CHAPTER 2

Porous Alumina Membrane Templates: Fabrication, Growth Mechanism and Characterization

This chapter discusses the fabrication and growth mechanism of porous alumina membrane (PAM) templates along with a brief description of general templated synthesis of nanomaterials. A generic approach to fabricate alumina templates with linear nanopore arrays through a two step anodization process is demonstrated, highlighting the relevance of all key parameters. As pore diameter is linearly proportional to the anodization voltage for a given area, it is easy to fabricate ordered linear nanopore arrays by merely tuning the anodization voltage. More importantly, anodization has been extended to the rational design of hierarchically branched templates such as Y-branched and two generation Y-branched PAM, where uniform Y-junctions are formed with regard to the position of the junction and the diameter of the arms. These templates with nanoporous arrays in linear as well as in branched forms have far-reaching implications in the design of interconnected and controllably branched nanoscale systems for next generation electronic devices.
2.1. Introduction

“Templating” essentially involves the replication of one structure into another under structural inversion. For example, the replication of molecular aggregates such as micelles is used as templates for the fabrication of mesoporous silica. Thus a template, in a general sense could be defined as a *structure-directing agent*. Templating is a versatile technique for the formation of nanostructured materials with structural units ranging from nanometers to micrometers. More importantly, size and shape of the resulting structures can be easily tuned by choosing the appropriate template structures/dimensions. The key for a successful template-assisted synthesis is to select a template which ensures the formation of a desired nanostructure that could be easily removed without any damage.

Templates that could be used for solid state synthesis include soft, hard, and complex templates. Soft templates, which can be subsequently removed by heat treatment, are normally surfactant based micelles, reverse micelles and polymers. Additionally, vesicles, ionic liquids, self-assembled colloidal crystals, foams, and air bubbles can also be considered as soft templates. An important advantage of the soft-template method is that it is scalable to bulk quantities of nanostructures, especially when the reduction is carried out in solution. On the other hand, hard template includes inorganic or polymeric materials, typically in the form of porous membrane. The inorganic hard templates (such as alumina membrane, mesoporous silica, ion-track etched mica, and macroporous silicon) can be leached away by using acid or alkali solution whereas, polymeric templates (such as ion track etched polycarbonate and polyester membranes) could be removed by using organic solvents. In the hard-template method, this porous membrane physically constrains the crystal growth. The main advantage of using a hard template over a soft one is that it allows unidirectional growth of nanostructures yielding dense arrays of uniform structures aligned on substrates, which are beneficial for their application in device fabrication. Moreover, they cover length scales from a few nanometers over micro to the macro scale. However, since these hard
templates are usually a thin membrane, it is difficult to scale-up to macroscopic quantities of nanowires, although efforts in that direction are underway.

Complex templates, which combine the soft and the hard templates, or two hard templates, or two soft templates of different length scales, have been used to prepare hierarchically bi-modal and tri-modal porous structures with the primary objective of minimizing diffusional resistance and improving the accessibility of various surfaces. For example, bimodal mesoporous–macroporous materials with interconnected pore channels can be prepared by using a surfactant template in combination with a colloidal-crystal template.\textsuperscript{2d,3}

Among these templates, hard templates like porous alumina membranes have many favourable characteristics including regular pore distribution, high pore density ($10^{11}$ pores/cm$^2$) and high aspect ratio. These porous membranes are generally fabricated through a controlled anodization of highly pure aluminium in acidic medium.\textsuperscript{4} Interestingly, these cylindrical pores of uniform diameter are arranged in a hexagonal array having little or no tilt with respect to the surface normal, resulting in an isolated and non-connected porous structure. The pore diameter could be tuned from ~ 5 nm to > 100 nm by varying the composition and concentration of the acidic electrolyte, temperature and the voltage of anodization. Also, the thickness of the porous layer is dependent on time, with longer anodization resulting in thicker templates (ranges up to several hundred micrometers). In addition, high chemical, thermal and mechanical stability of these templates allow convenient post-deposition processing, which is useful to release the nanostructures without any extensive damage.

Besides these cylindrical/linear nanopore arrays, Y-branched and hierarchically branched arrays are also obtained through mere tuning of the anodization conditions.\textsuperscript{5} The creation of these branched nanopore arrays provides a powerful way to produce interconnected nanostructures. For example, linear alumina templates fabricated through anodization could be extended for the formation of branched arrays. The rationale for creating Y-branched pores in PAM templates includes the reduction of anodizing voltage
by a factor of $1/\sqrt{2}$, which initiates the transformation of a linear pore during the anodization into a symmetrically divided Y.\textsuperscript{5c} Based on this rationale, it is possible to generate not just a single Y junction but multiple Y-branching by sequentially reducing the anodization voltage many times, each by a factor of $1/\sqrt{2}$. In general, the anodization voltage to generate 'n' number of pores from a single stem pore could be expressed as $(1/\sqrt{n}) V_A$, where $V_A$ is the anodizing voltage, and 'n' is the number of branched pores from that stem.

