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RESEARCH ARTICLE

Controlling the thickness of electrochemically produced porous alumina membranes: the role of the current density during the anodization

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Abstract A study of the thickness growth rate of anodized porous alumina membranes (PAMs) and its connection to the current density during the anodization process is presented. Several samples of PAMs were prepared in a hydrate solution of 0.3 M oxalic acid, under applied voltages of 40 and 50 V with varying solution temperatures in a purpose-built electrochemical cell. The thickness of the PAMs produced under these conditions was measured using cross section images taken by scanning electron microscopy (SEM). From these measurements, a linear expression between the growth rate of PAMs and the current density during the anodization is deduced, giving an efficiency value of 53 and 65 % for applied voltages 40 and 50 V, respectively. In steady state conditions, i.e., after the stabilization of the anodization current, this linear dependence is very conveniently transformed into linear dependence of thickness versus total anodization time, providing thus a simple method for controlling the thickness of the produced membranes. Finally, from the Arrhenius-type plot of the thickness growth rate versus temperature and the anodization current density vs temperature a mean value of 48.5 kJ mol^{-1} for the aluminum oxide formation activation energy E_a is deduced.

Keywords Porous alumina · Anodization · Activation energy · Growth rate

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1 Introduction

Porous anodic alumina membranes formed under aluminum anodic oxidation have received particular attention over the past 20 years due to their wide range of applications in optical, magnetic, and electric nano-devices, and their use as filters or templates for the fabrication of nanowires, nanotubes, and chemical sensors [1–8]. The membrane morphology is crucial for each particular application; hence, precise control during the fabrication process is of major importance. The morphology of PAMs is basically described by four parameters, the mean pore diameter (D_p), the inter-pore distance (D_{int}), the barrier layer thickness (L_b), and the thickness of the membrane (h). The dependence of the D_p, D_{int}, and L_b on the anodization parameters has been described in detail in a number of studies [9–14]. It is widely accepted that these three parameters are proportional to the applied voltage with the proportionality constant ranging from 1 to 1.5 nm V^{-1} for D_p [9, 10], from 2 to 2.5 nm V^{-1} for D_{int} [11, 12], and from 1 to 1.3 nm V^{-1} for L_b [13, 14].

Several attempts have appeared in the literature in order to explore the mechanism of pore formation during aluminum anodization [15–17]. Proposed mechanisms can be basically distinguished as based on (i) field assisted dissolution, (ii) oxygen bubble effect, and (iii) stress driven viscous oxide flow.

According to the model of field assisted dissolution, the oxide grows at the metal/oxide interface due to counter migration of Al^{3+}, O^{2-}, and field assisted dissolution of the alumina at the oxide/electrolyte interface. In contrast to chemical dissolution, field assisted dissolution involves the breakage of the Al–O bond with the aid of an external electric field. Increased current density at the bottom of the alumina pores raises the temperature locally easing thus the

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dissolution [18]. The initial pore growth sites are ridges, grooves, and other surface irregularities that pre-exist on the aluminum surface at the beginning of the anodization [19].

In the oxygen bubble effect model, oxygen bonded in the alumina structure undergoes conversion to oxygen gas either at the oxide bulk or at the oxide/electrolyte interface [20]. Additionally, the Al^{3+} ions released during this process are ejected from the oxide/electrolyte interface where they react with electrolyte anions [21]. Oxygen gas evolution initially takes place at impurity center sites or at defect sites with local high lattice stress leading to small pores formation. Oxygen gas generated this way causes the formation of bubbles exerting an isotropic pressure at the metal oxide interface. The oxide layer erupts under this pressure, and the barrier layer is dissolved. Repeated cycles of this procedure lead to the eventual formation of the pores. It is not yet very clear though through which mechanism, the oxygen ion loses electrons in order to be transformed to oxygen gas. A possible explanation of the oxide conductivity required for the above electron transfer is the ionization via a Pool–Frenkel mechanism of the incorporated species in the aluminum oxide originated from the free radicals of the electrolyte [20].

A slight variation of this model [22] adopts the migration of aluminum as neutral atoms (Al) and not as aluminum cations (Al^{3+}). Al atoms, reach the interface where they react with protons, converting to Al^{3+}.

