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Abstract
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Keywords
aluminum, electrochemical electrodes, sputtered coatings, porous materials, polarisation, modelling, reaction kinetics, corrosion inhibitors

Disciplines
Chemical Engineering

Comments
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An Electrical Model for the Cathodically Charged Aluminum Electrode

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ABSTRACT

A mathematical model was formulated for the surface film on aluminum which considered the film to consist of an inner barrier high-field conducting layer and an outer, porous, ohmically conducting layer. It included all relevant capacitive and faradaic processes, and incorporated the nonlinearity of conduction and reaction rate expressions. The model was used to investigate structural changes produced by cathodic polarization in acid solutions, which has been found to promote anodic pitting strongly in ac etching processes. The film's structural parameters were fit to experimental current transients following anodic potential steps after cathodic charging. The model was found to represent experimental current decays realistically over several orders of magnitude variation of current density (factor of 10^6) and time (factor of 10^10). To a first approximation, cathodic activation could be described in terms of a decrease of the inner layer thickness (b) from about 30 to 15 or 20 Å and an increase of the porosity (p) to 0.62. These changes were interpreted as being due to the rapid penetration of pores into the outer portion of the initial film. The pores may have been produced by electrochemical dissolution of the oxide during cathodic current flow through the film. The promotion of pitting by cathodic charging in chloride solutions suggests that some fraction of the pores may penetrate to the metal.

Introduction

Surface films on structural metals generally have a high electrical resistance which protects them from corrosion. However, the film resistance presents an obstacle to their use in applications where reactivity is desirable. In the case of aluminum, these include the use of the metal as a battery electrode, as well as its use in the chloride solutions for capacitor electrodes and lithographic plates. In the latter process, periods of anodic etching alternate with intervals of polarization at potentials where cathodic hydrogen evolution dominates the electrochemical process. Lin and Hebert found that in single cycles of ac etching, 10^5 pits/cm^2 nucleated in the first 10 ms of anodic polarization, an enhancement of more than 100 times over the case of no prior cathodic charging. Such cathodic "activation" of aluminum has been noted by other authors with regard to the rates of metal dissolution and hydrogen evolution at cathodic potentials. It apparently results from a modification of the surface film by the cathodic processes. In order to understand this activation, knowledge of the film's composition and structure, as they relate to its electrical resistance, is important. For this purpose, in situ characterization of the film is desirable, since oxidation reactions which may change the structure can occur once cathodic polarization is removed.

Previously, electrode processes during polarization at cathodic potentials in 0.1 N HCl or H_2SO_4 were investigated using the quartz crystal microbalance (QCM), infrared reflectance spectroscopy (IRS), and capacitive current transients. After polarization at the cathodic potential of -2.0 V vs. Ag/AgCl, the film had a "duplex" structure consisting of a thin, nonporous "barrier" oxide in contact with the metal and an outer porous layer in contact with the solution. Such two-layer films are frequently found from a modification of the surface film by the cathodic processes. In order to understand this activation, knowledge of the film's composition and structure, as they relate to its electrical resistance, is important. For this purpose, in situ characterization of the film is desirable, since oxidation reactions which may change the structure can occur once cathodic polarization is removed.

Experimental

Aluminum films with thicknesses of about 0.2 µm were deposited on quartz substrates by either dc magnetron sputtering or thermal evaporation. A cryopumped vacuum evaporator (DV-502A, Denton Vacuum, Inc.) was used to prepare the thermally deposited aluminum films. The evaporation process has been described elsewhere. Sputtered films were deposited at a rate of 23 nm/min, to a thickness of 200 nm, using a bias of 40 V on the substrate platform. The Ar pressure in the sputtering chamber was 0.67 Pa.

The electrodes were mounted in a glass electrochemical cell using an O-ring joint. The counter electrode was a platinum wire positioned about 9 cm from the working electrode, and the reference electrode (Ag/AgCl/4 M KCl) was placed between the working and counter electrodes,
about 3 cm from the latter. Prior to electrochemical polarization, the aluminum films were mounted in the cell and pretreated by immersion in 5 weight percent (w/o) H₃PO₄. The pretreatment time for the sputter-deposited films was 20 min, and that for the thermally deposited films was 10 min. After the pretreatment, the cell was rinsed thoroughly by deionized water to remove traces of phosphate ions before the 0.1 N H₂SO₄ solution was introduced into the cell. The open-circuit potentials of pretreated aluminum films were all about −1.05 V, suggesting an approximately uniform oxide film thickness. Potential control was accomplished using a potentiostat (EG&G Princeton Applied Research 273 or Schlumberger 1286). Rapid current transients were recorded to a resolution of 10 μs using a high-speed digital voltameter (Keithley 194A). No inconsistencies were found in measurements using either sputtered or thermally evaporated electrodes.

**Mathematical Model**

Figure 1A presents the physical structure model of a duplex-type surface film on aluminum. Phases (1), (2), (p), and (3) denote the metal, inner layer, porous layer, and bulk solution, respectively. Phase p was present only for cathodic polarization. Phases (1), (2), (p), and (3) denote the metal, inner layer, porous layer, and bulk solution, respectively. (B) Electrical network representation of the electrical model.