The structure of alumina membrane is described as close-packed array of columnar hexagonal cells which nearly appear like a honeycomb.\textsuperscript{4a,6} However, in real situation, the formation of defect free ordered pore arrays is often limited to a domain of few $\mu$m only. This is attributed to the non-idealities in the Al sheet such as defects and grain boundaries, where electric field is locally modified which impacts the pore growth direction and balance between neighbouring pores. Therefore the formation of regularly spaced vertical pores is limited to within the boundary of single Al grains. As a result, Masuda et al. have advocated a two-step anodization route and molding process to obtain long-range ordered channel array architecture on the order of millimeter.\textsuperscript{4c,d} In the latter case, shallow ordered textures (array of concaves) is made on the Al surface prior to the anodization step by a molding process and as a result, growth of an almost defect free channel array could be achieved throughout the textured area. In a two-step anodization route (which is cost effective compared to that of the previous one), the porous alumina obtained after the first anodization step is removed and subsequently a second anodization is performed. The removal of initial porous film leaves behind an ordered concave textured structure, which facilitates the growth of ordered pore arrays during the second step.

Apart from Al, anodization of Si, Ti and W also forms nanoporous films, and efforts to control their pore dimension similar to that of porous alumina are known, to be successful.\textsuperscript{7}
2.2. Growth Mechanism of Al₂O₃ Pore Arrays

The self-organizing nature of the porous alumina is explained by the dynamic nature of the native aluminium oxide. Aluminium is a highly reactive element and rapidly forms a thin native oxide upon the exposure to oxygen. When an electric field is applied during the anodization process, two opposing processes occur to rapidly establish a dynamic equilibrium. The first is the electrical breakdown of the oxide layer which is followed by an electrochemically mediated dissolution of the aluminium oxide. Breakdown occurs when an electric field exceeding the dielectric strength of the oxide is applied across the film. When this occurs, Al³⁺ ions under the mask will be injected into the aluminium oxide/electrolyte interface and the O₂²⁻/OH⁻ ions from the electrolyte move to the Al₂O₃/Al interface under the electric field and the aluminium under the broken down aluminium oxide thin film will continue to be anodized to grow a thicker at the Al₂O₃/Al interface. Ultimately, the aluminium oxide layer becomes sufficiently thick and the breakdown–growth cycle stops. A barrier type aluminium oxide is thus formed.⁸

Even though, this barrier oxide layer is stable, they are eroded in the presence of acidic electrolytes used for anodization. In particular, these oxides are isotropically etched by electrolytes such as sulphuric acid, oxalic acid, and phosphoric acid. Electrochemical etching is a field dependent process and also anisotropic in nature, dominating in regions where the field strength is maximum. As the oxide is eroded at the electrolyte/Al₂O₃ interface, it gradually thins to a point wherein the field across the oxide is again sufficient to cause breakdown resulting in additional oxide growth at the Al₂O₃/Al interface. The competition between dissolution of oxide layer at oxide/electrolyte interface and the oxide growth at metal/oxide interface sets up a dynamic equilibrium which is responsible for the porous oxide growth. (A schematic representation of the ion migration at the pore bottom under the applied electric field is shown in figure 2.1.). Here, the loss of Al³⁺ ions to the electrolyte has been found to be an essential prerequisite for the porous oxide growth.⁸
Figure 2.1. A schematic representation of ion migration responsible for the formation of porous structure under applied electric field; pores grow perpendicular to the surface with the migration of oxygen containing ions (O\(^2\)/OH\(^-\)) from the electrolyte through the oxide layer at the pore bottom and Al\(^{3+}\) ions which simultaneously drift through the oxide layer are ejected into the solution at the oxide/electrolyte interface; on the left unoxidized Al metal surface is depicted (wavy pattern denotes the electrolyte). [Adopted from ref. 9a]

The atomic density of aluminium in Al\(_2\)O\(_3\) is lower than that of metallic aluminium by a factor of two. As a result, volume expansion of Al\(_2\)O\(_3\) will be nearly twice than that of the Al metal developing mechanical stress during oxide formation. This stress is the possible origin of repulsive forces that appear between neighbouring pores.\(^9\) Since the oxidation takes place at the entire pore bottom simultaneously, the material can only expand in the vertical direction, so that the existing pore walls are pushed upwards, ultimately resulting into a parallel and uniformly ordered porous array having a hexagonal arrangement.

