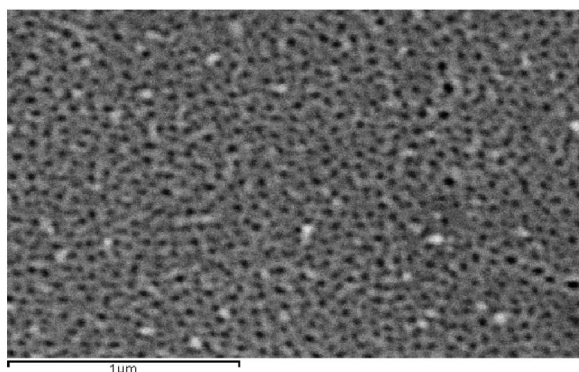


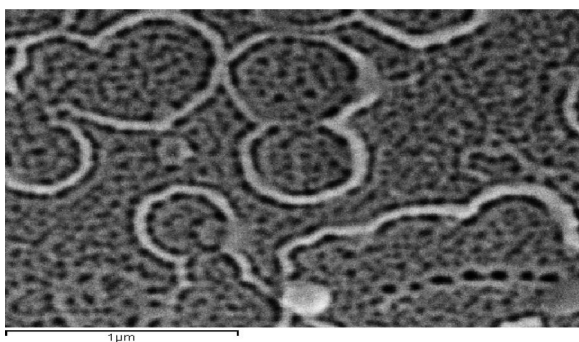
Figure 2 : Current time plot for anodization in phosphoric acid

Figure 3- 6 shows the surface morphology of AAO films. All the samples shows regular nanoporous array with different shapes structure. Figure 1 shows the porous film formed in oxalic acid. The film shows the cylindrical hexagonal pores with different pore diameter (30-50 nm) and interpore distance is about 80 nm. The film formed in phosphoric acid gives the porous structure but with irregular pores. The pore diameter and interpore distance is higher than that of film formed in oxalic acid. Figure 3 shows the morphology of film formed first in oxalic acid then in phosphoric acid. This anodizing sequence provides the regular array of pores with different shapes and decreases the irregularities due to adjoining of the pore wall in anodization of aluminium in pure phos-

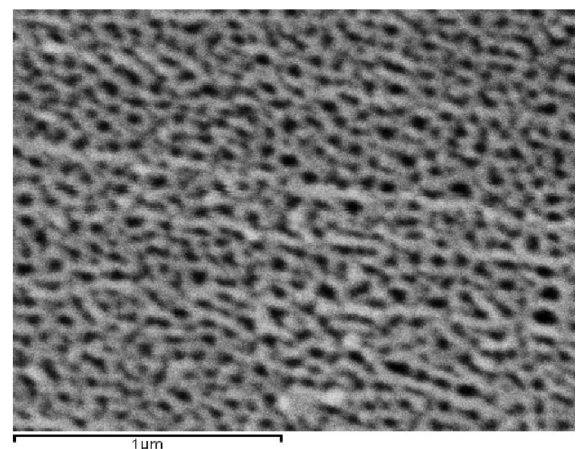
phoric acid. These pores are larger than pores formed in oxalic and in phosphoric acid. The sample d (film first formed in phosphoric and then in oxalic acid) shows the porous structure with pore diameter and interpore diameter almost similar to film formed in oxalic acid but less cylindrical. From SEM images it is revealed that film formed in oxalic acid have more symmetrical porous structure than in phosphoric acid.



