



# Automated synthesis and characterization of diverse libraries of macroporous alumina

Christof Brändli, Thomas F. Jaramillo, Anna Ivanovskaya, Eric W. McFarland \*

*Department of Chemical Engineering, University of California Santa Barbara, Santa Barbara, CA 93106-5080, USA*

Received 23 March 2001; received in revised form 9 July 2001

## Abstract

This paper describes the combinatorial fabrication of porous alumina membranes by electrochemical synthesis. Combinatorial methods were successfully applied to generate a 256 member library of porous aluminum oxide with different pore sizes and pore densities. An alternating anodization and etching sequence was performed. Diversity within the library was achieved by changing the anodization time, the number of etching and anodization steps and the applied potential during anodization. It could be shown that the pore size strongly depends on the anodization potential and the uniformity of the pores depends on the last anodization time. A new combinatorial system and approach are presented which have advantages over previous cells and methods in a variety of electrochemical research applications. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Anodization; Porous alumina; Automated synthesis; Combinatorial methods

## 1. Introduction

The controlled fabrication of high surface area, ordered porous materials is of general interest. Structures with submicron dimensions can exhibit interesting and sometimes unexpected physical and chemical properties [1–3]. Applications of such structured materials include electronic, optical, and magnetic devices, sensors, catalyst supports, and membranes. Several reliable synthesis routes have been developed for ordered nano-, meso-, and macroporous structures [4,5]. For many of these routes, the expense can be prohibitive and creation of bulk quantities is not possible. Solution chemistry, and specifically room-temperature electrochemistry, offers an inexpensive alternative to these methods without the need for complex fabrication facilities.

Macroporous aluminum oxide is a particularly versatile structure used as membranes, supports, and templates to generate nanosize particles of different materials. Masuda and Fukuda were the first to create well ordered, hexagonal arrays of alumina [6]. Subsequently, several groups have fabricated structured alu-

mina with various properties [7–16]. Martin et al. used electrodeposition, sol-gel deposition, and polymerization methods to synthesize nanoparticles, nanowires, and nanotubules of metals, semiconductors, and polymers inside the porous structure of alumina [7–9]. Moskovits et al. applied electrochemical deposition methods to fabricate semiconductor nanowire arrays inside the alumina host [10–12]. Magnetic nanowires of cobalt and iron have also been synthesized inside macroporous aluminum oxide by Metzger et al. [13–16].

The controlled anodic oxidation of aluminum in either basic or acidic media is well known [17,18]. In basic media, a barrier-type, corrosion-resistant, oxide film is produced which can be used as a dielectric (for electrolytic capacitors) or insulating film. Nanoporous aluminum oxide can be formed by anodization of aluminum in polyprotic acids. The pore diameter is primarily a function of the applied potential, typically in the range of 1.0–1.2 nm V<sup>-1</sup>. The kinetics and formation of ordered arrays of aluminum oxides have been studied experimentally by several groups [19–24]. Recently, Gösele prepared large monocrystalline hexagonally arranged arrays of pores with distances between the pore centers of 200–460 nm using electron-beam

\* Corresponding author. Tel.: +1-805-893-4343; fax: +1-805-893-4731.

E-mail address: mcfar@engineering.ucsb.edu (E.W. McFarland).

lithography to pre-pattern the aluminum surface, followed by anodization under controlled conditions [25]. To date, the most regular arrays of pores with the most uniform dimensions rely on repetitive anodization/etch cycles. During a first long-time anodization step, an aluminum oxide surface, which is rough and covered with disordered pores, is generated. By removing the oxide layer with a wet chemical etch solution, a patterned aluminum surface is revealed. The aluminum surface acts during a second anodization step as a template for the formation of regular pores of aluminum oxide.