2.3. Effect of Anodization Parameters on the Pore Dimension

Since a minor variation in one of the several key variables like anodization voltage, concentration and type of the electrolyte, and temperature can adversely affect the reproducibility of the critical dimensions of the alumina template, it is very important
to systematically investigate the effect of these parameters on porosity. The influence of some of the major parameters is discussed below:

2.3.1. Anodization Voltage ($V_a$)

The pore diameter ($D_p$) and inter-pore distance ($D_{int}$) are linearly proportional to the anodization voltage, in accordance with the theory established by O’Sullivan et al. and the proportionality constant ($\zeta$) is $2.5 \text{ nm V}^{-1}$\textsuperscript{.4a.g,6c,8a,10} (A schematic cross-section of the porous alumina is shown in figure 2.2, where the pore diameter, inter-pore distance and barrier layer thickness are clearly seen) This is ascribed to the high current density (diffusion limited current) and strong chemical dissolution enhanced by the electric field.

![Schematic representation of the cross-section of PAM with the barrier layer; $D_p =$ pore diameter, $D_{int} =$ inter-pore distance, $t_b =$ thickness of the barrier layer; hexagonal ordering of cylindrical pore arrays with barrier layer is clearly seen.]

Figure 2.2. Schematic representation of the cross-section of PAM with the barrier layer; $D_p =$ pore diameter, $D_{int} =$ inter-pore distance, $t_b =$ thickness of the barrier layer; hexagonal ordering of cylindrical pore arrays with barrier layer is clearly seen.

2.3.2. Type and Concentration of the Electrolyte

The type and the concentration of the electrolyte for a given anodization potential has to be selected properly to obtain a stable porous structure.\textsuperscript{4b,10d,9a,11} The electrolytes
typically used are sulphuric acid, oxalic acid, and phosphoric acid respectively. The optimal voltage depends on the electrolyte used for the anodization (e.g., 25 V for sulphuric acid, 40 V for oxalic acid, and 195 V for phosphoric acid for a given electrode with same inter-electrode distance) perhaps due to the conductivity and pH difference. For example, if aluminium is anodized in sulphuric acid at a high potential, breakdown of the oxide layer often takes place. In addition, the pore diameter is affected strongly by dissolution velocity of alumina which in turn is determined by the pH of the electrolyte. The lower the pH, the lower is the potential threshold for field-enhanced dissolution at the pore tip leading to a smaller size of the pores. Therefore, large pore diameters are formed by using phosphoric acid while smaller pores are obtained by sulphuric acid.

Change in the electrolyte concentration also has a significant effect on pore diameter. Upon increasing the electrolyte concentration, pore diameter enlarges linearly, although the inter-pore distance does not vary under a given anodization voltage. For example, Du et al. have observed an increase in the pore diameter from 50 nm to 80 nm respectively when the concentration of oxalic acid is increased from 0.3 to 0.5 M at an anodization voltage of 50 V. However, the inter-pore distance remains at 120 nm.

2.3.3. Temperature

During the anodization, temperature should be kept minimum (less than room temperature) to get uniform features and also to prevent complex species from being dissolved in certain electrolytes. A second reason to keep the temperature as low as possible is to avoid a local heating at the bottom of the pores during the course of anodization (specially, in the case of a high potential), to prevent inhomogeneous electric field distribution at the bottom. In fact, cracks and bursts of the oxide film are generated if porous alumina is formed without adequate temperature control. However, if the temperature is too low (well below 0°C), the growth rate of porous alumina will not be sufficient to facilitate a porous film formation.
Hence by accurately controlling temperature, anodization voltage (current density), type and concentration of the electrolyte, nanoporous structure with well defined pore diameter, inter-pore distance and porosity could be easily fabricated.

In chapter 1, a critical review has been provided on various methods of preparing high aspect ratio nanostuctures, demonstrating the importance of porous alumina membrane for the growth of metals like platinum and palladium using electrodeposition. In this chapter, we discuss our efforts to prepare such a porous alumina membrane having linear as well as hierarchically branched nanopore arrays through anodization. These nanoporous structures have been characterized by SEM, XRD, FTIR, BET and Electrochemical Impedance techniques. A few commercial PAM samples from Whatman International Ltd. have also been used to bench mark our membrane structures. Furthermore, contact angle studies of these porous membranes are also carried out to understand the wetting of different solvent into the PAM pore walls. These are valuable for the synthesis of different metallic/semiconducting nanostructures either by electrodeposition or by electro-less deposition after functionalization of the pores by selected organic molecules.