![Diagram](image)

Fig. 1. (A) Sketch of the surface film structure. (1), (2), (p), and (3) denote metal, inner layer, porous layer, and bulk solution, respectively. (B) Electrical network representation of the electrical model. The symbols are defined in the text.

An electrical network representation of the model is shown in Fig. 1B. Rᵢ is the ohmic resistance of the solution in the cell. Zᵢ is the porous-layer impedance, which accounts for both conduction and capacitive processes. Rₚ is a lumped resistance representing the electrochemical conduction resistance of the inner barrier layer; combined with the electrochemical charge-transfer resistance at the metal/film interface. Rₚ represents the kinetic resistance of the charge-transfer reactions, metal and oxide ion transfer, at the film/solution interface at the pore bottoms. Cₛ is the lumped capacitance of the inner layer and the film/solution interface at pore bottoms. In the following, model equations corresponding to these circuit elements are described.

During anodic film growth, Siejka et al.¹⁷ found that the metal/film interface was close to the potential of the metal in equilibrium with the oxide, −1.51 V for Al/Al₂O₃. Here, it is assumed that, during anodic polarization, the metal/film interface is at a constant potential, Vₘ, which was expected to be close to this value. The primary electrochemical reaction during cathodic polarization (i.e., the initial condition of the model) is cathodic hydrogen evolution.

Since the metal/film interface during anodic polarization is at equilibrium with respect to aluminum oxidation, the current through Rᵢ in Fig. 1B is determined by the potential drop through the inner layer, which drives ionic conduction. Lin and Hebert found that anodic ion conduction in this layer follows the high-field conduction equation¹⁸

$$i_a = i_{a0} \exp \left( \frac{\beta \phi_i}{\delta} \right)$$  \hspace{1cm} [1]

where \(\phi_i\) is the potential drop across the inner layer and \(\delta_i\) is its thickness. In 0.05 M H₂SO₄, \(i_{a0}\) was 9.8 × 10⁻¹² A/cm² and \(\beta\) was 4.86 × 10⁸ cm/V·s. The current during cathodic charging mainly results from reduction of hydrogen ions to hydrogen gas. Lin and Hebert¹⁰ determined that the cathodic current obeyed a Tafel rate expression of the form

$$i_c = -i_{c0} \exp \left[ \frac{-\alpha_i F}{RT} (\phi_i + V_i) \right]$$  \hspace{1cm} [2]

\(i_{c0}\) is 10⁻¹⁵ A/cm², while \(\alpha_i\) is 0.616 (the derivation of \(i_{c0}\) is given in the Appendix). In this expression, the cathodic interfacial and conduction resistances are “lumped” together, the current being given in terms of the potential drop across both resistances. Thus, it is not necessary to know which resistance controls, or even whether protons or electrons carry the current through the oxide (although electronic current is considered unlikely, due to the insulating properties of aluminum oxide). For the modeling calculations, it was necessary to combine Eq. 1 and 2 to provide a single equation which could describe the transition between cathodic and anodic reactions in the potential step experiments. This current, \(i(\phi_i)\), was formed by adding Eq. 1 and 2 along with two small additional exponential terms whose purpose was only to provide continuity of the current while the potential shifted between the anodic and cathodic regions. Despite the presence of these additional terms, Eq. 1 and 2 were dominant during anodic and cathodic polarization, respectively.

After passage through the inner layer, the current flows through the film/solution interface at the pore bottoms. According to Vetter and Gorn¹⁵ and Kirchheim,¹⁶ the reactions at the oxide-electrolyte interface are reversible oxygen transfer between the film and water in solution (current density \(i_p\)), and irreversible dissolution of metal ions from the film (current density \(iₐ\)). These reaction current densities are written in terms of the overpotential of the oxygen transfer reaction, \(\eta_{o₂}\), as
The parameter values here were derived by Lin and Hebert\textsuperscript{18} from the experimental results of Våland and Heusler\textsuperscript{9} and are: \( i_{\text{lo}} = 3.6 \times 10^{-6} \text{ A/cm}^2 \); \( \eta_{\text{lo}} = 2.6 \times 10^{-4} \text{ A/cm}^2 \); \( \alpha_1 = 1.11 \); \( \alpha_1^* = 1.76 \); and \( \alpha_2 = 0.24 \). On the basis of the network, the total current density \( i \) is related to \( \phi_p \) and \( \eta_p \) as

\[
i = i_p(x, \phi_p) + C_2 \frac{d(\phi_p + \eta_p)}{dt} = p(i_\text{lo} + i_p(\eta_p))
\]

\[+ C_2 \frac{d(\phi_p + \eta_p)}{dt} \tag{4}
\]

where \( p \) is the porosity, \( C_2 \), the lumped capacitance of the inner layer, includes the interfacial capacitances and the bulk capacitance. When \( i \) is anodic, film formation at pore bottoms results in pore filling and leads to an increased inner-layer thickness \( \delta \). The rate of increase of \( \delta \) is given by

\[
\frac{d\delta}{dt} = i_p \frac{V_{\text{el}}}{3F}
\]

where \( V_{\text{el}} \) is the molar volume of the film material, 20 cm\(^3\)/mol for ALOOH.\textsuperscript{20}

While the impedance of the porous layer was present in the model only when the cathodic charge was greater than 7 mC/cm\(^2\), it was necessary to include a fractional porosity \( p \) in Eq. 4 for all calculations, even when the cathodic charge was much smaller. These latter cases corresponded to a thin porous layer with a small resistance compared to that of the barrier layer. The effect of a small \( p \) was a large rate of increase of the barrier-layer thickness: the current, taking the shortest path through the oxide film, was concentrated to the pore bottoms, resulting in a large \( L \), and therefore a high rate of pore filling from Eq. 5.