The formation and growth of porous aluminum have been modeled theoretically in a reaction–diffusion model [26,27]. It was found that the rate of the electric-field-enhanced dissolution of the electrode material at the pore base is a characteristic parameter for the growth of the pores. Different reactions at the oxide/electrolyte and oxide/aluminum interfaces were considered and the electric field distribution in this system was calculated. Although the relationship between voltage and pore size was made explicit, several parameters were required which are not readily determined in real systems and studies to date have relied on empirically derived electrosynthesis conditions.

In chemical syntheses, with a large number of non-independent parameters contributing to the final product, traditional serial synthetic methods are relatively slow to identify optimum conditions. Combinatorial methods of chemical synthesis are developed to increase the rate at which empirical parameter optimization can be accomplished. With automated synthesis, experimental parameters can be varied widely within a short period of time. Electrochemical synthesis is ideally suited for a combinatorial approach since thermodynamic and kinetic variables are greatly affected by current, voltage, electrolyte, and reaction time. Fabrication of micro-, meso- and nanoporous structures is strongly dependent on these experimental parameters. The research pre-

sented here focused primarily on two questions: (1) Can an automated system be developed for rapid diverse electrosynthesis and applied to anodic fabrication of porous structures? (2) Can libraries of macroporous alumina be produced rapidly where large variations in synthesis conditions over the library give rise to structural variations in the alumina that show the same trends observed in conventional serial experiments?

## 2. Experimental

Libraries were fabricated on polycrystalline aluminum which had been deposited on Si wafers. Three inch Si(100) wafers were first cleaned with a 1:1 solution of conc.  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  (30%). Titanium (50 nm) followed by aluminum (2000 nm) were deposited by electron-beam evaporation on the cleaned Si wafers. The anodization electrolyte consisted of 0.3wt% oxalic acid. Between anodization cycles, a wet chemical etching solution of 1:1 chromic acid (0.4%):phosphoric acid (0.6%) was used for the selective aluminum oxide stripping. The library was immersed in this solution for 6 min at 60 °C for each etching step.

A fully automated scanning electrochemical cell was used for anodization (see Fig. 1). In brief, the system consisted of an electrochemical cell made of polypropylene fitted with a Pt counter electrode. A fully programmable xyz-scanning system (LabView, National Instruments) moved the electrochemical cell over the substrate to individually anodize each location at variable controlled potentials (using a Sorensen power supply SRL 60-35). Anodizations were performed at a constant cell potential in a two-electrode configuration. An automated pumping system filled and emptied the probe with electrolyte at each library location prior to movement.

The pore morphology was characterized by scanning electron microscopy (SEM). SEM imaging was performed at 5 kV (JEOL, JSM6300F). A prerequisite for the highest quality SEM images is a conducting substrate, nonetheless, the images of the uncoated oxide were of sufficient quality for qualitative analysis. To increase the contrast of the pore edges for sizing, the images were filtered using a gradient filter [28].

## 3. Results and discussion

The relationships between the pore size and the number of repetitive etching steps and anodization voltage were specifically examined. The synthesis parameter space for anodization and etching which was explored on the library is shown schematically in Fig. 2. Anodization potentials were varied from 10 to 60 V. The potential was applied for either 10 or 180 s.

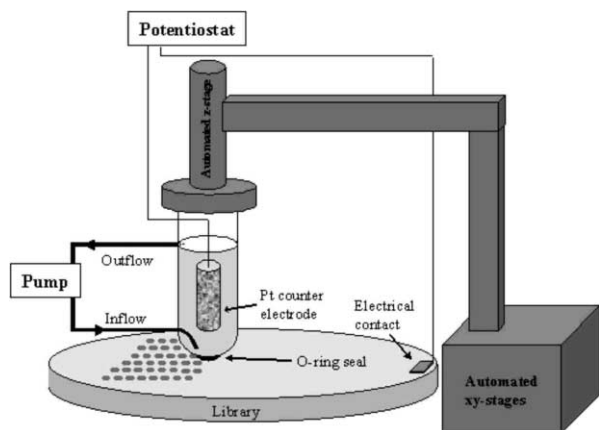


Fig. 1. Schematic diagram of the automated electrochemical setup.