2.4. Experimental Details

2.4.1. Materials

Aluminium sheet GR (99.9 % purity, thickness 0.14 mm) and oxalic acid GR (99.5 %) were purchased from Loba Chemie while, CuCl₂·2H₂O was purchased from Merck. Solvents such as ethanol (99.9 %) and perchloric acid (72 %) were procured from Merck and Rankem chemicals. Dimethyl sulfoxide (99 %), N,N'-dimethyl formamide (99.5 %), methanol (99.8 %), cylohexane (99.5 %) and hexane (95 %) were obtained from Loba Chemie, while toluene (99.5 %) was purchased from Qualigens. All reagents were used without further purification and deionized water (18 MΩ) from milli-Q system was used in all experiments.
2.4.2. Fabrication of Linear PAM

Alumina membranes with linear nanopore arrays were fabricated using a DC power supply (Spectron Model: PLC 3001 DtM) for anodization. First, clean Al foils were degreased in acetone followed by annealing for 5 h at 500 °C under Ar atmosphere in order to remove the crystal defects and to promote grain growth. Subsequently, the foils were electropolished in a mixture of ethanol and perchloric acid (70:20) at 5 V for 2 min to smoothen the surface morphology and the resultant foils were anodized in 0.25 M oxalic acid at 40 V (current density 5 mA/cm²) for 4 h at 5 °C using a Pt wire as the cathode under stirred conditions. However, the order of the pores achieved was often limited to a domain of few μm only and more importantly, the individual domains were separated by wide regions of defects. Hence as per Masuda’s suggestion of carrying out a two step anodization for ordered porous structures, we performed a further second anodization after etching the alumina layer from the first step in a mixture of 1.5 wt % chromic acid and 6 wt % phosphoric acid for about 30 min. Etching of these porous alumina layer produced a patterned aluminium substrate with an ordered array of concave shaped holes which subsequently served as initial sites to form a highly ordered nanoporous array during the second anodization step (which was performed under identical conditions) for 5 h.

A schematic representation of different stages involved during the formation of ordered linear nanopore arrays is shown in Figure 2.3, includes anodization of annealed and electropolished Al sheet to form porous alumina layer, which are however non-uniform. As a result, the porous layer is removed to obtain ordered concave textured structure and subsequently a second step anodization is performed to form ordered linear nanopore arrays. This porous alumina layer was then separated from the underlying aluminium substrate by etching in 1 M CuCl₂ solution for 30 min and finally the alumina barrier layer was carefully removed after a brief contact (2 min) with 5 wt % phosphoric acid to obtain a free standing porous alumina membrane.
2.4.3. Fabrication of Y-branched PAM

After the initial anodization to form the straight pore stems (see section 2.4.2 for the fabrication of linear PAM), the voltage was subsequently reduced to 28 V (by a factor of $1/\sqrt{2}$; current density 3.2 mA/cm$^2$) and finally a third step anodization was performed for 4 h. As a result, nearly all large diameter channels formed at 40 V, get bifurcated into two smaller diameter branches. These Y-branched nanochannels of alumina layer were then separated from the underlying substrate by etching in 1 M CuCl$_2$ or mercurous chloride (aqueous solution) for 30 min and finally the alumina barrier layer was carefully removed after a brief contact (2 min) with 5 wt % phosphoric acid to obtain a free standing alumina membrane.

2.4.4. Fabrication of Two-Generation Y-branched PAM

After the above third step (see section 2.4.3), the anodization voltage was further reduced to 20 V (by a factor of $1/\sqrt{2}$; current density 2.5 mA/cm$^2$) and continued for 4 h.
As a result of this, a second generation of branched channels was generated from each of the first generation branched channels (formed at 28 V). After the anodization process, a similar procedure (as discussed in section 2.4.3) was followed to obtain free standing PAM.

2.4.5. Structural and Morphological Characterization

2.4.5.1. Scanning Electron Microscopy (SEM)

Dimensions of the nanopore arrays were examined using a scanning electron microscope, Lieca Stereoscan 440 Model. A small piece of the membrane was mounted on a Cu substrate using a carbon tape. For comparative studies, the energy of the electron beam was kept constant while analyzing all the samples. Micrographs were recorded with a 20 kV electrical high tension and 25 pA camera attached on the high-resolution recording unit. Some micrographs were also recorded using a Hitachi S-4800 field emission scanning electron microscope.

2.4.5.2. X-ray Diffraction (XRD)

In order to understand the structure of ‘as-prepared’ PAM at room temperature and also to elucidate the purity, XRD studies were performed using CuKα (λ = 1.5405 Å) radiation on a Panalytical XPert Pro diffractometer. Diffraction patterns were collected at a step of 0.02° (2θ) and the background was subtracted with the linear interpolation method.