The stress viscous oxide flow model is recently introduced [23, 24]. According to this model, pores grow both due to ionic migration through the oxide and creep from the oxide toward the pore walls. The latter is a consequence of mechanical stress gradients arising inside the oxide bulk. More specifically, this compressive stress arises through the competition of incoming O^{2-} at the pore bottom with the electrolyte anions adsorbed at the surface. This mechanism has been confirmed both by simulations and experimentally, observing the movement of tracers. Another possible cause of this mechanical stress is the pressure exerted by the oxygen bubbles at the electrolyte/oxide interface, generated in a similar manner to that observed in solid oxide electrolyte cells [25].

Although thickness is a key parameter for a number of applications, the growth rate of PAM under potentiostatic anodization conditions is not studied as extensively as pore formation. In a recent work by Zaraska et al. [26], the effect of the anodization parameters on the PAM geometrical characteristics has been studied in detail. The anodization time versus the final thickness of PAMs fabricated under a variety of anodization conditions has been established in the above work. Although the extracted relation is very useful for estimating the thickness of the PAM, it is restricted to a number of specific anodization conditions and cannot be of more general use. Therefore, the need of establishing a relationship connecting the growth rate of PAM thickness with a more general anodization parameter remains very important to the ever-growing PAM community. It is widely known that different anodization parameters as for example the kind and temperature of the electrolyte have a direct effect on the current density transferred through the electrochemical cell. Obviously, the geometrical characteristics of the cell itself (such as the size and distance between the electrodes) have also an effect on current density. Current density is a parameter that can always be calculated independently of other experimental conditions. Therefore, the investigation of its relationship to the growth rate of PAMs could lead to a useful tool for the control of the final thickness of the membrane in a universal way, i.e., under any experimental conditions.

2 Experimental set up

For the experimental requirements of this work, an electrochemical cell has been designed (Fig. 1). PTFE has been chosen for the cell construction, a material combining substantial thermal and chemical resistance. The cell is filled with the electrolyte solution which comes into contact with the Al foil to be anodized via a 22-mm hole drilled in the bottom of the cell and sealed with an o-ring. A nickel grid (60 mesh) serves as the cathode electrode, while the Al foil is connected to the anode via a spring loaded contact. The cell with the sample fitted is placed on a Peltier cold plate with adjustable temperature settings.

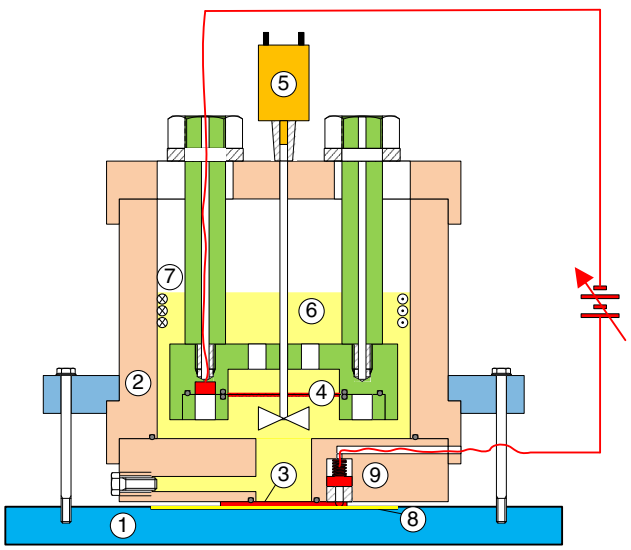

Fig. 1 Schematic representation of the experimental setup. *1* cold plate, *2* PTFE cell, *3* Al foil sample, *4* nickel electrode, *5* motor stirrer, *6* electrolyte solution, *7* heat exchanging coil, *8* thin electrical insulating membrane, and *9* spring loaded contact

Furthermore, the electrolyte solution is always kept at a constant temperature with the aid of a heat exchanging circuit immersed in the solution which is also continuously stirred by a motor stirrer attached on the cap of the cell. A thin plastic membrane is fitted between the sample and the cold plate for electrical insulation purposes.