**Figure 3 :** SEM image of AAO membrane anodized in 0.3 M oxalic acid at 40 V for 1 hour

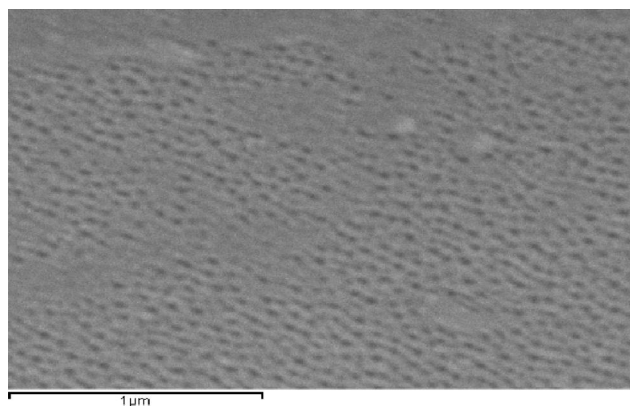


**Figure 4 :** SEM image of AAO membrane anodized in 0.3 M phosphoric Acid at 40 V for 1 hour

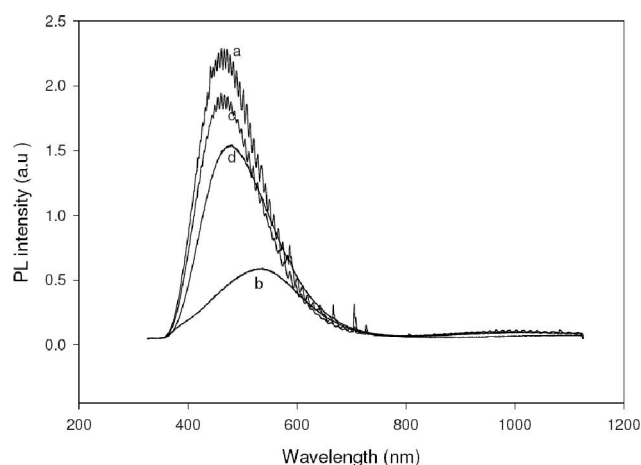


**Figure 5 :** SEM image of AAO membrane anodized first in 0.3 M oxalic acid then in phosphoric acid at 40 V for 30 minutes each

Photoluminescence spectra of samples (a-d) are shown in Figure 7. The PL spectra of sample a, c and d appears in the range of 360-540 nm. The maxima of peaks are at 460 nm (a), 470 nm (c) and 480 nm (d). The sample 'b' have weak intensity band at maxima, 530 nm.



**Figure 6 :** SEM image of AAO membrane anodized first in phosphoric acid (0.3) then in 0.3 M oxalic acid at 40 V for 30 minutes each



**Figure 7 :** The PL spectra of AAO (a) 0.3 M oxalic acid (b) phosphoric acid (c) firstly in oxalic acid then in phosphoric acid (d) firstly in phosphoric acid then in oxalic acid

The excitation wavelength was 325 nm. The result revealed that the anodizing sequence in phosphoric & oxalic acid has slight effect on the band maximum and intensities. The PL spectra results indicate that the PL is due to different type of luminescent centre present on film formed in oxalic acid and phosphoric acid electrolytes. The PL peak of film formed in phosphoric acid is produced at higher wave length having maxima at 530 nm. So that use of phosphoric acid in anodizing sequence shifts the PL band of film formed in oxalic acid towards higher wave length. The film formed in oxalic

## Full Paper

acid (sample a) has highest intensity. The intensities were decreases when the samples were anodized in sequence of oxalic and phosphoric acid (sample c and d). The PL band of film formed in phosphoric acid has very less intensity as compare to others. Though there are many studies concerting the luminescence mechanism of AAO membrane. In the anodization procedure there are two opposite process – film formation & film dissolution, oxygen ion transfer in the electrolyte & migrate through barrier layer under a high electric field by a vacancy mechanism. This indicates that many oxygen vacancies exist in PAA film. The F centres are produced due to partial oxygen vacancies. The luminescent centres exist in pore walls & barrier layers of PAA membranes. The blue PL of AAO membrane form in oxalic acid has been related with  $F^{15}$  centre &  $F^+$  centres<sup>[16]</sup> and surface hydroxyl group<sup>[17]</sup> showing a blue PL band around 460nm<sup>[18]</sup> proposed that the band around 470 nm is attributed to the transition in the  $F^+$  centres (oxygen vacancies with one electron). The electrolyte has a large influence in the light emitting property of alumina membrane. We have attributed the blue emission to  $F^+$  centers and oxalic ion impurities in case of film formed in oxalic acid and F center in film formed in phosphoric acid. Huang at al<sup>[18]</sup> explained the bands at higher wave length are due to F centers. Use of phosphoric acid in anodizing sequence shifts the peaks towards at higher wavelength. As shown in current voltage diagram the growth rate of pore nucleation in phosphoric acid is lower than as compare to oxalic acid thus lesser number of oxygen defect were created during anodization and therefore the PL peak of film formed in phosphoric acid is less intense.