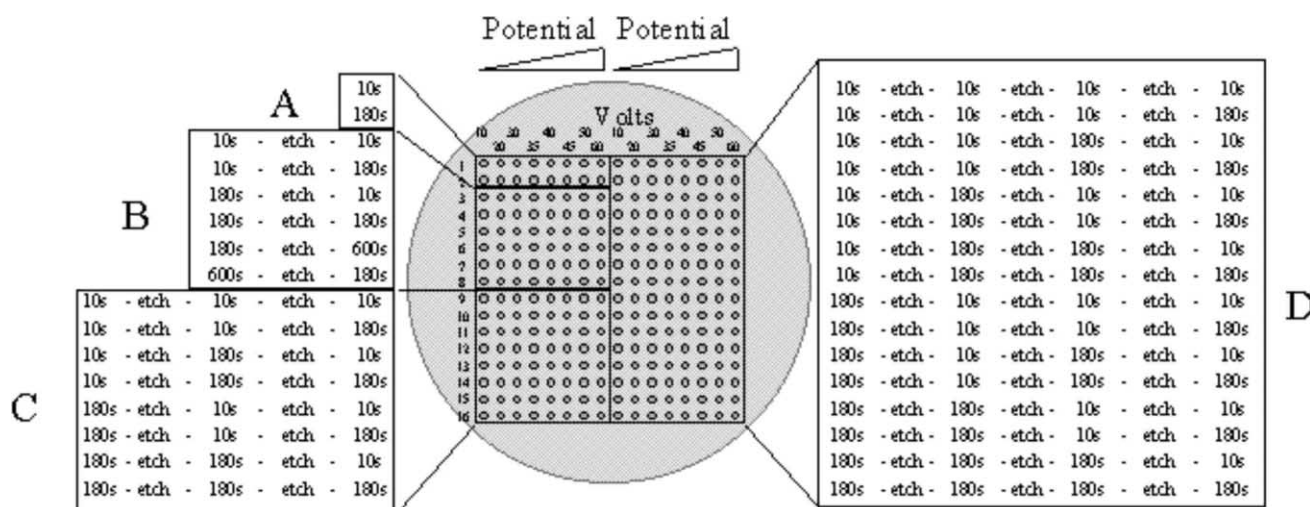


Fig. 2. Schematic library design.

One section of the library (A) was anodized with one cycle at potentials described above (row 1 for 10 s and row 2 for 180 s); another section (B) was anodized twice with one etching step in between; the times of the first and the second anodization were independently varied. Another section (C) of the substrate was anodized again either for 10 s or for 180 s with two etching steps in between. Section D of the library explored the alternating anodization/etch cycle for four anodizations and three etching steps. The two anodization times (10 and 180 s) were varied in such a way that all combinations could be obtained. The etching time was held constant for all steps.

The porous library was characterized with scanning electron microscopy (SEM). Fig. 3 shows SEM images at two magnifications after two 60 V anodizations, with one etching step in-between. Geometrically, the pores are approximately circular in cross-section. The pores homogeneously cover the entire anodized region. With this particular member of the library (60 V; Section B),

the long range uniformity of the anodization and the high porosity of the surface ( $\sim 10^{12}$  pores  $\text{cm}^{-2}$ ) are observed. As expected, the entire anodized surface is covered with perpendicular oriented porous structures. The high porosity and long range uniformity make such materials suitable for membranes and filters, catalyst supports, and as templates for nanostructure compounds.

