Advances of the research evolution on aluminum electrochemical anodic oxidation technology

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Abstract. This article gives an overview on the development of aluminum anodization technique in terms of fundamental aspects and practical applications in the past decades. Besides, the formation mechanism and structural characteristics of anodic alumina films as well as the factors affected the formation of porous anodic alumina films are also discussed. Anodic aluminum oxide (AAO) prepared by the anodization method can be divided into two categories: dense anodic alumina (DAA) and porous anodic alumina (PAA). This article also summarizes the optical properties, magnetic properties, solar absorption properties, and catalytic properties of porous anodic alumina film and its applications in nanomaterials, optical materials, magnetic materials, biosensors, solar cells, and so on. In addition, future developmental trend of porous anodic alumina film is covered.

1. Introduction
Aluminum is an active element. When aluminum is exposed to air, it oxidizes rapidly and forms a thin surface layer of oxide film with a thickness of 0.01-0.10 µm. However, this oxide layer is amorphous, thin, porous, and shows low mechanical strength. Although this layer can prevent further oxidation of the aluminum, it fails to fulfill the demands of aluminum and its alloys in terms of decoration, protection, and function in various applications. The anodization of aluminum in an electrolyte, first developed in the 1920s, offers a solution to this problem. Development of this process has led to widespread applications of anodized aluminum. This article reviews the preparation and processing methods of porous anodic alumina films. The formation mechanism of anodization is also examined, as it is essential to this process. Finally, the practical applications and the future development of porous anodic alumina films are discussed.

2. Characteristics and preparation of porous anodic alumina
Anodic aluminum oxide (AAO) prepared by the anodization method can be divided into two categories: dense anodic alumina (DAA) and porous anodic alumina (PAA). When aluminum is anodized in neutral electrolytes (boric acid, decanedioic acid, hexanedioic acid, etc.), a dense oxide film with a compact structure is formed. DAA is a good insulator and can be used in capacitors. When aluminum is anodized in acids or weak bases (phosphoric acid, sulfuric acid, oxalic acid, etc.), porous oxide film is formed because aluminum oxides are easily etched by the electrolytes. This type of film has unique structural characteristics as it is a thin and dense barrier layer formed on the aluminum surface. PAA has a packed array of columnar hexagonal cells with uniformly sized holes that are
perpendicular to the alumina surface and parallel to each other. Its structure is illustrated in figure 1 [1-5].

![Porous structure of aluminum oxide film.](image)

**Figure 1.** Porous structure of aluminum oxide film.

Studies of porous anodic alumina have identified several advantages: (1) barrier layer hardness that is higher than corundum; (2) good wear resistance, corrosion resistance, and chemical stability; (3) pore morphology and film thickness that are tunable by varying the electrolytic parameters; and (4) simple preparation without harsh reaction conditions or complicated experimental setups [3-8]. The following section will describe commonly used methods for preparing anodic oxide film in acidic electrolyte [2-19].

2.1. Sulfuric acid anodization
Films prepared with sulfuric acid anodization have the following characteristics: (1) thickness; (2) colorlessness; (3) high porosity (10-15% on average); (4) good absorption; (5) can be easily dyed; (6) high hardness; (7) high corrosion resistance; (8) high wear resistance; and (9) good colorability. Parameters affecting the film include the concentration of sulfuric acid, temperature, current density, oxidation duration, stirring, additives, and the composition of aluminum alloys. The advantages of this method are (1) simple and easy operation; (2) simple effluent handling; (3) low energy consumption; (4) low cost; (5) short oxidation duration; and (6) high production efficiency.

2.2. Chromic acid anodization
Chromic acid anodization produces films of inferior quality compared to films prepared with sulfuric acid. They are relatively thin (5-20 µm) and soft, with low porosity and high corrosion resistance. However, the films have low wear resistivity. They are less suitable for dyeing due to their gray color. These films offer good adhesion to organic coatings and can be used as the base for coatings, but the chromic acid anodization process requires high-energy consumption.

3. Oxalic acid anodization
Films prepared by oxalic acid anodization are relatively thick. They can be yellow or white, with color that darkens with increasing film thickness. They feature low porosity, high corrosion resistance, high wear resistance, and good insulation. However, the high-energy consumption of the anodizing process and the need for cooling lead to high cost. In addition, the electrolyte has low chemical stability.

Researchers have developed two-step anodization as an improvement on anodization using acid electrolytes to produce alumina with arrays of ordered pores over large areas. In 1995, Masuda et al [14] demonstrated two-step anodization to prepare a PAA template. First, aluminum was sonicated in a mixture of acetone, ethanol, and distilled water to remove impurities from the surface. Then, a mixture of ethanol and perchloric acid in a volume ratio of 4:1 was used as the electrolyte for electropolishing before the first anodization. After anodization, the formed oxide layer was removed using a mixture of chromic acid and phosphoric acid under certain temperature conditions. Subsequently, a second anodization was carried out to obtain an ordered PAA template.
This discovery has had a significant impact on the preparation and applications of PAA. Fan et al [2,15] fabricated porous anodic aluminum oxide (AAO) on glass substrates using electrochemical oxidation and subsequent etching. The pore depth was controlled by electrochemical anodization and/or chemical etching time.