To complete the model, it is necessary to specify the equations corresponding to the porous-layer impedance, \( Z_p \), in Fig. 1B, which was present in the network for cathodic charges larger than 7 mC/cm\(^2\). Since it is assumed that the current flows through the porous layer only via the aqueous pathways (pores), charging of the pore walls can be described by a differential charge balance mathematically equivalent to the diffusion equation

\[
\frac{\partial \phi_p}{\partial t} = \frac{\partial^2 \phi_p}{\partial x^2} \tag{6}
\]

where \( \alpha = \kappa/C_p \alpha \) is a diffusivity for charge. The boundary conditions for Eq. 6 are

\[
\phi_p(L, t) = 0 \tag{7}
\]

\[
i(t) = -\kappa \frac{\partial \phi_p}{\partial x}(0, t) \tag{8}
\]

where \( L \) is the thickness of the porous layer. \( L \) values were determined from QCM frequency measurements during cathodic film growth.\textsuperscript{4} \( \kappa \) was calculated from the cathodic transient and the corresponding porous-layer thickness, as described in detail in the Appendix. The present model for porous-layer charging is similar to ones developed for macroscopic porous electrodes.\textsuperscript{31} Transmission-line networks, which have also been used to model porous-layer impedance,\textsuperscript{26,27} are mathematically equivalent to the diffusion equation above when the number of circuit elements comprising them becomes large.

\[
V_{\text{Ag/AgCl}^{-}} = 0.27 \text{ V} + \phi_p(t) + \eta_p(t) \tag{9}
\]

The constant, 0.27 V, is the correction for the potential of a Ag/AgCl reference electrode with respect to a hydrogen reference electrode in equilibrium with the bulk solution at pH 1.5.

For \( \phi_p \), the initial condition was a linear potential profile corresponding to the initial current density. The initial conditions of \( \phi_p \) and \( \eta_p \) were determined from the current density immediately before the potential step, \( i(0^-) \). In experiments where the potential was stepped from the cathodic to the anodic side of the open-circuit potential, anodic currents of 1 to 10 mA/cm\(^2\) were typically found experimentally in 10 ms after the potential step, which, according to Eq. 3 above, are associated with an approximately constant \( \eta_p \) of 120 mV. Hence, in simulating these experiments, \( \eta_p \) was treated as a constant and not a variable. This procedure avoided the difficulty of setting an initial condition for \( \eta_p \), which was not known during cathodic polarization.

Equations 1 and 2 and 4 through 9 form a closed set of equations which were solved to obtain the current transients. The differential equations to be solved were ordinary differential equations (ODE) except Eq. 6, a partial differential equation (PDE). The orthogonal collocation method\textsuperscript{22} was applied to convert this PDE into a group of ODEs. The resulting system of ODE initial value problems was solved numerically by a Gear method (IVPAG Fortran subroutine from the IMSL Math/Library).

Results

\textbf{Surface film before cathodic charging.}—It was necessary to characterize the film prior to cathodic charging to provide a basis for comparison to experiments in which charge was applied. For this purpose, the steady conduction current was measured as a function of potential. A sequence of potentials was applied, and the current transient recorded at each potential. For a given potential, a stable current was obtained within 2 ms after the step. Since the total duration of the experiment was only 20 ms, it was assumed that no significant film growth occurred, and the stable currents were used for comparison to experiments in which film thickness. In Fig. 2, the stationary anodic currents are plotted on a logarithmic scale vs. the corrected potential, which was obtained by subtracting \( \eta_p \) and \( iR_3 \) from the applied potential. In terms of the electrical model, the corrected potential here is \( \phi_p + V_c = 0.27 \text{ V} \). The linear relation between \( \log i \) and the corrected potential in the figure

- \( i \) is the corrected current density (mA/cm\(^2\)).
- \( V_c \) is the potential difference due to conduction between the film/solution interface.
- \( V_{\text{Ag/AgCl}^{-}} \) is the potential of the aluminum electrode vs. a Ag/AgCl reference electrode.
- \( \eta_p \) is the overpotential due to the cell's ohmic resistance and the overpotential at the film/solution interface.
confirms that the pretreated oxide films were high-field conductors. The solid line represents a linear regression of the data, in which the slope and intercept are 7.43 V⁻¹ and 5.8, respectively. From Eq. 1, the slope is \( B_i/(\delta \ln 10) \), and the intercept is \( \log i_0 - B_i(V_e - 27 V)/6 \ln 10 \). \( V_e \) and \( \delta \) were calculated to be -1.57 V and 28.4 Å, using values of the conduction parameters \( i_0 \) and \( B_i \) known from independent experiments. This rest potential is reasonably close to the potential of aluminum in equilibrium with \( \text{Al}_2\text{O}_3 \), at -1.51 V, and was used in all transient calculations using the model. Also, the film thickness is in agreement with the value of 31 Å from x-ray photoelectron spectroscopy (XPS) measurements.