The dependence of pore size on potential is important for controlled fabrication of specific structures. The number of etching steps was also found to significantly effect the final pore size and the uniformity of the pores. An increase of almost 20 nm was observed with one additional etching step (two compared to three). For a given number of etching steps a linear dependence of pore size on potential was obtained. Fig. 4 shows pore size dependence on potential of row 16 in sections C (two etching steps) and D (three etching steps). The slopes of both curves lie in the range of  $1.1\text{--}1.2 \text{ nm V}^{-1}$ , however, row D (four anodization,

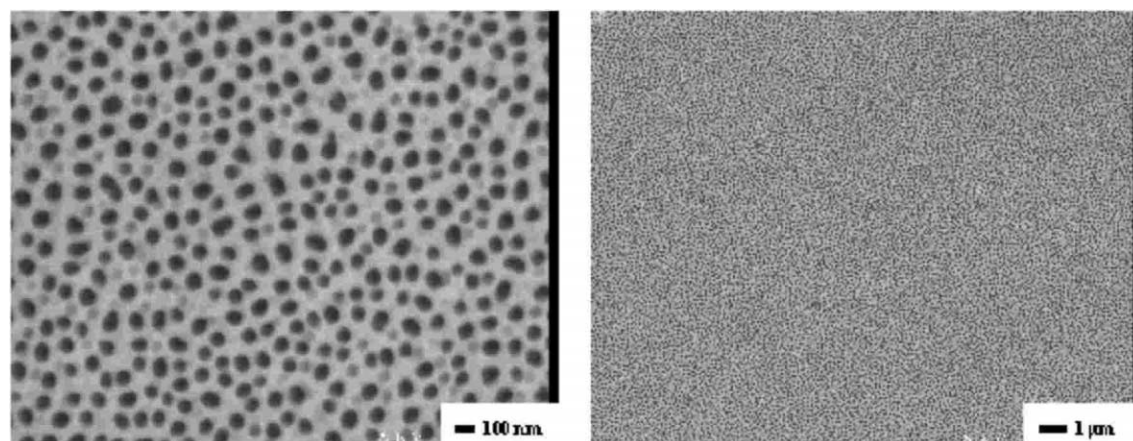


Fig. 3. Electron micrograph of the surface of an alumina membrane anodized at 60 V at two magnifications.

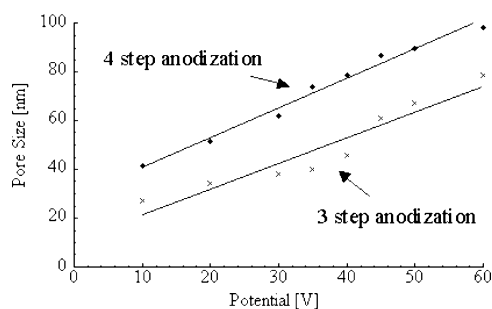


Fig. 4. Dependence of pore size on anodization potential at 180 s for three and four anodizations, respectively. A linear fit for both graphs is also shown.

three etching steps) had nominally 20 nm larger pores due to an extra anodization/etch cycle. Both sections were anodized for 180 s at each anodization.

An increase in long range uniformity was observed with an increased number of anodization/etch cycles. Although larger pores could be created even with a single step at high voltages and short (10 s) anodization times, three or more anodization/etch cycles with longer anodization times (180 s) resulted in more uniform pore distribution. Fig. 5 shows micrographs of library regions representing all anodization/etch cycles. Even at low anodization potentials, uniform pores are created. At higher potentials and increased anodization/etch cycles, it appears that the pores grow, and merge together, resulting in a nearly close-packed arrangement. This is believed to be the first step in the development of ordered, hexagonal alumina pores. Fig. 6 reveals an interesting feature observed for long anodization times and high potentials. A layer of small pores (e.g. 43 nm for 40 V; 53 nm for 50 V) lies