3 Experimental procedure

High purity aluminum foil (99.99 %) was used for the fabrication of PAMs. Prior to anodization the aluminum foil's surface received an electropolishing treatment at 60 °C for 60 s under an applied voltage of 20 V. The electropolish solution consisted of H_3PO_4, H_2SO_4, and distilled water in 4:4:2 (v/v), and the procedure was followed by washing the aluminum with distilled water and ethanol. Then, the anodization of the Al foil takes place in a hydrate solution of 0.3 M oxalic acid for applied voltages 40 and 50 V. In order to determine the porosity and the density of PAMs with adequate accuracy, the two-step anodization method was used as the pores formed during the second step of anodization is regularly distributed. Furthermore, there is no difference in oxide growth rate for the first and second anodizing step [27]. After the post-anodization chemical dissolution of the oxide, the alumina density was calculated by a gravitational method which resulted to a value of 3.1 g cm^{-3}. The porosity was estimated to 20 % for 40 V and 16 % for 50 V from SEM images with an error of 2 % for all samples. The duration of the anodization procedure varied between 3 and 4 h, while the temperature was kept constant for each PAM and varied from −0.5 °C upto 20 °C, which falls in the region of mild anodization conditions. Special precaution must be taken in order to accurately stabilize the temperature during the anodization procedure since the exothermic nature of the reactions taking place inside an electrochemical cell tends to increase the temperature resulting to the increase of the current density. Fresh electrolyte solution was always used, in order to avoid extra Al^{3+} remaining from previous anodizations that could contribute to the measured current and lead to erroneous values for the current density. The thickness of the produced membranes was measured using cross sectional views of scanning electron microscopy (SEM). In Fig. 2a, it is clear that porous alumina growth is uniform throughout the sample's section. The porosity was measured from top views of samples formed by a two-step anodization process (Fig. 2b, c).

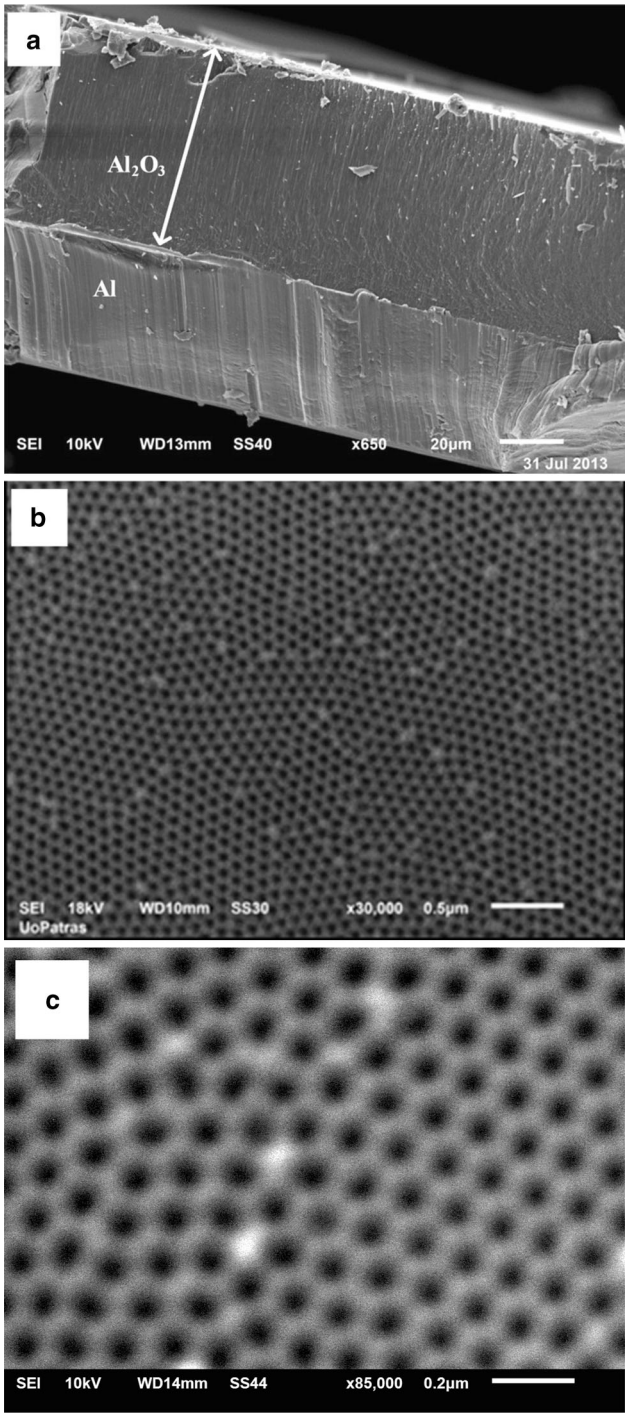

Fig. 2 SEM images **a** section view of PAM fabricated under 40 V, 7.5 °C with its aluminum substrate. **b** Top view of a sample after 2-step anodization under 40 V, 5 °C, 4 h. **c** Top view of a sample after 2-step anodization under 50 V, 14 °C, 3 h

4 Results–discussion

In Fig. 3, a typical current density graph against anodization time is presented. Within several seconds from the onset of the anodization, the current reaches a constant value, indicating that the aluminum oxide growth rate is stable over time.

