Influence of Anodizing Parameters on Pore Diameter of Anodic Aluminium Oxide (AAO) Films Using Taguchi Design

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Abstract Nanoporous anodic aluminium oxide (AAO) films were fabricated by using a two-step anodizing process of aluminium foils in oxalic acid electrolyte. The effect of synthesis conditions including applied voltage, electrolyte concentration and temperature on the pore diameter of AAO films was investigated. To reduce the number of experiments, the Taguchi L9 orthogonal array was adopted and the results were analyzed using minitab15 software. It was found that the pore size increased in direct proportion with the applied voltage. The proportion of the pore size with increasing electrolyte concentration was at first direct and then inverse and the maximum pore diameter was obtained in the case of 0.3 M. The pore size relation with increasing electrolyte temperature was at first inverse and then direct and the minimum pore diameter was seen at 10 °C. The diameter of the nanopores were predicted with the software in the range of 35–71 nm in different conditions of selected experimental parameters. Also, as a practical application of obtained AAO films, template-synthesis fabrication of polypyrrole nanowire arrays by electrochemical polymerization of pyrrole within the pores of the obtained AAO was successfully demonstrated.

Keywords Anodic alumina · Pore diameter · Taguchi design · Nanowire

1 Introduction

In recent years, nanoporous anodic aluminium oxide (AAO) films have attracted increasing interest due to their potential applications in ultrafiltration and gas separation [1], hemodialysis [2], Li rechargeable batteries [3] and so on. Also they are extensively used as templates for the fabrication of nanomaterials, such as metallic [4–6], metal oxide [7] and conducting polymer [8–11] nanotubes and nanowires. These nanostructures which are produced by filling the pores of the AAO template, have uniform and adjustable
pore diameter and length, and can be obtained reproducibly and economically. AAO films present many desirable characteristics including tunable pore dimensions, good mechanical and thermal stabilities in a wide range of temperatures, remarkable hardness and a well-developed and not expensive preparation process [12].

The phenomena of nanoporous anodic alumina film formation have been studied extensively over several decades, with considerable scientific attention towards explanation of the mechanism of self-organized growth of the porous layer. Although the mechanism by which pores grow is still in debate, several pore formation models have been proposed and developed [13–17]. The field-assisted mechanism of oxide growth is commonly used to describe the self-organized growth of anodic porous alumina films [13, 18, 19].

The porous structure of anodic alumina film develops from the barrier-type coating formed on aluminum at the start of anodizing. For the steady-state film growth, the average field across the barrier layer dictates the film growth, and the locally increased field at the pore base–electrolyte interface results in the so-called field-assisted dissolution of the oxide film. The steady-state growth of anodic alumina is a result of dynamic equilibrium between oxide growth at the metal–oxide interface and field-assisted oxide dissolution at the electrolyte–oxide interface. Oxide formation is associated with opposite direction migrations of $\text{Al}^{3+}$ and $\text{O}^2-/\text{OH}^- \text{ions}$ due to the applied electric field, the Al–O bond is weakened and so dissolution of the metal cations is promoted. Chemical dissolution of the oxide, by the acidic electrolyte also takes place during anodizing, although dissolution of alumina by the electrolyte is of little concern [13, 14, 20].

A two-step anodizing process can be used to fabricate more ordered and regularly arranged nanopore arrays with straight holes throughout the oxide film in comparison with the pores produced in the first anodizing step which are not parallel to each other [21]. Nanoporous alumina films are in the form of high-density hexagonally ordered arrays including of parallel and cylindrical channels with uniform diameters. The pore characteristics in terms of pore diameter, interpore distance and AAO film thickness are dependent on the anodizing parameters such as applied voltage, anodizing time, solution temperature, chosen electrolyte and its concentration [22].

As aforementioned, nanotubes and nanowires have been extensively fabricated by deposition of various materials inside the pores of AAO templates and thus pore diameter is one of the most important structural features of porous alumina membranes, since it affects the characteristics of the produced nanostructures. Therefore, pore diameter was chosen to study in the current research. The relation between pore diameter and anodizing parameters of AAO films fabricated by anodizing in different electrolytes has been reported. Different relations have been observed during anodizing in different electrolytes [13, 19, 23]. For example, Sulka and Parkola [19, 23] reported the relation between pore size and anodizing potential conducted in sulfuric acid at various anodizing temperatures. Belwaker et al. [22] investigated the effect of applied voltage and electrolyte concentration on pore characteristics of AAO membranes anodized in sulfuric acid. They examined the influence of anodizing applied voltages of 30 and 40 V in 2.7 wt% oxalic acid electrolyte, too. Since fewer researches had focused on the effect of anodizing parameters on the pore diameter of AAO films produced through anodizing in oxalic acid electrolyte, it was investigated in the current research. The significance of oxalic acid as the anodizing electrolyte is that the AAO films obtained in oxalic acid are the primary and widely used templates for synthesizing nanostructures. This is because aluminium anodizing in oxalic acid electrolyte is very stable and easy to control, but the anodizing process in sulfuric acid and phosphoric acid is not stable and burning effect may happen during anodizing [24].

Finally, The novelty and objective of this study is to determine the effect of anodizing parameters of AAO films synthesized in oxalic acid electrolyte, including applied voltage, electrolyte concentration and temperature on the pore diameter by using of Taguchi experimental design. In order to understand the effect of parameters, the traditional way, i.e., varying one parameter and keeping others constant is often used. By means of Taguchi technique, the number of experiments that cause an increase in time and cost is reduced. Taguchi design can determine the effect of factors on characteristic properties [25]. In addition, we also demonstrated practical application of the produced AAO films in synthesizing polypyrrole nanowires within the pores of AAO by electrochemical polymerization.

2 Experimental

2.1 Experimental Design

In the Taguchi method, the parameters of the system which mainly affect the output objective function, are known as the control factors. In this research, oxalic acid was chosen as the electrolyte with the concentrations of 0.2, 0.3 and 0.4 M, at temperatures of 3, 10 and 17 °C and the applied voltages were 30, 40 and 50 V. So, three control factors with three levels were chosen and their effect on the pore diameter of the synthesized AAO was studied in this work. The process parameters and their selected levels are presented in Table 1.

For three parameters at three levels, the traditional full factorial design would require $3^3$ or 27 experiments. The orthogonal array can provide an efficient means to perform the experiments with the least number of trials. In the current