Two-step anodization has become the most commonly used method of preparing PAA. Li et al [16] successfully prepared highly ordered PAA film in oxalic acid electrolyte by modifying the two-step anodization method developed by Masuda. Later, Li et al [17] prepared a PAA template with cell diameters of 77 and 96 nm using oxidation voltages of 40 and 50 V in a \( \text{H}_2\text{SO}_4\)-\( \text{Al}_2\text{(SO}_4)_3\)-\( \text{H}_2\text{O} \) electrolyte system. In addition, Dou et al [18] successfully synthesized an ordered PAA template with nanopores using two-step anodization in oxalic acid electrolyte. Highly ordered PAA templates with larger pore diameter were demonstrated by Gao et al [19] using oxidation under constant current density. These recent improvements to the anodization process have further advanced its potential.

3.1. Hard stamping anodization

Masuda et al [20-22] developed hard stamping anodization based on the concept of acid dissolution of alumina to induce porous structure. In this method, a SiC mold with ordered arrays of convexes is pressed onto the aluminum surface using an oil press to generate the corresponding array of concaves on the surface of aluminum. This step is followed by a conventional anodization process to obtain an ordered PAA template, as shown in figure 2.

![Figure 2](image)

**Figure 2.** SEM images of polymer fiber arrays prepared by nanoimprinting using anodic porous alumina.

3.2. Y-shaped, tube-in-tube, bone-shaped, and parallel channels in PAA templates

Prior research has demonstrated that pore density is inversely proportional to the square of the anodizing voltage. Using this concept, Gao et al successfully obtained Y-shaped branched channels in PAA films by reducing the anodizing voltage in each step by \( (V/2)^{1/2} \), as illustrated in figure 3. The discovery of one-dimensional Y-shaped nanostructures played a critical role in the development of electrical transport in nano-circuits [23,24].

Lee et al [24] prepared PAA film with a specific pore diameter and further anodized the film into a coaxial tube-in-tube structure with different inner and outer diameters under the same reaction conditions, as illustrated in figure 4.

![Figure 3](image)

**Figure 3.** Y-junction copper nanowires.

![Figure 4](image)

**Figure 4.** The linearly joined tubes with different diameters.

![Figure 5](image)

**Figure 5.** SEM micrographs of the bone-shaped PAA film cross-section.
Xu et al [25] obtained PAA film with bone-shaped pores using a four-step anodization. The first three anodization steps were conducted in 0.3 mol/L oxalic acid under a constant current of 40 V and for oxidation times of 5 h, 5 min, and 40 min, respectively. The last step was conducted in 0.04 mol/L oxalic acid at a temperature of 17°C, under constant current of 80 V, and for an oxidation time of 3 min. The bone-shaped pores are illustrated in figure 5.

PAA film with ordered nano-channels parallel to the base was synthesized by Costel et al [26] under low voltage (3 ~ 5 V). The length of the ordered channels was more than several hundred nanometers and the smallest pore diameter was about 3 ~ 4 nm.

3.3. Radial, triangle/diamond-shaped PAA template

Lee et al [26,27] used hard and mild anodization methods to prepare PAA templates with long channels and tunable pore diameters, as illustrated in figure 6. Ruy et al [28] employed a reoxidation method to anodize Al wires to prepare PAA templates with radial morphology, as illustrated in figure 7. The diameters of the Al wires were maintained within the range of millimeters or micrometers to ensure the intactness of the hexagonal columnar arrays of the PAA templates.

**Figure 6.** SEM micrographs of AAO membranes formed by MA for 2 h (left column) and by HA for 2 h (right column).

**Figure 7.** Radial morphology of the two-step anodization method.

**Figure 8.** FESEM images of diamond and hybrid triangle-diamond patterns (All scale bars are 500 nm).

Smith et al [29] made use of the non-equilibrium dynamics present during the growth of PAA and the tessellation effects during cellular formation to prepare extended, uniform, and partially
compressed hexagonal columnar structure, giving rise to the formation of diamond-shaped, spherical, and triangular pores, as illustrated in figure 8.

3.4. Zigzag-shaped PAA templates with conical channels

Lee et al [26,30] used pulsed anodization to prepare aluminum oxide nano-channels with tunable pore diameter, as illustrated in figure 9. The advantage of this method is that the electrolyte does not need to be changed because the nano-channels and the pore diameter are tuned by the pulse voltage and anodizing duration.

![Figure 9. Modulation of pore diameter.](image)

![Figure 10. Cross-sectional SEM images of PAA substrates with conical holes with different aspect ratios.](image)

Yusuke et al [31] prepared conical pores with inverted honeycomb structure and different aspect ratios, as illustrated in figure 10. The authors also proposed the concept of oriented growth to explain the important role of surface structure of PAA templates in the perpendicular growth of channels.

Losic et al [32] reported a new anodization process, termed cyclic anodization to achieve improved control over internal pore shape, as shown in figure 11. By changing the period of the current oscillation, control over the geometry of pore structures was achieved and AAO with asymmetrical (ratchet-type) and symmetrical (circular) periodic pore geometries, with different lengths, periodicity and gradients were fabricated [33]. Similarly, AAO membranes with conical holes were observed by Yamauchi et al [31]. The conical holes were achieved by repeating and alternating anodization at 40 V and chemical etching with 5% phosphoric acid solution at 30°C.