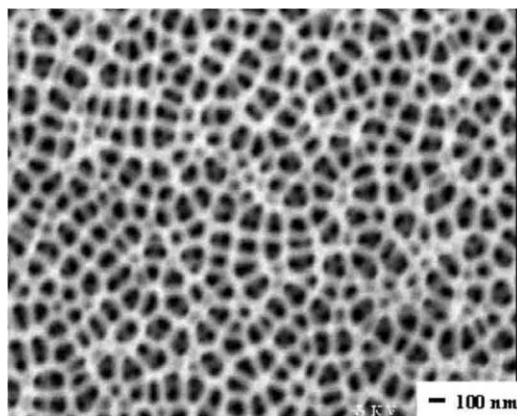


Fig. 6. Electron micrographs of a sample anodized four times at 180 s and 50 V. An underlying small pore size structure is produced underneath a larger network of alumina pores.

underneath a layer of larger pores (92 nm for 40 V; 106 nm for 50 V). This could very well be a result of the relatively short etching step. For samples with deeper aluminum oxide layers (from longer anodization times and/or higher anodization potentials), not all the oxide is removed during the etching step. Therefore, upon the next anodization step, the unetched, porous aluminum oxide structure is enlarged and smaller pores are generated in the underlying material.

To evaluate if longer anodization times improve the quality of the pores we introduced two rows (7 and 8 in section B) which were anodized at 180 s/600 s and 600 s/180 s, respectively. Densely packed pores were obtained. Compared to the shorter anodization time, it can be seen that longer anodization time creates pores of greater density and uniformity. There is no signifi-

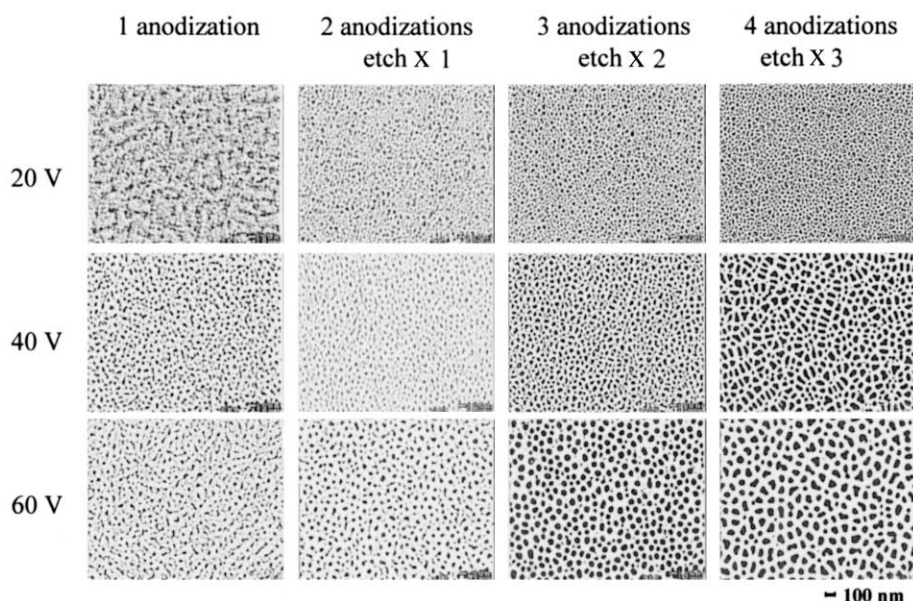


Fig. 5. Electron micrographs showing different anodization/etch sequences for 180 s anodization at different potentials.

cant difference between these two rows at higher voltage, but at lower voltage, longer times result in deeper pores. Since we did not analyze the pore depth, we cannot quantify this observation.

#### 4. Conclusion

In conclusion, an automated system for electrochemical synthesis of combinatorial libraries is developed and utilized for high speed, controlled electro-oxidation of aluminum. A macroporous aluminum oxide library with 256 members was synthesized demonstrating on a single substrate trends in morphological and geometrical properties as a function of oxidation voltage. These trends were consistent with work done previously using conventional, single sample, methodologies. In addition, the relationship between etching, pore size, and voltage was determined. This automated electrosynthesis methodology will be utilized in future work involving selective depositions into the macroporous substrates.

