Research paper

Use of High-Voltage Cyclic Voltammetry to Characterize Bulk and Interfacial Conduction Processes in Anodic Alumina Films

Shinsuke Ide, Pratyush Mishra, Kurt R. Hebert*

Department of Chemical and Biological Engineering, Iowa State University, Ames, IA 50011, United States

ABSTRACT

A high-voltage cyclic voltammetry method is introduced that enables separate determination both the bulk conduction kinetics of anodic films and kinetics associated with interface processes. The results confirm that ionic conduction in the oxide follows a high-field exponential dependence on the electric field with a field coefficient of approximately 33 nm/V, consistent with reported values for barrier-type films formed in neutral solutions. The correlation of the pre-exponential current density with the incorporation level of different acid anions from the anodizing bath suggests that conduction is enhanced by anionic contaminants. Current densities associated with self-ordered pore formation in different solutions seem to be associated with a common narrow range of electric fields. The large size of the interface potential drop suggests that it derives from the elevated conduction resistance of an anion-contaminated oxide layer close to the solution interface. Such resistive surface layers are thought to be the source of compressive stress that drives oxide flow during self-organized pore formation.

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1. Introduction

Porous anodic oxide (PAO) films on metals such as aluminum and titanium are widely investigated as controllable templates for functional materials [1,2]. Porous anodic alumina, the focus of the present work, consists of hexagonally-ordered arrays of parallel cylindrical pores embedded in amorphous aluminum oxide. The dimensions of the porous layer geometry are sensitive to the composition of the anodizing solution as well as to the voltage and current density during anodizing. The anodizing voltage determines the interpore spacing of porous alumina according to a universal scaling ratio of 2.5 nm/V; however, self-organized porous films in sulfuric, oxalic and phosphoric acids are obtained only at specific voltages of respectively 25, 40 and 195 V [3]. While it is well-known that acid anions incorporate in porous anodic alumina films, the reasons for the decisive influence of acid type on geometry have not been determined.

Mechanistic studies of PAO formation would be significantly aided by improved knowledge of ionic conduction in the oxide. The rate of anodic oxide growth is controlled by high-field electrical migration of metal and oxygen ions through the film [4]. Ono et al. showed that formation of highly-ordered porous films in different acids occurs at the same threshold electric field strength, but at different current densities according to acid-specific ionic conduction kinetics [5]. Since acid anions incorporate to varying extents in anodic alumina [6], this may suggest that conduction kinetics depend significantly on contamination with electrolyte species. Ionic conduction in anodic films is further complicated by the possibility of spatially nonuniform conduction resistance. Evidence now suggests that pore growth is assisted by oxide flow away from the pore base and toward the pore walls [7–12]. Finite element calculations indicated that such flow is driven by compressive stress in the oxide close to the pore base [8]. Recently, we measured stress distributions in barrier anodic oxide films formed by anodizing Al in phosphoric acid [11]. Compressive stress was found to accumulate within a several nanometer-thick layer adjacent to the barrier oxide-solution interface; the same layer also contained elevated concentrations of incorporated phosphate ions. Compressive stress buildup and anion accumulation in the oxide close to the interface suggest locally elevated ionic conduction resistance. In addition, kinetics of ion-transfer reactions at the film interfaces may influence the current-potential characteristics of relatively thin anodic films [13,14].

Only limited measurements of ionic conduction are available in the literature for the conditions of PAO growth. Ebihara et al. used a mathematical model incorporating the pore base geometry to derive bulk conduction characteristics from steady-state current measurements during Al anodizing in sulfuric and oxalic acids [15].

Dell'Oca and Fleming used ellipsometry to validate the high-field conduction rate law for growth Al barrier oxides in phosphoric acid [16]. In the work reported here, we introduce a new method using high-voltage cyclic voltammetry (CV) to determine separately the interfacial and conduction kinetics of anodic alumina barrier films formed during the early stages of anodizing in solutions of sulfuric, oxalic and phosphoric acids. Cyclic voltammetry has been applied to investigate oxide thickness nonuniformities [17], aluminum passive film dissolution induced by chloride ions [18,19], coupled ionic conduction and oxide dissolution in solutions of various oxyanions [20,21], and the effects of potentiodynamic conditions on anodizing [22]. With the exception of the latter work, these studies did not consider high potentials relevant to PAO formation. In the present article, we show that for sufficiently large voltage sweep rates, cathodic-direction scans of CV reveal the combined conduction characteristics of the bulk oxide and its interfaces. Using experiments where the anodic potential limit of CV is varied to reveal the effect of oxide thickness on conduction, diagnostic plots are constructed from which bulk and interface conduction rate laws are separately determined. The results demonstrate effects of anion incorporation on both bulk and interface layer conduction and provide evidence for resistive surface layers.