**Anodic current transients induced by potential steps following cathodic charging.**—These transients, measured after various periods of cathodic charging, revealed the structural changes induced by cathodic polarization. Figure 3 shows the early portion of anodic transients measured by Lin et al. at -0.9 V after various periods of cathodic charging at -2.0 V. The critical cathodic charge, at which growth of the porous outer layer was detected with QCM and IRS, was 7 mC/cm²; only the top curve in the figure had a charge greater than this value. Hence, the differences between the bottom three transients were attributable to modification of the initial film by cathodic charge, as opposed to growth of an overlying porous layer. The presence of distinct time constants which control the transient over different time domains is indicated by approximately linear regions of the log \( i \) vs. time plot. The exponential decay at times less than 0.5 ms has been identified already as due to capacitive charging of the inner layer. When \( C_2 \) was approximately fully charged, porous-layer charging and oxidation dominated the current decay.

In fitting the model to experimental transients, values of parameters for kinetic and transport processes (i.e., high-field conduction, hydrogen evolution, and metal and oxygen ion transfer at the film surface), which had been determined independently, were fixed at the values given above in the Mathematical Model section. When the porous layer was present \( (Q > 7 \text{ mC/cm}^2) \), its resistance was included in the model; the layer thickness and conductivity were taken from QCM measurements, as described in the Appendix. Other parameters relating to the structure of the duplex film were adjusted for best agreement with experimental transients. The measurements of the adjusted parameters for the dashed curves in Fig. 3 are listed in Table I. The first three variables, \( R_n \), \( C_n \), and \( \delta(0) \), were calculated as follows: \( R_n \), the solution resistance, was set to the ratio of the step change in potential \( (1.1 \text{ V, from } -2.0 \text{ to } -0.9 \text{ V}) \) to the change in current at the potential step \( (i(0)^+ \text{ to } i(0)^-)) \). \( C_n \) was determined from \( R_b \), along with the slope of the initial linear decay of \( i(0)^+ \) in Fig. 3 at times smaller than 0.5 ms. The initial value of \( \delta \) was estimated from the current density at the end of this \( C_b \) charging process (at time \( t_c \)), according to the following equation

\[
V_{\text{Ag/AgCl}} + 0.27 V - V_a = \frac{\delta(0)}{B_n} \ln \left( \frac{i(t_c)}{i(0)} \right) + \frac{i(t_c)}{L} + i(t_c)R_3 \quad (10)
\]

Here, the porous layer (if present) was assumed to be uncharged at \( t_c \), so that the potential drop through it was the same as at the cathodic potential. After \( t_c \), the remaining portion of the transients in Fig. 3 were fit using the porosity \( p \) and the time constant of porous-layer charging, \( \tau_p = L^2/\alpha \). When no growth of the porous layer had occurred \( (Q < 7 \text{ mC/cm}^2) \), only \( p \) was available for fitting. As discussed above, the presence of a fractional porosity with no porous-layer resistance in the model is physically realistic when the porous-layer resistance is small compared to that of the barrier-layer; \( p \) still determines the rate of growth of the barrier-layer thickness by Eq. 4 and 5. Generally, Table I shows that cathodic activation of aluminum is accompanied by a decrease of the effective inner-layer thickness and an increase of the porosity. The process of cathodic activation will be described further in the Discussion section.

Figure 4 shows the early portion of another current transient measured after the potential was stepped from -2.0 to -0.9 V, for which the electrolyte was 0.1 M H₂SO₄, rather than 0.1 M HCl. The simulated transient is shown in the figure, and the model parameters in Table I. In this experiment, a porous layer was detected with QCM, and its thickness was determined to be 10 Å. Its resistance was estimated to be 5 Ω-cm² from \( \Phi_0(0) = -0.025 \text{ V and } i(0)^- = -5 \text{ mA/cm}^2 \). This porous-layer thickness was somewhat greater (27 Å) for the top curve in Fig. 3, the lower currents in Fig. 4 are due to the larger cell resistance and inner layer thickness.

### Table I. Adjusted parameters used to fit the current transients in Fig. 3 and 4.

<table>
<thead>
<tr>
<th>( Q_m ) (mC/cm²)</th>
<th>( R_n ) (Ω-cm²)</th>
<th>( C_n ) (mF/cm²)</th>
<th>( \delta(0) ) (Å)</th>
<th>( \tau_p ) (ms)</th>
<th>( p )</th>
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<td>0.05</td>
</tr>
</tbody>
</table>

*Polarization in 0.1 M H₂SO₄. All others in 0.1 M HCl.*

---

**Fig. 3.** Anodic current transients at 0.1 N HCl, after potential steps from -2.0 to -0.9 V. Dashed curves are calculated results, and solid curves are experimental data. Cathodic charges passed at -2.0 V from top to bottom were 60.2, 2.59, 0.65, and 0.002 mC/cm².