2.4.5.3. Fourier Transform Infrared Spectroscopy (FTIR)

Detailed information on the different functional groups present in the porous membrane has been investigated using FTIR analysis. Different modes are employed for analysis depending on the nature of the sample and required sensitivity. For example, FTIR measurements were carried out in the diffuse reflectance mode at a resolution of 4 cm⁻¹ on a Perkin-Elmer FTIR Spectrum One spectrophotometer.
2.4.5.4. Contact Angle Measurements

Contact angle measurement is a surface sensitive technique, which quantitatively unravels the wetting of a solid by a selected liquid, enabling a simple and effective method to determine the surface tension, and its relation to the structure and composition of a surface. All contact angle measurements were performed on a GBX model (DIGIDROP contact angle instrument) using proprietary Windrop software. The contact angle ($\theta$) was measured using sessile solvent drop method. Prior to the measurements, the membrane was dried at 100°C for 1 h and allowed to cool to room temperature. Wetting behavior of PAM was carried out using seven different solvents such as H$_2$O, dimethyl sulfoxide (DMSO), N,N'-dimethyl formamide (DMF), methanol, toluene, cyclohexane and hexane. The measurements were performed after fixing the membrane on the sample holder. Extreme care was taken in monitoring contact angle values within 2 - 3 min to avoid the evaporation effects. At room temperature (27°C) and at constant humidity (40-50%), all contact angle measurements showed a standard deviation of ± 2°. However, since the contact angle depends on the liquid purity, temperature, as well as the statistical errors in the actual reading of the contact angles by different people, average values were taken typically after 5-6 measurements.

2.4.5.5. Determination of Pore Size Distribution

The Brunauer Emmett Teller (BET) method continues to be the most widely used method for the evaluation of surface area, pore volumes and pore size distributions of porous solids from N$_2$ physisorption isotherm data. The BET equation can be represented as follows:

\[
\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c^2} \frac{p}{p_0}
\]
where, $v$ = volume of N$_2$ adsorbed by the sample under pressure $p$, $p_0$ = saturated vapor pressure at the same temperature, $v_m$ = volume of N$_2$ adsorbed when the surface is covered with a unimolecular layer, and $c$ = constant for a given adsorbate.

The equation suggests that the plot of \( \frac{p}{v(p_0 - p)} \) versus \( \frac{p}{p_0} \) should be linear, and from the intercept \( \frac{1}{v_m^c} \) and slope \( \frac{c-1}{v_m^c} \), the values of $v_m$ and $c$ can be determined as follows: $v_m = (\text{slope} + \text{intercept})^{-1}$. Thus the specific surface area ($S$) of a sample can be determined as follows: $S = \frac{N_0 v_m A}{22414m}$, where $N_0$ = Avogadro number, $m$ = amount of solid adsorbent, $A$ = cross-section of the gas molecules (16.2 $\text{Å}^2$ for N$_2$), and $S$ is expressed in cm$^2$ g$^{-1}$ unit.

Several computational procedures are available for the derivation of pore size distribution of mesoporous samples from physisorption isotherms. Most popular among them is the Barrett-Joyner-Halenda (BJH) model, which is based on speculative emptying of the pores by a stepwise reduction of $p/p_0$, and allowance being made for the contraction of the multilayer in those pores already emptied by the condensate.

The pore size distribution of PAM was determined by BET method using Quantachrome Autosorb Automated Gas Sorption System with N$_2$ gas adsorption–desorption measurements at 100°C.

2.4.5.6. Electrochemical Impedance Measurements

Electrochemical Impedance is an important electroanalytical technique based on the measurements of the frequency dependent response of an electrochemical cell after applying a small-amplitude sinusoidal signal under a potentiostatic control. It offers the possibility of obtaining information on important parameters such as ohmic resistance, double layer capacitance, charge transfer kinetics at the electrode/electrolyte interface and also about mass transfer phenomenon. In the present work, electrochemical
impedance studies were performed in 0.1 M KCl containing equal proportions of K₄[Fe(CN)₆]/K₃[Fe(CN)₆] couple (5 mM each) using Autolab PGSTAT30 (ECOCHEMIE) instrument equipped with a frequency response analyzer.

2.5. Results and Discussion

2.5.1. SEM Analysis

Figure 2.4a shows a typical scanning electron micrograph of the “as-prepared” porous alumina membrane (top-view) by the two step anodization process using 40 V, revealing an ordered hexagonally packed nanopores with an average diameter of 65 nm. Indeed, pores are seen over the entire surface of the sample and the distance between two adjacent pores (inter-pore distance) amounts to ca. 100 nm. More specific cross-sectional view of the membrane is shown in figure 2.4b to highlight the periodic linear array with a pore length of ca. 56 μm. Interestingly, a slightly higher anodization voltage (50 V; current density 7 mA/cm²) as indicated in figure 2.4c reveals the formation of the same hexagonal array, despite with a slightly higher pore diameter (80 nm) and inter-pore distance of 120 nm respectively. Further, the porosity and pore density of PAM film at different anodization voltage could be estimated as follows:

Porosity ($P$), after assuming an ideal hexagonal arrangement of the pores, is given by,\(^{12}\)

$$P = \frac{2\pi}{\sqrt{3}} \left( \frac{r}{D_{\text{int}}} \right)^2$$

(2.2)

where, $r$ is the pore radius and $D_{\text{int}}$ is the inter-pore distance.