The measured current corresponds primarily to the movement of O^{2-} anions arriving at the metal/oxide

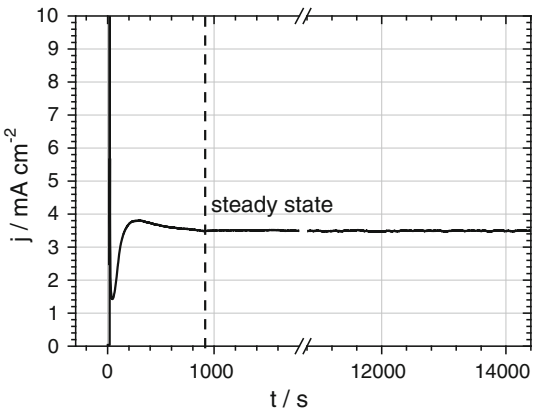

Fig. 3 Current versus time graph for anodized sample at 40 V and 7.5 °C

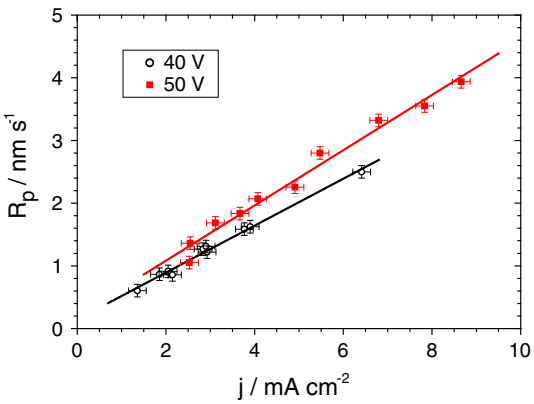

Fig. 4 Plot of thickness growth rate R_p versus steady state current density j for the samples anodized under 40 and 50 V in 0.3 M oxalic acid and at temperatures varying from −0.5 °C upto 20 °C

interface and also to the current of Al^{3+} cations which are ejected to the electrolyte. At the metal/oxide interface, Al^{3+} cations are formed and their mass $m_{Al^{3+}}$ according to Faraday's law is

$$m_{\left(Al^{3+}\right)_{n=100\%}} = \frac{M_{Al}}{z\,F}\; i\; t \tag{1}$$

where M_{Al} is the molar mass of aluminum, i is the total current of the anodization, t is the duration of the process, F is Faraday's constant, and z the number of electrons involved in the reaction. Three electrons are produced in the aluminum oxidation process ($z = 3$), while at the anode, two O^{2-} convert to O_2 gas by losing four electrons. Some of the Al^{3+} ions migrate through the bulk of the oxide and reach the oxide/electrolyte interface and are ejected directly into the solution, not participating in the formation of the oxide. Reaction of oxygen evolution and possible migration of aluminum cations contributes to the current measured at the external circuit not taking part into the oxide formation. Thus, the obtained mass of porous oxide according to Faraday's law is

$$m_p = \frac{M_{Al_2O_3}}{z\,F}\; i_{O^{2-}}\; t = \frac{M_{Al_2O_3}}{z\,F}\; i\; T_{O^{2-}}\; t \tag{2}$$

where $M_{Al_2O_3}$ is the molar mass of Al_2O_3, z = 6 in this case, and $T_{O^{2-}}$ the transport number of O^{2-},

$$T_{O^{2-}} = \frac{i_{O^{2-}}}{i} \tag{3}$$

The transport number $T_{O^{2-}}$ is the fraction of current carried by the O^{2-} anions, and it is actually the current efficiency of the oxide formation. The mass of porous alumina, m_p is related to the thickness h, via the density, $d_{Al_2O_3}$ and the porosity, p