**Fig. 4.** Anodic current transient in 0.1 M H₂SO₄ after a potential step from -2.0 to -0.9 V. The solid curve is experimental data, and the dashed curve was calculated using the model. The cathodic charge passed at -2.0 V was 24 mC/cm².
The long time behavior of the current in the experiment of Fig. 4 is shown in Fig. 5, along with the simulation result. Since the times occupied by this transient were greater than the capacitive time constants of the porous and inner layers, charging current was not included in the model calculation: the porous layer was treated as an ohmic resistor. The initial conditions of the simulation were taken as the calculation results from Fig. 4 at 20 ms. Because the inner layer thickness in Fig. 5 was generally larger than at early times, its resistance was dominant over those of the porous layer and the cell; the current decayed due to inner layer growth. In order to fit the long-time current decay, it was necessary to adjust the porosity \( p \) from its value in Fig. 4, 0.12, to the somewhat larger value of 0.2. This can be explained if the outer part of the film had a greater void fraction than the inner portion, which was filled first. Such a nonuniform porosity as a function of depth would be expected if, during growth of the porous film, the extent of chemical dissolution were greatest on the older part of the film closest to the bulk solution.

**Experiments with two sequential anodic potential steps.**—In some experiments in H\(_2\)SO\(_4\), the potential was stepped from the cathodic potential of −2.0 V to −0.9 V, as above, and then stepped again to −0.4 V. Figure 6 shows current transients measured at −0.4 V in 0.1 M H\(_2\)SO\(_4\) for various “interruption times” at −0.9 V. The cathodic time was 5 s, the same as in Fig. 4. Analysis of these transients with the model gave additional information about the progress of oxidation after cathodic charging. Also, in a subsequent paper they will be compared with parallel experiments in HCl so as to show the effect of this oxidation on the resistance of the metal to pitting. The calculated values of the adjusted model parameters for Fig. 6 are given in Table II. As before, the kinetic and transport parameters were set independently, and \( R_\text{K}, \tau_\text{K}, \) and \( C_\text{K} \) were fit as described in the last section. The remaining variables in Table II, \( R_\text{P} (=L/k) \) and \( \delta(0) \), were calculated directly from the experimental transients, using the following equations

\[
i(1 - f) (R_\text{P} + R_\text{K}) + (\eta_\text{P} - \eta_\text{K}) + (\delta - \phi_1) = -0.5 V \quad \text{[11]}
\]

\[
i f (R_\text{P} + R_\text{K}) + \eta_\text{P} + \phi_2 = -0.13 V - V_\text{r} \quad \text{[12]}
\]

The superscript “1” refers to the final condition at −0.9 V and “2” to the condition at −0.4 V immediately after both capacitive charging processes. \( \eta_\text{P} \) and \( \eta_\text{K} \) were determined from \( f_1 \) and \( f_2 \) using Eq. 3. Then Eq. 11 and 12 were solved for \( R_\text{P} \) and \( \delta(0) \), and \( \delta(0) \) was obtained from \( \phi_2 \) using the high-field-conduction kinetic expression, Eq. 1. Only \( R_\text{P} \) and not \( L \) and \( k \) individually, was needed for the model calculation. From Table II, it is clear that the inner layer thickness \( \delta \) increases during the time at −0.9 V. The resulting decreased electric field in the inner layer produced the strongly decreased currents as a function of interruption time, as shown in Fig. 6.

In Fig. 7, the initial inner layer thickness \( \delta(0) \) for the various interruption times at −0.9 V is compared with \( \delta(t) \), as predicted by the simulation of the experiment in Fig. 4 and 5. The two results for \( \delta(t) \) are seen to be quantitatively consistent, the inner-layer thickness increasing according to a logarithmic growth law. This time dependence is frequently observed during growth of passive films. The agreement of the two determinations of \( \delta \) is evidence that conduction in the inner layer, as well as film growth by pore filling, have been properly modeled. The prediction of \( \delta \) was further verified with an independent experiment in which cathodic charging was carried out as in Fig. 4, after which the potential was held for 20 s at −0.9 V and then rapidly stepped through a series of more anodic potentials. After each of these last steps, the current reached a stable value within 2 ms. These stationary currents were analyzed as in Fig. 2 to obtain the film thickness of 32 Å, which is close to the value of 34 Å at 20 s in Fig. 7.