Also, the pore density ($\rho$, pores/cm²) is given by,\(^{13}\)

$$\rho = \frac{2}{\sqrt{3}D_{\text{int}}^2} \times 10^{14} \text{ cm}^2$$

(2.3)

Accordingly, Table 2.1 summarizes both the porosity and pore density of the PAM film formed at two different voltage, where it could be seen that porosity increases upon increasing the voltage whereas pore density decreases.
Figure 2.4. SEM images of porous alumina membrane fabricated after a two step anodization in 0.25 M oxalic acid at 5 °C; (a & b) top and cross-sectional view of porous alumina membrane fabricated at an anodization voltage of 40 V; (c) top view of porous alumina membrane fabricated at 50 V.

Table 2.1. Different structural parameters of PAM fabricated at two different anodization voltages; anodization was performed in 0.25 M oxalic acid at 5 °C.

<table>
<thead>
<tr>
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<th>PAM (40 V)</th>
<th>PAM (50 V)</th>
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<tbody>
<tr>
<td>Pore Diameter (nm)</td>
<td>65</td>
<td>80</td>
</tr>
<tr>
<td>Interpore Distance (nm)</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>38</td>
<td>40</td>
</tr>
<tr>
<td>Pore Density (pores/cm²)</td>
<td>$1.1 \times 10^{10}$</td>
<td>$8 \times 10^{9}$</td>
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Typical field-emission scanning electron micrographs (FESEM) of alumina membranes with Y-branched nanochannels (cross-sectional view) fabricated via an extended two step anodization are shown in figure 2.5a-c at different magnifications.
More specifically, the images depict Y-branched nanochannels with stems and branches of about 100 and 50 nm diameters respectively, although these parameters could be controlled systematically by varying temperature, anodization time, nature and concentration of the electrolyte. Furthermore, the angle between the two branches is about 10° as shown in the micrograph. The Y-junctions are uniform with regard to both the position of the junction (i.e., orientation) and the diameter of the arms. Similarly, figure 2.6 shows the SEM image of two-generation Y-branched PAM fabricated through an extended three step anodization, where the micrograph shows the first generation and second generation branches. However, it is difficult to mention the diameter of the branches from this low magnification.

Figure 2.5. FESEM images of Y-branched PAM (cross-sectional view) fabricated via an extended two step anodization: Y-branched nanochannels consist of stems and branches having diameter 100 nm and 50 nm respectively; (a-c) show images at different magnifications; inset shows the schematic view of Y-branch alumina membrane.
Figure 2.6. SEM image of two-generation Y-branched PAM (cross-sectional view) fabricated through an extended three step anodization; branched nanochannels are marked by circles; schematic view of two-generation Y-branch alumina membrane is shown in the inset.

2.5.2. XRD Analysis

Figure 2.7 reveals the XRD pattern of the free-standing PAM template recorded at room temperature, demonstrating that the ‘as-prepared’ PAM has an amorphous nature. However, sharps peaks at 2θ values 44.1°, 65.1° and 78.2° respectively are observed corresponding to the (200), (220) and (311) planes of metallic Al [JCPDS 4-787]. This reveals the presence of trace amount of Al debris in the PAM membrane even after the treatment with cupric chloride.
Figure 2.7. XRD spectrum of the free-standing PAM fabricated through a two-step anodization at 40 V in 0.25 M oxalic acid; the pattern reveals amorphous structure of alumina membrane; sharp and intense peaks correspond to the metallic Al.

2.5.3. Wetting Behaviour of Linear PAMs: Results of Contact Angle Measurements

One of the important applications of PAM is in the preparation of high aspect ratio nanostructures through different routes including both electrodeposition and electroless deposition. However, attempts to fill the pores by natural convection or capillarity effect alone are unsuccessful because of the extremely slow nature of diffusion inside porous structures (Knudsen diffusion). Therefore, it is important to study liquid-solid interactions in order to understand how the interfacial properties affect the influx and outflux of molecules/ions into the pores of the membrane. With this objective, the contact angle studies have been carried out on PAM membranes to understand the wetting behaviour between a liquid and a porous solid surface.
Figure 2.8 reveals the droplet profile observed with various solvents on PAM (pore diameter 65 nm). A closer look at ‘θ’ values corresponding to various solvents reveal the following order \( \text{H}_2\text{O} > \text{DMSO} > \text{DMF} > \text{Toluene} > \text{Cyclohexane} > \text{Methanol} > \text{Hexane} \). A higher ‘θ’ value is observed for the case of \( \text{H}_2\text{O} \) (70.3 ± 2°), whereas hexane shows comparatively lower value (7 ± 2°). Most important properties that affect ‘θ’ are dielectric constant, dipole moment of the solvent, and surface tension. In the present case, the interaction of membrane with the liquid is through the hydroxyl and oxalate groups (these groups are present on the surface as well as on the pore walls) and hence the wetting of the alumina membrane is partly decided by the density of these groups. The presence of these groups is confirmed by FTIR studies (figure 2.9), where the appearance of peak at 1650 cm\(^{-1}\) and 1210 cm\(^{-1}\) is attributed to the carbonyl (C=O) and C-O stretching of –COO\(^-\) moiety respectively. In addition, peaks at 1410 and 1530 cm\(^{-1}\) are assigned to the symmetric and asymmetric stretching of carboxylate ion and apart from
these, a broad band at around 3200 cm$^{-1}$ corresponding to the –OH stretching of hydroxyl group is also observed.$^{16}$

![Figure 2.9. DRIFT spectrum of free-standing linear PAM; the stretching frequencies of different functional groups present in the membrane are mentioned.]