![Figure 11. (a)-structural modulation of AAO; (b)-Modulated AAO pores.](image)

4. Mechanism of anodization

Anodic aluminum oxidation is an electrochemical process during which an external current passes through an electrolyte, in which aluminum serving as an anode is connected to the positive electrode of an external power supply and a cathode is connected to the negative electrode. The formation and dissolution of oxide film occur simultaneously during anodization but the dominating process is
determined by their reaction rates. The formation mechanism of anodic alumina film is complicated and has not yet been fully understood. Based on the ion migration phenomenon observed during the oxide film formation in chromic acid, phosphoric acid, and oxalic acid, several models have been proposed to explain the reaction mechanisms of anodic alumina.

4.1. Critical current density model
In the 1970s, O’Sullivan and Wood [34] studied the morphology and formation mechanism of PAA. They proposed that the mechanism was associated with the formation and dissolution of anodic alumina under an electric field. In the 1980s, Xu et al proposed the critical current density model by investigating the ion migration phenomenon during the growth process of anodic alumina film. The authors also explained the formation mechanism of oxide films at the film/electrolyte interface using a dissolution-precipitation theory. The experiment showed that aluminum and oxygen ions migrated through the oxide film in opposite directions during the formation of anodic alumina film. The fraction of aluminum ions migrating in the same electrolyte remained constant. There is a critical current density in this model. A compact barrier layer was formed when the applied current density was greater than the critical current density, causing the aluminum ions to form new film material at the film/electrolyte interface. On the contrary, a loosely packed porous layer was formed when the current density was lower than the critical current density. In this case, aluminum ions migrated towards the electrolyte, leading to the formation of oxide film at the film/electrolyte interface. This theory, which describes the possible formation of porous anodic alumina in acidic and neutral electrolyte as well as the concept of barrier anodic film, challenges the conventional views on film morphology and electrolytes used for anodization.

4.2. Volume expansion stress model
In 1992, Shimizu et al [35] studied the structure of anodic alumina and proposed that the barrier layer was formed as the result of simultaneous inward migration of O\(^{2-}\) and outward migration of Al\(^{3+}\). At this layer, O\(^{2-}\) filled up the vacant space after outward migration of Al\(^{3+}\) and formed Al\(_2\)O\(_3\). The volume of newly formed Al\(_2\)O\(_3\) was smaller than the volume of outward migrated Al\(^{3+}\). As the oxidation reaction proceeded, the total volume of the aluminum foil decreased as the oxide layer continued to form, following the mechanism that involved the inward migration of O\(^{2-}\) and outward migration of Al\(^{3+}\).

Tensile stress was formed when the volume of aluminum oxide film was reduced, leading to the formation of cracks in the oxide surface. In addition, temperature increased as the current density concentrated at the cracked areas, causing the existing cracks to close up. Repeated cracking and closing of the oxide surface eventually led to the formation of pores and the porous layer. These were the conditions of pore and layer formation in the volume expansion stress model.

In 1998, Jessensky et al used the anodization method to prepare porous oxide film with uniform hexagonal arrays and proposed the volume expansion stress model [36]. This model qualitatively analyzed the effects of self-assembly in the growth process of ordered pores and explained the formation mechanism of porous layers, as shown in figure 12. The results showed that highly ordered arrays of hexagonal pore structures were formed in oxalic acid or sulfuric acid electrolyte while the pore diameter was dependent on the anodizing voltage. The volumetric loss caused by the outward migration of Al\(^{3+}\) was offset by the inward migration of O\(^{2-}\), leading to the formation of a barrier layer. The volume of the newly formed oxide layer was smaller than the volume of aluminum being consumed. Thus, the total volume became smaller and induced tensile stress in the surface. As the tensile stress continued to build, cracks formed in the barrier layer. As the current density was concentrated at the cracked areas, the temperature of those areas became high enough to cause volume expansion, closing up the existing cracks. Repeated cracking and crack closure led to the formation of pores and porous layers. Self-assembled pores in compact hexagonal arrays resulted in the lowest free energy. Conversely, because the spherical pore had the smallest surface area, it yielded the most stable structure.
4.3. Field-assisted dissolution model
In 1978, Thompson et al [37] proposed an acid-assisted dissolution model, which is also known as the field-assisted dissolution model. As illustrated in figure 13, the anodization process can be divided into three stages: the formation of the barrier layer, the formation of pores, and the dynamic equilibrium in dissolution. Experimental results showed that the anodization process required a dynamic equilibrium between the growth and dissolution of oxide film in an acidic electrolyte. A compact barrier layer was formed on the surface of aluminum when external voltage was applied, but this newly formed barrier layer was partially dissolved in acidic electrolyte. Pore nuclei started to form at the active sites on the film surface when the thickness of the barrier layer exceeded the critical value. As a result, the electric field was concentrated at the base of these areas. Rising temperature caused by increasing current at the base of the affected areas accelerated their dissolution rates. The final porous layer was formed when the pore nuclei continued to grow in a vertical direction. The barrier layer at the interface with the aluminum base was formed by the inward migration of $O^{2-}$ and $OH^-$ ions after passing through the film and by the outward migration of $Al^{3+}$ ions under the influence of the electric field. The porous layer started to grow steadily when dynamic equilibrium was reached between the growth and dissolution of film, as illustrated in figure 13.