#### Acknowledgements

This research was funded by a generous gift of the Paul Glenn Foundation and made use of the MRL Central Facilities supported by the National Science Foundation under Award No. DMR96-32716. C.B. thanks the Swiss National Science Foundation for a postdoctoral fellowship. T.F.J. thanks the GEM Consortium and the Rohm&Haas Company for their graduate education fellowship support.

#### References

- [1] C.P. Collier, R.J. Saykally, J.J. Shiang, S.E. Henrichs, J.R. Heath, *Science* 277 (1978) 1997.
- [2] E.W. Wong, P.E. Sheehan, C.M. Lieber, *Science* 277 (1971) 1997.
- [3] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, *Science* 283 (1999) 512.
- [4] A.K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem. Int. Ed.* 38 (1999) 3269.
- [5] J.Y. Ying, C.P. Mehnert, M.S. Wong, *Angew. Chem. Int. Ed.* 38 (1999) 56.
- [6] H. Masuda, K. Fukuda, *Science* 268 (1995) 1466.
- [7] V.M. Cepak, C.R. Martin, *Chem. Mater.* 11 (1999) 1363.
- [8] C.R. Martin, *Science* 266 (1961) 1994.
- [9] B.B. Lakshmi, P.K. Dorhout, C.R. Martin, *Chem. Mater.* 9 (1997) 857.
- [10] D. Routkevitch, T. Bigioni, M. Moskovits, J.M. Xu, *J. Phys. Chem.* 100 (1996) 14037.
- [11] D. Routkevitch, A.A. Tager, J. Haruyama, D. Almalawi, M. Moskovits, J.M. Xu, *IEEE Trans. Electron Devices* 43 (1996) 1646.
- [12] D. Almalawi, C.Z. Liu, M. Moskovits, *J. Mater. Res.* 9 (1994) 1014.
- [13] X. Bao, F. Li, R.M. Metzger, *J. Appl. Phys.* 79 (1996) 4866.
- [14] F. Li, R.M. Metzger, W.D. Doyle, *IEEE Trans. Magn.* 33 (1997) 3715.
- [15] F. Li, R.M. Metzger, *J. Appl. Phys.* 81 (1997) 3806.
- [16] R.M. Metzger, V.V. Konovalov, M. Sun, T. Xu, G. Zangari, B. Xu, M. Benakli, W.D. Doyle, *IEEE Trans. Magn.* 36 (2000) 30.
- [17] G.E. Thompson, G.C. Wood, *Nature* 290 (1981) 230.
- [18] J.P. O'Sullivan, G.C. Wood, *Proc. Roy. Soc. Lond. A* 317 (1970) 511.
- [19] A.P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, *Adv. Mater.* 11 (1999) 483.
- [20] A.P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, *J. Appl. Phys.* 84 (1998) 6023.
- [21] O. Jessensky, F. Müller, U. Gösele, *J. Electrochem. Soc.* 145 (1998) 3735.
- [22] O. Jessensky, F. Müller, U. Gösele, *Appl. Phys. Lett.* 72 (1998) 1173.
- [23] L. Zhang, H.S. Cho, F. Li, R.M. Metzger, W.D. Doyle, *J. Mater. Sci. Lett.* 17 (1998) 291.
- [24] V.V. Konovalov, G. Zangari, R.M. Metzger, *Chem. Mater.* 11 (1999) 1999.
- [25] A.P. Li, F. Müller, U. Gösele, *Electrochem. Solid State Lett.* 3 (2000) 131.
- [26] V.P. Parkhutik, V.I. Shershulsky, *J. Phys. D Appl. Phys.* 25 (1992) 1258.
- [27] Y.E. Makushok, V.P. Parkhutik, J.M. Martinez-Duart, J.M. Albella, *J. Phys. D Appl. Phys.* 27 (1994) 661.
- [28] The public domain NIH Image program (developed at the US National Institutes of Health and available on the Internet at <http://rsb.info.nih.gov/nih-image/>) and the Adobe PHOTOSHOP program were used for image analysis.