$$d_{Al_2O_3} = \frac{m_p}{V_{ox}} = \frac{m_p}{S_{ox}(1-p)h} \tag{4}$$

where S_{ox} is the oxide surface area. The thickness of the porous oxide vs. current density combining Eqs. (2), (4) is

$$h = \frac{M_{Al_2O_3}\; i\; T_{O^{2-}}\; t}{z\,F\; d_{Al_2O_3}(1-p)\; S} = \frac{M_{Al_2O_3}\; j\; T_{O^{2-}}\; t}{z\,F\; d_{Al_2O_3}(1-p)} \tag{5}$$

and finally, the rate of growth R_p is obtained as a function of the current density:

$$R_p = \frac{dh}{dt} = \frac{M_{Al_2O_3}\; j\; T_{O^{2-}}}{z\,F\; d_{Al_2O_3}(1-p)} \tag{6}$$

In Fig. 4, the obtained growth rate R_p versus current density j is plotted for anodizations under 40 and 50 V at various temperatures. For the calculation of the current density j, the steady state value of the current was taken into account (see Fig. 3). According to the preceding analysis, the slope λ of the linear fit to the experimental points corresponds to

$$\lambda = \frac{M_{Al_2O_3}\; T_{O^{2-}}}{z\,F\; d_{Al_2O_3}\;(1-p)} \tag{7}$$

Using Eq. (7), the current efficiency for oxide formation T_O^{2-} is estimated, provided that the porosity and density of alumina are the same for all samples. The porosity of the PAMs has been reported to be depended on the time and the temperature of anodization under prolonged time and relatively high temperature due to dissolution mechanisms of the pore wall [28]. However, under the mild anodization conditions of the present work, the porosity was estimated from SEM images to 20 ± 2 % for all samples prepared under 40 V and 16 ± 2 % for samples anodized under 50 V at different temperatures.

On the other hand, it was recently suggested that porous formation is due to stress gradients at the barrier layer and not due to alumina dissolution [29, 30]. This was experimentally confirmed by the observation of tungsten tracers

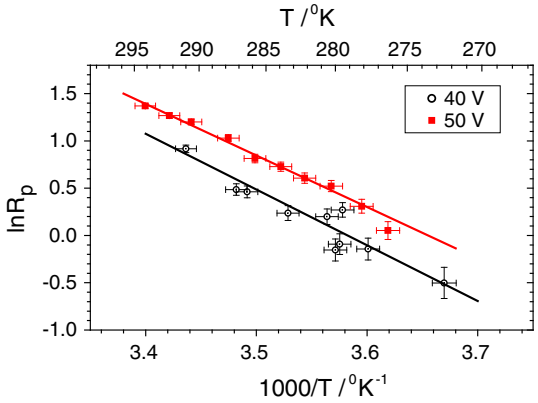

Fig. 5 Arrhenius-type plot of thickness growth rate R_p versus 1000/T of aluminum samples anodized at 40 and 50 V in 0.3 M oxalic acid in the temperature range of −0.5 upto 20 °C

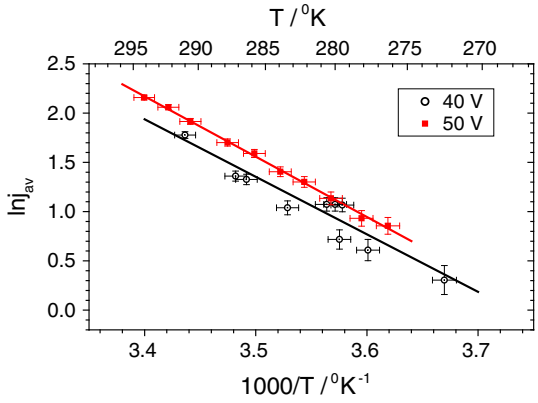

Fig. 6 Arrhenius-type plot of anodization average current density j_{av} versus 1000/T of aluminum samples anodized at 40 V in 0.3 M oxalic acid in the temperature range of −0.5 upto 18 °C and for samples anodized at 50 V in 0.3 M oxalic acid in the temperature range of 2–20 °C

dragged by the oxide which flowed toward the pore wall [31]. It is therefore apparent that the porosity depends mostly on the oxide displacement, rather than the chemical dissolution of the oxide, a procedure with very low formation enthalpy $\Delta H = -1675.7$ kJ mol^{-1} [22]. Small deviations in porosity due to chemical dissolution are possible either after long anodization times or at high temperatures [32].