Even though, water exhibits higher values of dielectric constant ($\varepsilon$) and dipole moment ($\mu$), a higher value of surface tension ($\gamma$) is primarily responsible for the poor interaction with the pore walls. In other words, in water the cohesive force ($\gamma_{lv}$, surface tension at the liquid-vapor interface) is strong enough to overcome the adhesive force ($\gamma_{sl}$, surface tension at the solid-liquid interface) and as a result prevents it from spreading.$^{17}$ In contrast, hexane has comparatively lower surface tension (than that of water) to ensue stronger adhesive force ($\gamma_{sl}$) than the cohesive force ($\gamma_{lv}$) and as a result, wetting of pore walls occurs. Similarly, wetting behaviour observed with solvents such as DMSO, DMF, methanol, toluene, and cyclohexane as judged by the contact angle values ($\theta$) are in agreement with the corresponding surface tension values.
Similar studies with planar aluminium sheet (with native oxide film) is also carried out and the corresponding droplet profiles with various solvents are shown in figure 2.10. A similar trend as observed in the case of PAM is also obtained for planar alumina sheet although a comparison of the contact angle values on both samples, reveals a slightly higher \( \theta \) value for the planar alumina (especially in the case of polar solvents). This could be attributed to the hydroxyl and oxalate functional groups present on the surface and pore walls of PAM and also due to the porous structure of the membrane, which in turn increases the surface roughness. Table 2.2 summarizes the contact angle with various solvents (along with surface tension) on both planar and porous alumina. It has been already observed that upon increasing the surface roughness of hydrophilic surfaces, the surface will exhibit enhanced hydrophilicity. All these factors are responsible for the comparatively lower \( \theta \) for the PAM with respect to planar alumina. However, considering the wetting behaviour of non-polar solvents such as toluene on both surfaces, it is observed that the angle \( \theta \) is comparatively lower for planar one compared to that on porous membrane. This could be partly attributed to the hydrophilic-hydrophobic interaction on the porous membrane, which leads to a slightly higher angle on porous alumina. However, further studies are desired to pinpoint the exact reason for this behaviour.

![Figure 2.10. Solvent droplet profiles with different solvents on planar alumina at room temperature; the wetting angle \( \theta \) observed with each solvent is also shown.](image)

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**Figure 2.10.** Solvent droplet profiles with different solvents on planar alumina at room temperature; the wetting angle \( \theta \) observed with each solvent is also shown.
Table 2.2. Variation of contact angle ‘θ’ with different solvents on both porous alumina membrane and planar alumina; surface tension of corresponding solvents are also included.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Contact Angle (θ) (degree)</th>
<th>Surface Tension (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAM</td>
<td>Planar Alumina Sheet</td>
</tr>
<tr>
<td>Water</td>
<td>70.3</td>
<td>88</td>
</tr>
<tr>
<td>DMSO</td>
<td>36.4</td>
<td>50.7</td>
</tr>
<tr>
<td>DMF</td>
<td>26.1</td>
<td>33.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>8.5</td>
<td>20.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>10.3</td>
<td>4.5</td>
</tr>
<tr>
<td>Hexane</td>
<td>7</td>
<td>*</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>9.1</td>
<td>*</td>
</tr>
</tbody>
</table>

*Unable to measure

Further, the “critical surface tension” $\gamma_{\text{crit}}$ (a measure of interfacial surface energy) of a material is estimated from the Zisman plot (the cosine of the contact angle (θ) versus the surface tension of various solvents). As the surface tension of the solvent decreases, contact angle also decreases and the extrapolation of this plot to $\cos \theta = 1$ gives the critical surface tension value. Accordingly, figure 2.11a,b shows the Zisman plot of both planar alumina and PAM and corresponding $\gamma_{\text{crit}}$ value is 28.5 and 17.8 dyne/cm respectively. The lower value of $\gamma_{\text{crit}}$ for the PAM with respect to planar alumina is attributed to the increased surface roughness and porosity of the former.
2.5.4. Determination of Pore Size Distribution from BET Adsorption Isotherm

$N_2$ adsorption-desorption studies based on BET isotherm are valuable for estimating the surface area and pore size distribution of the porous materials.\cite{19} Accordingly, we have evaluated the pore size distribution of PAM fabricated at an anodization voltage of 40 V. However, the pore size distribution obtained reveals a bimodal distribution with a pore size of 40 and 60 Å respectively, which is an order less than that from SEM analysis (here the pore diameter was estimated based on BJH analysis during desorption process). The reason for this discrepancy is perhaps due to (i) normally, this technique is employed mainly for powder samples and hence getting reliable data for membrane is difficult due to very small surface area, and (ii) between the well-defined cylindrical alumina nanopores, amorphous alumina film is present on the surface which is perhaps more accessible for gases with pore diameters of around 40 and 60 Å thus masking the true nanoporous size distribution.