While the inner layer is the dominant resistance of the electrical network for anodic conduction at steady state, the resistance of the porous layer, if present, is appreciable at early times. As a test of the model’s ability to describe conduction in the porous layer, the transient currents at early times were predicted in experiments similar to those in Fig. 6. Figure 8 shows currents measured after 5 s of cathodic charging, followed by 20 ms at −0.9 V and then 4 ms at one of a series of higher anodic potentials (−0.7, −0.6, −0.25, and −0.1 V). The model parameters derived from an experimental current transient at −0.9 V were used to predict the current at a time of 4 ms at each of the higher potentials. These calculated currents are shown in

![Fig. 5. The same anodic current transient in Fig. 4, shown over a 20 s period. The dashed curve is the calculated result, and the symbols represent experimental data.](image)

![Fig. 6. Anodic current transients in 0.1 M H\(_2\)SO\(_4\), after 5 s cathodic charging at −2.0 V, approximately 24 mC/cm\(^2\) charge passed, followed by various times at −0.9 V and then steps to −0.4 V. Zero time corresponds to the potential step from −0.9 to −0.4 V. Dashed curves are calculated results, and solid curves are experimental data. The holding times at −0.9 V from top to bottom are 0.02, 0.1, 1, 3, and 20 s.](image)
The results in this section support important aspects of the electrical model: inner layer and porous layer conduction, and anodic pore filling. In the following Discussion, the model results are interpreted with regard to the mechanism of cathodic activation.

**Discussion**

The model results in Table I indicate that during the early moments of cathodic charging ($Q < 3 \text{ mC/cm}^2$), the barrier-layer thickness $s$ decreased abruptly from the initial thickness of 28 Å to 15 or 20 Å, and the porosity $p$ increased to 0.02. These structural changes were responsible for the difference between the current transients in Fig. 3, i.e., for the "activation" of the aluminum electrode which was also associated with a much greater susceptibility toward pitting corrosion. In this initial period of charging corresponding to the first 4 mC/cm$^2$ of charge, the QCM frequency increased by 2 to 3 Hz, suggesting film dissolution. However, this frequency shift is equivalent to only about 2 Å of uniform film dissolution, much smaller than the decrease of $s$ given by the electrical model. An interpretation of these observations is that, in the initial moments of cathodic charging, pores were formed in the outer part of the film. In these pores, where the aqueous pathways for conduction, the outer portion of the layer, containing these pores, would have been much more conductive than a barrier oxide. The electrically effective layer thickness of the film (i.e., $s$) would then correspond only to the inner pore-free part. Apparently, the newly formed porous part of the film was thin enough so that its resistance did not appear in the electrical measurements.

The cathodic activation of aluminum by formation of pores in the oxide film is supported in recent papers by Hassel and Lohrengel $^{24}$ and Takahashi et al. $^{25,26}$ The former authors based their conclusion on similar anodic current transients as those in Fig. 3. The latter investigators detected pits formed during cathodic polarization of anodized aluminum surfaces. These pits arose by dissolution of exposed metal at the base of pores in the oxide generated during cathodic polarization, some fraction of which penetrated the entire film.

In general, pores can be generated by dissolution processes when the rate of dissolution is partially controlled by the rate of transport through the solid. $^{27}$ This principle can be applied to give a possible mechanism for cathodic pore formation, as follows: when cathodic polarization was applied, the potential drop at both the film/solution interface and the oxide was constant. Hence, at microscopic irregularities, where the film was locally thinner than elsewhere, the magnitudes of both the electric field in the oxide and the interfacial potential drop were increased, and dissolution occurred faster. With greater penetration of the film, the rate of localized dissolution increased even further, leading to the formation of pores. When the applied potential was switched to an anodic value, the dominant electrochemical process became film growth, the rate of which was also limited by transport through the film. As a result, current flow was directed to the thinnest parts of the film (the pore bottoms), and the pores were filled. The role of topographic irregularities as sites for pore initiation is supported by results of Takahashi et al. $^{25,26}$ who found that the formation of pores was enhanced in experiments where the metal had been scratched, or where the oxide was initially flawed.

Despite the ability of this mechanism to explain pore formation qualitatively, questions remain about whether it can explain the apparent high rate of pore formation in these experiments. The smallest charge of 0.002 mC/cm$^2$ in Table I corresponds to a time of about 2 ms; the pore penetration of 8 Å during this time implies that oxygen

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**Fig. 7. Growth of the inner layer thickness during the period at $-0.9 \text{ V}$ in 0.1 M H$_2$SO$_4$, after 5 s cathodic charging at $-2.0 \text{ V}$. The solid curve is from the simulation of the longtime transient at $-0.9 \text{ V}$, shown in Fig. 5, and the symbols are initial film thicknesses fitted from the current transients after additional potential steps from $-0.9$ to $-0.4 \text{ V}$ (Fig. 6).**

**Fig. 8.** Anodic currents in 0.1 M H$_2$SO$_4$ after 5 s cathodic charging at $-2.0 \text{ V}$ (approximately 24 mC/cm$^2$ charge passed), followed by 20 ms at $-0.9 \text{ V}$ and then a constant time of 4 ms at different, more anodic potentials. Open symbols are calculated results, and closed symbols represent experimental currents. The solid line is a linear regression fit to the simulation results.
ions were removed at an equivalent current density of 0.7 A/cm². Seemingly, this current density is too large to be explained by the oxygen ion transfer kinetic expression (Eq. 3), unless it represents pores which are located at pre-existing defective regions of the film. It should be noted, though, that this kinetic expression represents an averaged dissolution rate, while microscopic fluctuations in the dissolution rate may be responsible for the creation of individual pits. The current density for such a process, such as mechanical cracking might be involved.38 Whatever the process controlling pore formation, no marked dependence of it on the electrolyte anion was detected; similar porous layers were generated in both HCl and H₂SO₄ solutions.