4.4. Quasi-static mathematical model of field distribution within the film
In a study reported by Xu et al [38,39], several assumptions related to the quasi-static field were made to explain the formation mechanism of porous layers. The author assumed that the geometrical and charge distributions at the film/electrolyte and film/aluminum interfaces varied over time during anodization. At the same time, changes at the interfaces could be rapidly re-distributed. Based on these assumptions, the term “quasi-static field” was used to refer to the two static fields in the film that possessed equipotential surfaces. Therefore, the strength of electric fields in the film and the potential of pore formation at different stages could be calculated using the finite element method. Experimental results showed that the field distribution in the film was non-uniform during the growth of the porous layer. In addition, the electric field played a critical role in the growth of pores: the pores grew along the field that possessed the highest intensity. The porous layer was formed when the anodizing current was lower than the critical value. The growth of pores went through a series of stages that included uniform dissolution, formation of pore nuclei, competition in pore development, expansion of pore diameter, and formation of a curved shape at the base of the pores, followed by steady growth.

4.5. Dynamics model of functional integrity
Patermarakis et al [40] studied the dynamics model of the functional integrity of PAA film in sulfuric acid electrolyte under a constant current condition. Experimental results showed that the transference numbers of $Al^{3+}$ and $O^{2-}$ ions at the metal/oxide interfaces were determined by the current density and temperature. The transference numbers of ions increased with the current density but dropped when
the temperature was increased. These phenomena were associated with the density of the oxides at the metal/oxide interfaces and the oxidation conditions. Generally, aluminum was partly converted into unstable oxides, while its remaining part was converted into amorphous $\gamma$-Al$_2$O$_3$. This process that occurred at the oxide/electrolyte interfaces led to the porous layer formation.

4.6. Oxygen bubble mold effect model

In 1995, Palibroda et al [41,42] proposed that the formation of the porous layer could be divided into three stages by observing the anodization of aluminum under an electron microscope. The breakdown of the barrier layer under a high current condition played a crucial role in the growth rate of the porous layer. Electron avalanche breakdown resulted in the generation and release of oxygen gas, leading to pore formation. This concept differed from the acid-assisted dissolution theory.

Based on the Wood model and the electron avalanche breakdown theory, Zhu et al [43] proposed the oxygen bubble mold effect model after many years of effort, as illustrated in figure 13. The authors found that oxygen was released during the anodization of aluminum and the morphology of the oxide film was determined by the amount of oxygen. The Wood model proposed that the inner walls of pores were contaminated by electrolyte species, while Zhu et al proposed that the outermost layer of the oxide film was contaminated by electrolyte species. The contaminated layer in each model is illustrated in figure 14(a). The contaminated layer was caused by the growth and dissolution of the oxide layer. At the beginning of the reaction, cations passed through the oxide layer to enter the electrolyte while the anions passed through the electrolyte to enter the oxide layer. During these processes, the accumulation of anions and cations at the boundary of the oxide layer leads to the formation of a contaminated layer. Unlike the acid-assisted dissolution theory, the oxygen bubble mold effect model proposed that the pore formation was attributed to the evolution of oxygen gas, as illustrated in figure 14(b). Pores that connected to the electrolyte formed during the evolution of oxygen gas. As illustrated in figure 14(a), three interfaces were involved in the preparation of oxide film: the electrolyte/contaminated layer, the contaminated layer/barrier layer, and the barrier layer/aluminum interfaces.

![Figure 14](image_url)

(a) Formation of contaminated layer
(b) Hole formation

**Figure 14.** Oxygen bubble mold effect growth model of porous template.

5. Factors affecting the formation of oxide film

Several reaction parameters in the oxidation process determine the properties and structure of oxide films. Previous experiments have established a close correlation between the structural properties of anodic alumina (e.g., pore diameter, distance between neighboring pores, pore density, thickness of oxide film, and crystallinity of oxide film) and the preparation conditions. Therefore, the structural properties of the AAO template can be tuned by the preparation conditions. Numerous factors affect the formation of oxide films, including anodizing voltage (or anodizing current), electrolyte type, electrolyte concentration, oxidation temperature, and oxidation duration.
5.1. Effect of oxygen evolution on the formation of the porous layer
Zhu et al [44, 46] studied the anodization process in three different electrolytes (ammonium dihydrogen phosphate solution, hexanediamine-boric acid-ethylene glycol solution, and monosubstituted phosphate-ethylene glycol solution). They proposed that oxygen evolution on the aluminum surface affected the formation of the porous layer. This was the reason that a barrier layer of oxide film can be eventually converted into a porous layer. Experimental results showed that the porous layer could still be formed without prior dissolution of the barrier layer in the same electrolyte. In addition, the formations of oxide film precursors and pores were attributed to oxygen evolution.

Wang et al [47] studied the anodization of hard aluminum alloys. Experimental results showed that a large amount of bubbles formed during oxide film formation; this phenomenon changed the current distribution on the surface of the oxide film, leading to a lower heat transfer rate between the electrolyte and the reaction surface. Furthermore, bubbles covering the surface of oxide film increased the local temperature, accelerating the electrochemical dissolution of oxide film. Hence, pores tended to be generated at those areas covered with bubbles.

