Self-Ordered Aluminum Anodizing in Phosphonoacetic Acid and Its Structural Coloration

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Ordered anodic porous alumina with large-scale periodicity was fabricated via phosphonoacetic acid anodizing. Aluminum specimens were anodized in a 0.1–0.9 M phosphonoacetic acid solution under various electrochemical operating conditions, and optimum anodizing at 205–225 V exhibited self-ordering growth of the porous alumina. These self-ordering voltages during phosphonoacetic acid anodizing filled an undiscovered vacant region in the linear relationship between the self-ordering voltage and the cell diameter. The nanostructured aluminum surface formed via self-ordering phosphonoacetic acid anodizing produced a bright structural coloration with a visible light wavelength of 500–700 nm, which is useful for optical nanoapplications.

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Anodizing time, \( t \)/ min

Current density, \( j \)/ Am\(^{-2}\)

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Current density, \( j \)/ Am\(^{-2}\)

The change in the current density, \( j \), with time, \( t \), during anodizing in a) 0.3 M, b) 0.1 M, and c) 0.9 M phosphonoacetic acid solutions at different applied voltages of \( U = 205–245 \) V. d) SEM image of the fracture cross-section of the specimen anodized at 225 V for 180 min.

the surface of the specimen. It was clear from these investigations that phosphonoacetic acid anodizing created an anodic porous alumina, and thus revealed that phosphonoacetic acid has the potential to be a new electrolyte for the fabrication of anodic porous alumina.

As the concentration decreased to 0.1 M (Fig. 1b), the maximum applied voltage without oxide burning increased to 240 V from 225 V. However, the current density was much lower than that obtained in 0.3 M phosphonoacetic acid, and thus it was expected that the growth rate of the porous alumina was much slower than that of 0.3 M phosphonoacetic acid. When the concentration increased to 0.9 M (Fig. 1c), the peak current density without oxide burning exhibited a relatively high value, although the maximum voltage without oxide burning decreased to 205 V in 0.9 M phosphonoacetic acid (Fig. 1c). From these electrochemical measurements, the following important behaviors could be summarized: a) the highest anodizing voltage without oxide burning decreased with increasing the phosphonoacetic acid concentration and b) the current density at the highest voltage increased with increasing the concentration. Therefore, the growth rate of the anodic oxide increased with the concentration.

The porous alumina anodized in the different conditions mentioned above was selectively dissolved in a \( \text{CrO}_3/\text{H}_3\text{PO}_4 \) solution for regularity analysis. Figures 2a–2c show the SEM images of the nanostructured aluminum surface anodized in a 0.3 M phosphonoacetic acid solution at 283 K and 210–225 V for 180 min. At 210 V, a disordered aluminum dimple array measuring approximately 530 nm in diameter was distributed on the aluminum surface. The regularity of the dimple array slightly improved with applied voltage, and a relatively well-ordered dimple array with a diameter of approximately 550 nm was observed on the aluminum anodized at the maximum voltage of 225 V (Fig. 2c). This improved behavior via maximum high-voltage anodizing without oxide burning can typically be observed during the self-ordering of porous alumina.\(^{29}\) Such self-ordering behavior is achieved by the highly viscous flow of the anodic oxide under high current density/growth rate conditions.\(^{22,33,34}\)

In a 0.1 M phosphonoacetic acid solution at 240 V (Fig. 2d), the size of the dimples slightly increased due to the high applied voltage; however, a disordered dimple array was observed on the aluminum surface. It was difficult to obtain ordered porous alumina via phosphonoacetic acid anodizing in such low concentration under whole anodizing conditions because of the low current density during anodizing. Conversely, the regularity of the dimple array improved as the concentration increased. An ordered aluminum dimple array of 500 nm in dimple diameter was obtained on the aluminum surface anodized in a 0.9 M phosphonoacetic acid solution at 205 V (Fig. 2e), although several defects and non-hexagonal dimples still remained in the arrangement. Through phosphonoacetic acid anodizing, a high solution concentration easily caused the formation of an ordered dimple array due to the high current density and highly viscous flow. Various constant voltage anodizing processes were explored at different solution temperatures from 273–323 K. As a result, it was found that the temperatures from 283–288 K were the most suitable conditions for ordered porous alumina fabrication during phosphonoacetic acid anodizing (Fig. 2f, cell diameter: 515 nm).
The nanostructured aluminum surface with honeycomb distribution obtained by phosphonoacetic acid anodizing exhibited the characteristic bright rainbow distribution under white light irradiation. Figure 3a shows the surface appearances of the nanostructured aluminum specimen via phosphonoacetic acid anodizing at 205 V and different viewing angles. The aluminum surface clearly exhibited bright structural colors including violet, aqua blue, light green, and red hues. Such structural coloration was generated by the interference from the periodically ordered aluminum dimple array with large-scale cell diameters. Therefore, it could be determined that the dimple array formed via phosphonoacetic acid anodizing has good regularity on the entire surface of the specimen. Figure 3b shows the changes in the reflection spectrum, $R$, from the nanostructured aluminum surface at different angles under white light irradiation. The selective color reflections were measured at approximately 500–700 nm. In particular, the lights were strongly reflected in the green and yellow wavelengths, which their wavelengths were similar to the intervals (i.e., cell diameter) of the ordered dimple arrays. The structural coloration based on the ordered dimple array could be employed in various optical applications and as the templates for optical devices.

The self-ordering voltage of the porous alumina, $U_s$, for the fabrication of highly ordered anodic porous alumina in various aqueous electrolyte solutions.

**References**