The present results conflict with the mechanism of cathodic activation given by Lin and Hebert. They assumed that a substantial fraction of the cathodic hydrogen evolution overpotential was at the metal/film interface and argued that in this case the step to the cathodic potential would induce hydroxide formation in the part of the film closest to the metal. It now appears that the changes in film structure produced by cathodic charging instead initiate near the film/solution interface. If the hydrogen overpotential at the metal/film interface is in fact small (i.e., the rate of hydrogen evolution is limited by proton or electron transport across the film), the cathodic potential step should not alter the film composition near the metal/film interface, which should remain close to Al₂O₃. Thus the assumption of transport-limited hydrogen evolution may explain the observation of an inner barrier layer in the film.

At small cathodic charges, the porosity controlled the time needed for the film to recover its resistance, after the step to the anodic potential. At the smallest Q, with a porosity of 0.001, the current decayed to 0.1 mA/cm² in about 3 ms. According to Eq. 1, this current corresponds to an inner layer thickness of 26 Å, the same as the initial film thickness. Thus, the small porosity allowed the film to be recovered very rapidly when the cathodic polarization was removed. With greater cathodic charge, the porosity increased, and thus more time was required to return the inner layer to its initial thickness (more than 10 ms according to Fig. 3). If the purpose of cathodic charging is to activate the surface toward reactions occurring under subsequent anodic polarization, the amount of time for which the interface remains reactive at the anodic potential should be considered.

When the cathodic charge exceeded 7 mc/cm², a porous film began to grow on top of the barrier layer. The presence of this porous film delays pit nucleation upon anodic polarization.12 As discussed above, because of the exponential high-field conduction law in the inner layer, the resistance of this porous layer was significant when the current was on the order of mA/cm², but it was not important at the much smaller currents found during steady-state conduction at anodic potentials. The structural parameters of the porous layer can be roughly estimated from the simulation results in Table I. If the pores are modeled as cylindrical in shape and their orientation is taken as perpendicular to the metal/film interface, the specific surface area of the porous layer is 2πr, where r is the pore radius and n is the number of pores per unit area. Also according to this model the porosity p is πr²n. The volume capacitance density of the porous layer, αCₑ, was 1770 F/cm² when Q, was 60.2 mc/cm². No Cₑ could be found specifically for aluminum oxide; using an order-of-magnitude estimate of 100 μF/cm², 18 is 1.8 × 10⁻³ cm⁻¹, that is, the radius of a pore is 2 p/a, or about 2.3 Å, and n is 1.2 × 10¹⁰ cm⁻², giving a pore-to-pore distance of about 0.9 nm. These calculations make use of the value of p of 0.2 from long-time current decays. Estimates of microcrystallite sizes within hydrated anodic alumina films are somewhat higher, ranging from 1 to 10 nm.30 However, given the crude nature of these calculations, agreement with expected pore sizes to within an order of magnitude is considered satisfactory.

The inner layer thicknesses determined by fitting current transients in this work represent values which are averaged over the entire surface. Since there was undoubtedly a distribution of pore lengths, some localized areas perhaps had a significantly smaller film thickness than the average. When the metal is polarized above the pitting potential after cathodic charging in 0.1 M HCl, the number of pits, which is on the order of 10⁶ pits/cm², is much smaller than the number of pores in the oxide calculated above. Therefore, it is possible that some fraction of the pores penetrated entirely through the oxide, and that the pits formed at these sites. As noted above, Takahashi et al.24 found evidence that such exposure of the metal can occur during cathodic charging.

Conclusions

A mathematical model was formulated for the surface film on aluminum which was fit to experimental current transients following anodic potential steps, in order to determine structural parameters of the film. The model assumed a duplex film structure composed of an inner barrier high-field conducting layer and an outer, porous, ohmically conducting layer. It included all relevant capacitive processes and interfacial reactions, including pore filling by oxide growth at potentials higher than the open-circuit potential. Nonlinear conduction and reaction-rate expressions were incorporated in the model. Of interest in this work were changes in the film structure which result from cathodic polarization in acidic solution, which, in chloride-containing solutions, are observed to increase dramatically the rate of pitting corrosion if the metal is brought to an anodic potential soon after cathodic charging.

The model was found to represent experimental current decays realistically over several orders of magnitude variation of current density (factor of 10⁶) and time (factor of 10⁴). When a well-developed porous outer layer was present (at long cathodic times), it controlled conduction when the current was high, while the resistance of the inner layer dominated when the current was small. To a first approximation, cathodic activation could be described in terms of a decrease of the inner layer thickness (8) from about 30 to 15 or 20 Å and an increase of the porosity (p) to 0.02. These changes were interpreted as being due to the rapid appearance of pores in the outer portion of the initial film. The pores may have been produced by electrochemical dissolution of the oxide during cathodic current flow; however, the rate of pore penetration is seemingly large compared to dissolution rates expected from the kinetics of this reaction. The promotion of pits by cathodic charging in chloride solutions may be due to the penetration of a small fraction of the pores entirely through the film.