5.2. Effect of anodizing current (or anodizing voltage) on the formation of PAA
There is a linear relationship connecting the distance between neighboring pores and the oxidizing voltage at which the oxide film reaches a stable stage, given that the electrolyte type and concentration are held constantly [45,46]. Several studies showed that an AAO template could only be successfully prepared when the oxidizing voltage (or current density) was controlled within a certain range [41–47]. The reaction was difficult to produce when the oxidizing voltage was too low. On the contrary, when the oxidizing voltage was too high, the dissolution rate of aluminum was higher than its formation rate. Therefore, a highly ordered template could only be achieved by controlling the oxidizing voltage within a certain range. Other studies showed that oxidizing voltage had a linear relationship with both the pore diameter and the distance between neighboring pores [44–48].

Vrublevskya et al [48] studied the effects of current density on the volume expansion of the PAA layer. Experimental results showed that the electrolyte concentration did not affect the volume expansion coefficient of the PAA layer under a constant current density condition. The volume expansion coefficient increased when the temperature of the electrolyte was decreased or when the current density was increased. The relationship between the volume expansion coefficient (K) of the PAA layer and the anodizing voltage (U) could be expressed as follows: \( K = 1.092 + 0.007U \). Therefore, there was a linear relationship between the logarithm of current density and the volume expansion coefficient of the PAA layer. Montero-Moreno et al [49] studied self-assembled anodization under a constant current condition. The authors used two-step anodization to prepare high-quality oxide film and compared it with oxide film prepared under a constant current condition. Experimental results showed that the thickness of oxide film increased when the current density was increased. Additionally, when the current density was increased, the fraction of alumina with crystalline phase decreased while the fraction of alumina with amorphous phase increased.

Formation of oxide film is a competition between growth and dissolution processes. High current density can cause the temperature to rise and accelerate the dissolution of the oxide film. Under this circumstance, the dissolution rate is higher than the growth rate of oxide film, affecting the formation of film. Therefore, there is a threshold current density. When the current density is lower than the threshold value, the growth process of oxide film is slow, leading to a decrease in film thickness. In some cases, the film may not even be generated under such a condition.

5.3. Effect of the composition of electrolyte
The composition of electrolyte, including concentration and type, affects the properties of the oxide film. Generally, different types of electrolytes contain different types of anions when other reaction conditions remain constant. Experimental results showed that the properties of oxide film (color, thickness, and orderliness) were affected by the type of anion. For example, electrolytes such as sulfuric acid, chromic acid, and oxalic acid solutions showed good dissolving power. Therefore, the
porous layer of anodic oxide film formed under this condition was relatively thick and the barrier layer was relatively thin. On the contrary, the oxide film was almost covered by the barrier layer when a boric acid electrolyte with less dissolving power was used.

Liu et al [50,51] studied the morphology and structure of oxide films prepared by anodizing aluminum in acidic electrolytes, such as sulfuric acid, oxalic acid, and chromic acid solutions. Experimental results showed that the electrolytes could be sorted by pore diameter in the following descending order: chromic acid > oxalic acid > sulfuric acid. However, the porosity was sorted in the opposite order. Additionally, oxide film prepared in different electrolytes varied widely in adhesive force and compactness. In 2003, Ono and Masuda [52] discovered the effect of electrolyte type on the distance between neighboring pores. Under the same reaction conditions, the electrolytes could be sorted by distance between neighboring pores in the following descending order: phosphoric acid > chromic acid > oxalic acid > sulfuric acid. Anodic alumina prepared in different electrolytes could be used for different applications best suited to their characteristics.

In 2008, Yang et al [52-55] found that the current density had a significant increment when a mixture of sulfuric acid and oxalic acid in a 1:1 ratio was used as the anodizing electrolyte. Under this condition, a thin barrier layer could be formed. If the anodizing voltage was further reduced, the pore diameter of the alumina film grew larger.

5.4. Effect of oxidation duration
The oxidation duration determines the thickness and compactness of the oxide film. Under longer oxidation duration, the film becomes thicker and more compact and shows higher corrosion resistance. However, heat released during the oxidation process accelerates the dissolution rate of the oxide film if the reaction duration is too long. As a result, the oxide film grows thicker in the initial stage, but eventually the growth process is retarded due to the dissolution process. In addition, long reaction duration affects the surface morphology of the film, reduces its smoothness, and hinders the binding behavior between the film and the base. More severely, a dusting phenomenon occurs, causing a significant drop in corrosive and wear resistances. Therefore, oxidation duration must be controlled in order to prepare an oxide film with the desired properties.

5.5. Effect of electrolyte concentration and temperature
Ion transfer rate is mainly affected by the electrolyte temperature. Consequently, the dissolution, formation, and heat transfer rates of oxide film are also affected by the electrolyte temperature. Therefore, electrolyte temperature is an important parameter in controlling the structure and distance between neighboring pores of oxide film. Under certain reaction conditions, the dissolution rate of oxide film increases when the electrolyte temperature is increased, causing the film to be thinner. Oxide film cannot be formed when the temperature is too high. On the contrary, the film thickness increases when the electrolyte temperature is decreased, producing oxide film with higher compactness and corrosive resistance. However, the duration required to prepare oxide film with the desired thickness becomes extremely long when the electrolyte temperature is too low. This is not suitable for mass production because the production efficiency is low and the energy consumption is high. Oxide film with different structures and properties can be obtained under different conditions and reaction parameters.