From the slope of the graph R_p versus j (Fig. 4) and the above mentioned values for the alumina density $d_{Al_2O_3}$ and porosity p, the current efficiency was estimated to 53 and 65 % for samples prepared under 40 and 50 V, respectively, in a good agreement with previously published results [33]. Notably, the linear behavior depicted in Fig. 4 implies a constant transport number T_O^{2-}, for each value of anodization voltage (potentiostatic conditions) which is independent of temperature. From a practical point of view, the linear dependence of R_p versus j provides a very useful tool for in situ controlling the thickness of PAMs during the fabrication process.

In the framework of the present study, the effect of the solution temperature on the alumina growth rate was also investigated.

The linear behavior of lnR_p versus 1000/T shown in Fig. 5 implies an Arrhenius-type relation between the thickness growth rate and the temperature. Assuming that the reaction rate for the alumina formation is a pseudo-first order reaction (the concentration of Al^{3+} is in abundance), the growth rate is given by Eq. (8):

$$R_p = \frac{dh}{dt} \sim r \tag{8}$$

where r is the chemical reaction rate for the pure alumina formation given by Eq. (9):

$$r = A_o e^{-\frac{E_a}{RT}} \tag{9}$$

where R is the universal gas constant, E_a is the activation energy, and A_0 is a constant. Thus, the activation energy can be calculated from the slope of the linear fit of the plot lnR_p versus 1000/T as shown in Fig. 5.

In Fig. 6, the average current density, j_{av}, instead of the steady state current density, j, is used in the Arrhenius-type plot lnj_{av} versus 1000/T (although the two values do not differ significantly). This is justified from the fact that the thickness growth rate R_p is also a time averaged value derived from the final thickness over the total duration of the anodization. The mean activation energy resulting from Figs. 5, 6 for 40 V is 49 kJ mol^{-1} (0.51 eV), while this mean value in the case of 50 V is 48 kJ mol^{-1} (0.50 eV) which are in good agreement with the value of 0.52 eV reported in the literature [34].

Different experimentally determined activation energies E_a are reported in the literature between anodizations carried out in oxalic, phosphoric, and sulfuric acid. For anodization under potentiostatic conditions (100–150 V) in H_3PO_4, the activation energy was found equal to 75.2 kJ mol^{-1} [35]. (The higher the value of the activation energy, the slower a reaction proceeds). It is evident that the reaction of the electrolyte anions with the aluminum will determine the porous alumina formation rate, and this explains the different values of the growth rate when various acids are used as electrolytes for anodization (oxalic, phosphoric, sulfuric etc.). The increase in the value of $T_{o^{2-}}$ (higher growth rate) with the applied voltage (Fig. 4) implies a direct relationship of the available oxygen anions per unit time with the number of incorporated anions [36]. The incorporation rate increases with the applied voltage [37, 38]. The calculation method for oxygen transport number proposed in the present work which is based on measuring the current in the external circuit is direct and

more accurate, avoiding errors induced in methods using tracers [39].

5 Conclusions

In the present work, the effect of current density on the growth rate of porous alumina has been investigated in detail. Using the described electrochemical cell, a number of samples have been prepared under potentiostatic conditions (40 and 50 V in 0.3 M oxalic acid) at different temperatures, and the growth rate has been assessed by SEM analysis. It is found that the growth rate increases linearly with the current density; therefore, this is a useful parameter in order to control the final thickness of the membrane in a universal way. This linear dependence implies a constant value of current efficiency for oxide formation, which for the above conditions was found equal to 53 and 65 % for 40 and 50 V, respectively, and independent of temperature. Moreover, the rate of alumina growth exhibits an Arrhenius-type behavior with the temperature, which allows the estimation of a mean value for the activation energy E_a of alumina formation. Notably, a very close value for E_a can be deduced from the $\ln j_{av}$ versus $1000/T$ plot without the need of using SEM analysis for thickness determination. The estimated mean value of E_a equals to 48.5 kJ mol^{-1} and the dependence of this value, as reported in the literature, upon the acid used, favors models that focus on the role of the electrolyte anions such as the "viscous" flow model. Further investigation is needed in order to clarify the role of these anions on the growth of the porous oxide.

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