### CONCLUSION

The film formed in oxalic acid has more symmetrical porous structure than film formed in phosphoric acid and sample anodized first in oxalic acid decrease the irregularities of film formed in phosphoric acid during anodization. The PL measurements shows there is different luminescent centers present in film formed in oxalic acid and phosphoric acid solution.

### ACKNOWLEDGEMENT

Naveen Kumar thanks the University grant com-

mission, Delhi, India for providing final assistance under UGC major research project 40-77/2011(SR) and Jitender thanks CSIR, New Delhi, India for the award of Junior Research Fellowship from the University Grant Commission, New Delhi as a major research project (40-77/2011 SR).

### REFERENCES

- [1] I.Liang, H.Chik, A.Yin, J.Xu; *J.Appl.Phys.*, **91**, 2544 (2002).
- [2] H.Masuda, M.Satoh; *Jpn.J.Appl.Phys.*, **35**, L126 (1996).
- [3] K.B.Jirage, J.C.Hulteen, C.R.Martin; *Science*, 655 (1997).
- [4] O.J.Lee, S.K.Hwang, S.H.Jeong, P.S.Lee, K.H.Lee; *Synth.Met.*, **148**, 263 (2005).
- [5] S.A.Knaack, J.Eddington, Q.Leonard, F.Cerrina, M.Onellion; *Appl.Phys.Lett.*, **84**, 3388 (2004).
- [6] X.J.Wu, F.Zhu, C.Mu, Y.Liang, L.Xu, Q.Chen, R.Chen, D.Xu; *Coord.Chem.Rev.*, **254**, 1135 (2010).
- [7] T.S.Shih, P.S.Wei, Y.S.Huang; *Surface and Coatings Technology*, **202**, 3298 (2008).
- [8] H.Zhuo, F.Peng, L.Lin, Y.Qu, F.Lai; *Thin Solid Films*, **519**, 2308 (2011).
- [9] Y.L.Shi, J.Wang, H.L.Li; *Appl.Phys.A*, **75**, 423 (2002).
- [10] M.Fang, Y.Wang, X.Peng, X.Liu, C.Zhen; *Materials Letters*, **57**, 4187 (2003).
- [11] O.Takayama, M.Cada; *Appl.Phys.Lett.*, **85**, 1311 (2004).
- [12] Y.Yamamoto, N.Baba, S.Tajima; *Nature*, **289**, 572 (1981).
- [13] J.Wang, C.W.Wang, S.Y.Li, F.Zhou; *Appl.Phys.A*, **94**, 939 (2009).
- [14] P.P.Pershukevich, D.V.Shabrov, V.P.Osipov, J.Schreiber, A.Lapina; *Journal of Applied Spectroscopy*, **78**, 524 (2011).
- [15] Y.Du, W.L.Cai, C.M.Mo, J.Chen, L.D.Zhang, X.G.Zhu; *Duy, Cai, Applied Phys Letter*, **74**, 2951 (1999).
- [16] G.S.Huang, X.L.Wu, Y.F.Mei, X.F.Shao, G.G.Siu; *J.Appl.Phys.*, **93**, 582 (2003).
- [17] G.S.Huang, X.L.Wu, G.G.Siu, P.K.Chu, G.S.huang; *Solid State Communications*, **137**, 621 (2006).
- [18] G.S.Huang, X.L.Wu, L.W.Yang, X.F.Shao, G.G.Siu, P.K.Chu; *Appl.Phys A*, **81**, 1345 (2005).