The intensity of the oxidation reaction is affected by the degree of erosion of the electrolyte, while the degree of erosion is affected by the concentration and temperature of the electrolyte. If the electrolyte concentration is too low, no oxidation reaction can be initiated; therefore, oxide film cannot be formed. An electrolyte concentration that is too high also inhibits the formation of oxide film because the dissolution rate is greater than the growth rate of the oxide film. Therefore, the electrolyte concentration must be controlled within an optimal range during the preparation of anodic alumina to ensure successful formation of pores. Zaraska et al [55] conducted anodization of aluminum using phosphoric acid solution and high anodizing voltage. Experimental results showed a regular pattern in current density under different concentrations of phosphoric acid: the current density decreased rapidly
in the beginning of the reaction, followed by a subsequent increase before reaching a stable stage. This pattern was generally followed during the preparation of AAO film. The current density increased when the concentration of phosphoric acid was increased, requiring less time to reach the stable stage. The thickness of the barrier layer and the distance between neighboring pores increased as well. Xu et al [56-58] conducted the anodization of aluminum under different concentrations of phosphoric acid. They found that the distance between neighboring pores decreased when the concentration of phosphoric acid increased, but the increment was small. In summary, the distance between neighboring pores was affected by the electrolyte concentration, but different electrolytes could have different degrees of influence on the distance between neighboring pores.

Experimental results showed an initial increase followed by a decrease in pore diameter and the distance between neighboring pores when the temperature was increased. In an experiment conducted at high temperature, the distance between neighboring pores of the AAO film was larger than that obtained at low temperature. The distance between neighboring pores was even smaller when the oxidation temperature was set at zero. This was attributed to the greater influence of temperature on the dissolution of film than on the growth of film. The temperature used for anodization should be controlled because high temperature may reduce the orderliness of pores and the composition of the oxide film.

6. Application of alumina film

Based on previous investigations and understanding of the microstructures and properties of anodic alumina, future prospects of PAA film are focused on two areas: (1) utilization of its porous structure to develop new membranes for precise separation [54,55], and (2) development of new materials by depositing foreign substances such as metals, semiconductors, and polymeric materials into the nanopores of PAA film.

6.1. Nano-template application

Nanotechnology has emerged as a popular, advancing technology, with numerous studies investigating nanomaterials. Owing to the unique properties of nanomaterials, they have been widely used in various fields, including electronics components, medical equipment, and material synthesis. Highly ordered porous oxide film can be achieved through a simple anodization of aluminum foil. Moreover, the pore diameter of the oxide film can be tailored by changing the preparation conditions and parameters. Nanomaterials with various sizes and shapes can be prepared using this porous alumina film as the template. As a result, porous aluminum oxide film is used in the synthesis of nanostructured array systems with a variety of morphologies, such as nano-columns, nano-wires, and nano-dots.

6.2. Optical and optoelectronic applications

The current era is dominated by information technology (IT). The transmission and display of optoelectronic information is the central technology of the growing optoelectronic information science industry. The unique functions of PAA film make it a promising material for use in research and development of optoelectronic materials. In addition, nano-sized porous film prepared by the anodic oxidation method can be applied to the development and preparation of ultrafine optoelectronic material. Furthermore, luminescent films and photosensitive films used for imaging can be achieved by introducing fluorescent and photosensitive materials into PAA film. For example, fluorescent film that can emit green light can be achieved by introducing Tb3+ onto the oxide film. Through deposition of certain metals onto porous aluminum oxide film, new optical and optoelectronic properties can be achieved in the creation of optical phase plates, polarization plates, and other optoelectronic devices. Tang et al [58] prepared Cu/Al2O3 composites using the deposition method. Experimental results showed that the Cu composites induced a redshift in spectrum and exhibited better optical performance compared with single-phase porous aluminum oxide film.

In order to effectively utilize solar energy, materials should have high absorption coefficients in the
visible range of the solar emission spectrum, but low emission rates in the range of the thermal emission spectrum. For example, functional film that can selectively absorb solar energy can be prepared by electrodepositing Ni on nanoporous aluminum oxide film in a phosphoric acid solution. The selective absorption characteristic of these films can be measured using reflectance.

6.3. **Catalytic applications**

Catalysis is useful for enhancing reaction efficiency, reducing energy consumption, and providing good selectivity and recyclability. Two commonly used catalysts are molecular sieve and ion exchange resins. However, these two types of catalysts show relatively low catalytic efficiency and are unstable at high temperatures, limiting further development of the technology. Aluminum substrate has good thermal conductivity. Owing to the unique structure of porous aluminum oxide film, it shows a good processability and its properties can be easily modified. In addition, the porous aluminum oxide film has a large inner surface area. Therefore, it can be used to develop functional film with good thermal conductivity and high catalytic efficiency. The Al₂O₃/TiO₂ functional thin films fabricated by Zhang et al. [59] showed good photocatalytic properties and improved the catalytic efficiency of traditional porous aluminum oxide film.