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APPENDIX

A calculation is presented here which shows how the conductivity of the porous layer k and the hydrogen exchange current density were obtained. During the cathodic charging period at ~2.0 V, the cathodic current at first increased (within ~8 s) to about 0.9 mA/cm². During this decay, mass measurements with the QCM, combined with infrared spectroscopy, showed that the mass of the porous outer part of the film increased at a constant rate, while no change of the barrier-layer thickness was detected. Lin and Hebert11 showed that the decay of the cathodic current was caused by the increase of its film’s conduction resistance with its thickness. Assuming that the deposited film was an ohmically con-
ducting porous layer with approximately uniform conductivity, the current $i$ and $\phi_p$ are related by

$$\phi_p = \frac{i}{k} \tag{A-1}$$

The potential drop across the metal/film/solution system is

$$V_{Ag/AgCl} + 0.27 V - V_i = \phi_p + i0 + \frac{i}{k} \left( \frac{L}{k} + R_p \right) \tag{A-2}$$

$L$ can be calculated from the mass increase and the density of the film. According to Eq. 1, $\phi_p$ is approximately constant since the cathodic current decays only within a small range. Since the film growth rate $(2.6 \text{ A/s})$ was constant with time, $i_{0}$ was also constant; a value of $0.11 \text{ V}$ was found from Eq. 3. Rearranging the above equation, one obtains

$$\Delta m = \frac{k}{\rho} \left( V_{Ag/AgCl} + 0.27 V - V_i - \phi_p - \eta_0 \right) - k\rho R_p \tag{A-3}$$

When $\Delta m$ was plotted vs. $1/i$, a linear relationship was found, confirming that the deposited film was an ohmic conductor. The slope and the intercept were $1.46 \times 10^{-8} \text{ A-g/cm}^4$ and $-1.78 \times 10^{-3} \text{ g/cm}^2$. Using the density of aluminum hydroxide, $2.4 \text{ g/cm}^3$, for $p$, and taking $R_p$ as $30 \Omega \text{ cm}^2$, the conductivity of the porous layer, $k$, was calculated from the intercept to be $2.5 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$. Dzimitrowicz et al. found a comparable ionic conductivity of $6 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ for bulk $\text{Al(OH)}_2 \cdot \text{H}_2\text{O}$, a material known to conduct ions through its aqueous pores. This experimentally obtained porous layer conductivity was used in simulations of experiments in $0.1 \text{ M HCl}$. $\phi_p$ was then found from the slope to be $-25 \text{ mV}$. The value of $i_{0}$ was estimated from Eq. 2 using the cathodic current and $\phi_p$.

LIST OF SYMBOLS

- $a$: surface area/volume in porous layer, $\text{cm}^{-1}$
- $B_i$: field coefficient, $\text{cm/V}$
- $C_i$: capacitance of inner layer, $F/\text{cm}^2$
- $C_O$: capacitance of oxide/solution interface, $F/\text{cm}^2$
- $F$: Faraday's constant, $96,487 \text{ C/eq}$
- $i$: current density
- $i_{a0}$: anodic high field conduction current density $\text{A/cm}^2$
- $i_{a1}$: pre-exponential current density in high-field conduction, $\text{A/cm}^2$
- $i_{a2}$: metal ion dissolution current density, $\text{A/cm}^2$
- $i_{a0}$: exchange current density for metal ion dissolution, $\text{A/cm}^2$
- $i_{a1}$: current density through inner layer, $\text{A/cm}^2$
- $i_{a2}$: cathodic hydrogen evolution current density, $\text{A/cm}^2$
- $i_{a3}$: exchange current density for hydrogen evolution, $\text{A/cm}^2$
- $i_{a4}$: oxygen transfer current density, $\text{A/cm}^2$
- $i_{a5}$: exchange current density for oxygen transfer, $\text{A/cm}^2$
- $L$: thickness of porous layer, $\text{cm}$
- $P$: porosity of porous layer, dimensionless
- $R$: universal gas constant, $8.3143 \text{ J/mol-K}$
- $R_1$: resistance of inner layer, $\Omega$/$\text{cm}^2$
- $R_2$: resistance of bulk solution, $\Omega$/$\text{cm}^2$
- $Q$: resistance of oxide/solution interface, $\Omega$/$\text{cm}^2$
- $C$: cathodic charge, $\text{C/cm}^2$
- $T$: absolute temperature, $\text{K}$
- $t$: time, $\text{s}$
- $V_{Ag/AgCl}$: potential with respect to Ag/AgCl reference electrode, $\text{V}$
- $V_{R}$: specific volume of film material, $\text{cm}^3/\text{mol}$
- $R_p$: rest potential, $\text{V}$
- $x$: coordinate through porous layer, $\text{cm}$

Greek symbols:

- $\alpha$: charge diffusivity in porous layer, $\text{cm}^2/\text{s}$
- $\alpha_{\text{a0}}$: transfer coefficient for metal ion dissolution
- $\alpha_{\text{a1}}$: transfer coefficient for hydrogen evolution

REFERENCES