2. Experimental Methods

Aluminum specimens were cut from 0.1 mm thick 99.99% purity aluminum foil (Toyo Aluminum Corp.). The surface preparation procedure consisted of first degreasing samples with acetone and then rinsing with deionized water. After drying, samples were etched at room temperature in 10 wt% sodium hydroxide solution and then dipped in 30 vol% nitric acid. All solutions were prepared from reagent grade chemicals and deionized water. Anodizing was carried out in aerated acidic solutions at room temperature (23 °C). The anodizing cell was a glass two-electrode cell with Al electrode working area 0.95 cm^2 and a platinum wire counter electrode. Various acid anodizing baths were used, consisting of 0.3 M and 0.5 M H_2SO_4, 0.2 M and 0.3 M $H_2C_2O_4$ or 0.4 M H_3PO_4. Cylic voltammetric scans were initiated about 5 s after immersing the electrode. The applied potential was swept between the initial potential of 0 V and the maximum potential of 30 V, using a high-voltage potentiostat/galvanostat (Gamry Instruments Reference 3000). In all these solutions, barrier anodic oxide films were formed during the voltage sweeps, since the anodic potential limits were smaller than the potentials at which pores initiate. To establish the counter electrode potential during anodizing, three-electrode cells were set up using the anodizing baths as solutions, along with the Pt wire as a working electrode and a mercury/mercurous sulfate reference electrode. The Pt potential was swept in the cathodic direction from the open circuit potential, and the range of potentials corresponding to currents passed during anodizing was determined.

3. Results and Discussion

3.1. Cyclic Voltammetry Results

Fig. 1 shows examples of voltammetric cycles in 0.5 M H_2SO_4 at different scan rates. During the anodic sweep, the current density increases rapidly to a plateau over a potential range of about 2–4 V. The current density on the plateau increases with scan rate. At 10–20 V, the plateau current density begins to slowly increase, and then upon reversal of the scan direction at 30 V, the current density drops to low values within a potential range of 5–7 V. The cyclic voltammetric response in Fig. 1 is similar to that reported previously near the open circuit potential [17,18,20,21,23,24], as
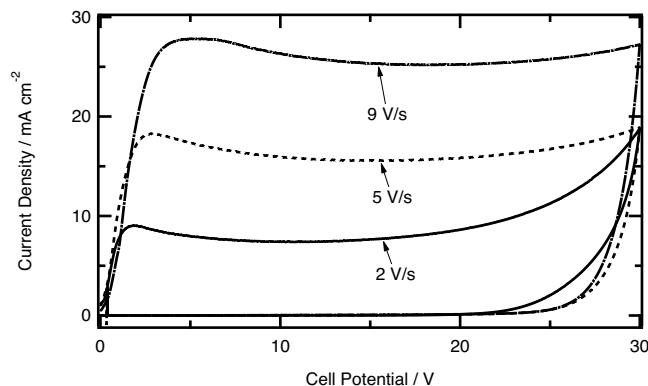

Fig. 1. Cyclic voltammetry with various scan rate in 0.5 M sulfuric acid. In each potential cycle, the current density is highest during the anodic-direction scan.

well as during anodic oxide growth at higher potentials [22]. During the anodic-direction scan, anodic oxide grows at the roughly constant plateau current density in a similar fashion as galvanostatic anodizing experiments. Indeed, the scan rates in Fig. 1 and those of CV experiments in other anodizing baths were selected because the plateau current densities represent those often used for constant current porous oxide growth [25]. The plateau current density determines the approximately constant electric field in the anodic oxide through the conduction rate law, and also dictates the rate of oxide growth through Faraday's Law. The scan rate relates directly to the oxide growth rate, as it is approximately equivalent to the product of the electric field and the growth rate. The rapid decrease of current density during the cathodic scan is influenced by the highly sensitive dependence of current density on electric field according to the high-field ionic conduction rate law [4]. The main goal of the present experiments was to extract both bulk and interfacial conduction kinetics from the cathodic scans.

Depending on the oxide solubility and the sweep rate, significant oxide dissolution may occur during the cathodic scans, complicating the interpretation of the CV response [18,20]. A second voltammetric cycle was applied to reveal the extent of oxide dissolution. Fig. 2(a) compares the first and second cycle CV response in 0.5 M sulfuric acid. Several CV experiments are shown at a common scan rate of 9 V/s but different anodic potential limits. The current-potential curve for the second anodic-direction sweep is displaced by about 0.5 V in the positive direction from that of the first cathodic-direction scan. In contrast, oxide dissolution would induce a *negative* potential shift of the second anodic-direction scan [18,20]. The absence of such a negative shift implies that no significant oxide dissolution occurred, as a result of the large scan rate of 9 V/s. The small displacement of the second scan toward anodic potentials is apparently attributable to a small amount of oxide growth during the first cathodic-direction and second anodic-direction scans. Thus, the high scan rates chosen here eliminate dissolution as a complicating factor for interpretation of the first cathodic scan.

The absence of significant oxide dissolution during cyclic voltammetry means that the first cathodic-direction scan reflects the current-voltage characteristics of the oxide film formed by anodizing to the anodic potential limit. As discussed above, the maximum anodizing potential is empirically found to determine the oxide thickness, according to the "anodizing ratio" of about 1.0 nm/V [26]. Therefore, the cathodic-direction scans of the first CV cycles in Fig. 2(a) may be interpreted as a series of current-potential characteristics for films of different controlled