6.4. **Magnetic applications**

Functional films with magnetic properties can be obtained by filling the pores of the ordered porous aluminum oxide film with magnetic metal or alloy materials. The obtained functional films can be further processed into a variety of magnetic products, such as tapes, disks, and magnetoresistance devices. Studies have shown that during the crystallization of magnetic metal located in the pores of PAA film, the orientation of the magnetic material was consistent with the direction of the magnetic axis, improving the retentivity and vertical magnetism of the functional film. Such films are commonly used as vertical magnetic recording media and magnetoresistance devices. Deng et al. [60] fabricated highly ordered CoPt nanotube by introducing metallic magnetic material into the pores of the aluminum oxide film through an electrochemical method. Investigation with various characterization techniques (TEM, SEM, XRD, and VSM) showed that the CoPt nanotubes had good magnetic storage performance.

6.5. **Separation membranes**

Separation membranes have a wide range of applications, including wastewater treatment, ion separation, and biomedicine. By controlling the conditions of anodization in the production of porous aluminum oxide film, different thicknesses and sizes can be obtained, in addition to highly ordered pores. The film is a new material for separation membranes because it is selective and can be used to separate molecules with different sizes. Aluminum oxide film has several advantages over the conventional polymer membrane, such as good chemical stability, strong corrosion resistance, good thermal conductivity, and good recyclability. It can be used as a separation membrane for gas, liquid, and blood at room temperature. Furthermore, it can be used for gas separation at high temperatures in processes such as desulfurization and deoxygenation of flue gases.

El-Safty et al. [61] used anodized aluminum oxide film as a separation membrane for sewage purification treatment. Experimental results showed that the removal rate of solid particles greater than 0.1 µm was close to 100%. The removal rates of BOD₅ and CODCr reached 83% and 67%, respectively. After the anodized aluminum oxide film was used, the sewage turbidity dropped about 40° and the treated water became colorless. The used oxide film was easily washed without significant silting and was reusable. Additional uses of porous aluminum oxide film include wear- and corrosion-resistant materials, hard materials, and lubricants.

7. **Future prospects**

With its ordered porous structure, aluminum oxide film has potential as an effective material in a wide range of applications with high commercial value. Over the past several years, significant progress has
been made with regards to structural engineering and surface fiction of nanoporous AAO material. Access to these structures is achieved by changing anodization conditions such as current, voltage and type of electrolytes during electrochemically self-ordering of AAO. However, the mechanism of pore formation is still not fully understood. In addition, there is still a need for further investigation of PAA and development of better PAA films. The preparation process should be optimized to reduce cost and increase efficiency. The physical and chemical properties of the PAA template should be investigated, and the parameters more finely adjusted.