2.5.5. Electrochemical Impedance Behaviour of PAM

Impedance is a powerful tool to understand the electrochemical behaviour of these porous membranes. Using this technique, the rate of thinning of barrier layer at the bottom of the porous structure has been studied extensively.\cite{20} Moreover, ionic transport
through the porous electrodes, in general have been extensively investigated using impedance. The work of de Levie marks the start of the theory of the impedance of porous electrodes derived from various mathematical models. Two of the most successful models are the cylindrical pore model and the macro homogeneous model. The impedance of the porous electrode under the influence of potential gradient, and concentration gradient and both had been analysed using the cylindrical pore model. However, the cylindrical pore models do not take into account the distribution of pores in the electrode, which is very significant for practical applications of porous electrodes. The macro homogeneous model proves to be a better representation as it takes into consideration the distribution of pores by volume averaging. Using the macro homogeneous model and linear polarization study, Ralph et al. have derived the impedance response of porous electrode under the influence of both the concentration gradient and the potential gradients. Interestingly, using this model they have demonstrated the effect of porosity of these electrodes on the impedance response.

Normally, the impedance response of the porous electrodes in presence of a redox couple, shows two semicircles: the high frequency semicircle is due to charge transfer process and the lower frequency semicircle for diffusion process. With a decrease in porosity of these membranes, both the charge transfer and mass transfer resistance increases. Accordingly, figure 2.12a-c shows the impedance response of Al sheet and alumina membrane with different porosity (38 % and 40 %) in presence of 1:1 mixture of both K₄[Fe(CN)₆] and K₃[Fe(CN)₆] couple in 0.1 M KCl, where with increase in porosity, suggests an increase in the charge transfer resistance (R_{CT}). For example, the R_{CT} value of planar Al sheet is 465 Ω, whereas 485 Ω and 1.6 kΩ are obtained for PAM with 38 % and 40 % porosity respectively. The corresponding enlarged view of the high frequency region is also shown in figure 2.13a-c where the ohmic resistance (R_{Ω}) of the three samples vary as: PAM (40%) > PAM (38 %) > Al sheet. However, several fluctuations are observed especially at lower frequency region perhaps due to pitting corrosion of Al (in side of the membrane) aggrevated by chloride ions and hence further studies in other electrolyte (e.g., sodium sulphate) are desired to explore this.
Figure 2.12. Complex plane impedance plots of (a) planar Al sheet; (b and c) PAM with 38 % and 40 % porosity using 10 mV AC signal recorded in the frequency range of 50 kHz to 0.1 Hz.

Figure 2.13. Complex plane impedance plots of a) planar Al sheet; (b and c) PAM with 38 % and 40 % porosity; the enlarged view of the high frequency region is shown; variation in $R_q$ with increase in porosity is clearly seen.
Thus a combination of all the above techniques provides an elegant way to characterize porous alumina membranes which clearly suggests the formation of PAM with well-defined nanopore arrays. Hence, this porous membrane could be effectively utilized for not only as scaffold platform for synthesizing nanostructural array for various material but also could be extended to various other diverse applications such as DNA translocation, size-exclusive filtration, gas separation, and as photonic crystal.

2.6. Conclusions

This chapter discusses various experimental details of the fabrication and growth mechanism of porous alumina template in order to illustrate the critical importance of controlling some of the major factors affecting the nanopore array formation. The methodology for preparing alumina template with linear nanopore arrays having diameter ca. 65 nm and ca. 80 nm through a two step anodization route is described along with extension for the fabrication of hierarchically designed alumina templates including Y-branched as well as two generation Y-branched nanopore channels. The approach developed in this chapter could serve as an efficient and reliable route for the synthesis of high aspect ratio nanostructures such as linear, Y-junction, and multilevel Y-junctions. Considering, the tremendous applications of the junctions nanostructures especially in molecular electronics, we further believe that present route could be extended for other such porous oxides realizing their complete potential. Further, we anticipate that a slight modification of the above template-design strategy could facilitate the fabrication of other potential junction structures such as X, and T.
2.7. References


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19 Gregg, S.J.; Sing, K. S. W. *Adsorption Surface Area and Porosity*; Academic