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**References**

[1] Ren Y, Ma Z and Bruce P G 2012 *Chem. Soc. Rev.* 41(14) 4909-27
[2] Fan Q H, Galipeau D, Ghimire B, Gupta R K, Dubey M and Mandal N 2014 *J. Coat. Sci. Technol.* 1 69-77
[3] Martin C R 1996 *Chem. Mater.* 8(8) 1739-46
[4] Yanagishita T, Nishio K and Masuda H 2005 *Adv. Mater.* 17(18) 2241-3
[5] Colombo P 2008 *Science* 322(5900) 381-3
[6] Thompson G E and Wood G C 1981 *Nature* 290 230-2
[7] Bennett S P, Menon L and Heiman 2008 *J. Appl. Phys.* 104 024309
[8] Poordt P, Lankhorst A, Roozeboom F, Spee K, Maas D and Vermeer A 2010 *Adv Mater.* 22(32) 3564-7
[9] Li A P, Muller F, Birner A, Nielsch K and Gosele U 1999 *J. Vac. Sci. Technol.* 17(4) 1428-31
[10] Nielsch K, Choi J, Schwirn K, Wehrspohn R B and Gosele U 2002 *Nano Lett.* 2(7) 677-80
[11] Jani A M M, Losic D and Voelcker N H 2013 *Prog. Mater. Sci.* 58(5) 636-704
[12] Keller F, Hunter M S and Robinson D L 1953 *J. Electrochem. Soc.* 100(9) 411-9
[13] Thompson G E, Furnaux R C, Wood G C, Richardson J A and Goode J S 1978 *Nature* 272 433-5
[14] Masuda H and Fukuda F 1995 *Science* 268(5216) 1466-8
[15] Hu Z, Shrestha M and Fan Q H 2016 *Thin Solid Films* 598 131-40
[16] Li F Y, Zhang L and Metzger R M 1998 *Chem. Mater.* 10 2470-80
[17] Li Y, Ling Z Y, Chen S S and Wang J C 2008 *Nanotechnology* 19(22) 225604-9
[18] Dou W H, Xu Q M and Zhao H L 2007 *Dept. Appl. Mater.* 22(8) 49-53
[19] Gao Y B, Peng Z, Song G J, Yong-Wei M A and She X L 2007 *Mater. Rev.* 21(7) 136-8
[20] Yanagishita T and Masuda H 2015 *Mater. Lett.* 160 235-7
[21] Li J, Papadopoulos C and Xu J 1999 *Nature* 402 253-5
[22] Gao T, Meng G, Zhang J, Sun S and Zhang L 2002 *Appl. Phys. A* 74(3) 403-6
[23] Tian Y H, Meng G W, Gao T, Sun S H, Xie T, Peng X S, Ye C H and Zhang L D 2003 *Nanotechnology* 15(1) 189-91
[24] Lee J S, Gu G H, Kim H, Jeong K S, Bae J and Suh J S 2001 *Chem. Mater.* 13(7) 2387-91
[25] Xu T T, Fisher F T, Brinson L C and Ruoff R S 2003 *Nano. Lett.* 3(8) 1135-9
[26] Cojocaru C S, Padovani J M, Wade T, Mandoli C, Jaskierowicz G, Wegrowe J E, Fontcuberta Morral A and Pribat D 2005 *Nano. Lett.* 5(4) 675-80
[27] Lee W, Ji R, Gösele U and Nielsch K 2006 *Nat. Mater.* 5 741-7
[28] Sanz R, Hernández-Vélez M, Pirotka K R, Baldonedo J L and Vázquez M 2007 *Small* 3(3) 434-7
[29] Smith J T, Hang Q L, Franklin A D, Janes T D and Sands T D 2008 *Appl. Phys. Lett.* 93 043108-12
[30] Lee W, Schwirn K, Steinhart M, Pippel E, Schol R and Gösele U 2008 *Nat. Nanotechnol.* 3 234-9
[31] Yamauchi Y, Nagaura T, Ishikawa A, Chikyow T and Inoue S 2008 *J. Am. Chem. Soc.* 130...
10165-71
[32] Losic D, Lillo M and Jr L D 2009 Small 5(12) 1392-7
[33] Jani A M M, Losic D and Voelcker N H 2013 Prog. Mater. Sci. 58(5) 636-704
[34] O’Sullivan J P and Wood G C 1970 Proc. R. Soc. Lond. 317(1531) 511-43
[35] Shimizu K, Kobuyashi K, Thompson G E and Wood G C 1992 Philos. Mag. A 66(4) 643-7
[36] Jessensky O, Muller F and Gösele U 1998 Appl. Phys. Lett. 72(10) 1173-5
[37] Thompson G E, Furneaux R C and Wood G C 1978 Nature 272(565) 433-5
[38] Xu Y, Thompson G E and Wood G C 1989 J. Chin. Soc. Corr. Pro. 9(1) 1-10
[39] Xu D S, Chen D P, Xu Y J, Shi X S, Guo G L, Gui L L and Tang Y Q 2000 Pure Appl. Chem. 72 127-35
[40] Palibroda E 1995 Electrochim. Acta 40(8) 1051-5
[41] Palibroda E, Farcas T and Lupsan A 1995 Mat. Sci. Eng. B 32(1-2) 1-5
[42] Zhu X F, Liu L, Song Y, Jia H B, Yu H D, Xiao X M and Yang X L 2008 Monatsh. Chem.-Chem. Month. 139(9) 999-1003
[43] Zhu X F, Han H, Song Y, Ma H T, Qi W X, Chao L and Chen X 2012 Acta Phys. Sin. 61(22) 228202-7
[44] Cao G B, Zhu W, Li J R and Li Z X 2014 Mater. Rev. 28 153-9
[45] Zhu X F, Li D D and Meng D W 2006 J. Nanjing Univ. Sci. Tech. 30(5) 644-8
[46] Wang P and Wei X W 2005 Surf. Tech. 34(6) 28-32
[47] Vrublevsky I, Parkoun V, Schreckenbach J and Mark G 2003 Appl. Surf. Sci. 220 51-9
[48] Montero-Moreno J M, Sarret M and Müller C 2010 Micropor. Mesopor. Mat. 136 68-74
[49] Liu F X and Xia Z C 1994 Mater. Prot. 27(1) 19-22
[50] Yang P X, Zhang X M and An M Z 2008 Electroplat. Pollut. Control 28(4) 28-30
[51] Ono S, Saito M and Asah H 2005 Electrochim. Acta 51(5) 827-33
[52] Michalska-Domańska M, Norek M, Stepniowski W J and Budner B 2013 Electrochim. Acta 105 424-32
[53] Hussain T, Shah A T, Shehzad K, Mujahid A, Farooqi Z H, Raza M H, Ahmed M N and Nisa Z U 2015 Int. Nano Lett. 5 37-41
[54] Zaraska L, Jaskula M and Sulka G D 2016 Mater. Lett. 171 315-8
[55] Zaraska L, Brudzińska A, Wierzbia J and Sulka G D 2016 Electrochim. Acta 198 259-67
[56] Xu Y F, Liu H, Li X J, Kang W M, Cheng B W and Li X J 2015 Mater. Lett. 151 79-81
[57] Tang H J, Wu F Q, Wang H L, Wei Y H and Li Q S 2006 J. Appl. Phys. 100(6) 064316-22
[58] Zhang X Y, Chen T Q and Wang C Y 2005 J. South China Univ. of Techno. (Nat. Sci. Ed.) 33(9) 67-72
[59] Deng C H, Qiao X Y, Yan Y N, Wang F, Fn J P, Zeng H and Xu X H 2016 IEEE T. Magn. 52(4) 1-5
[60] El-Safty S A, Sakai M, Selim M M and Alhamid A A 2015 Chem. Asian J. 10(9) 1909-18