Participation of Aluminum Hydride in the Anodic Dissolution of Aluminum in Alkaline Solutions

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The mechanism of anodic alkaline dissolution of aluminum was investigated through the analysis of cyclic voltammetry (CV) and potential step experiments. Attention was focused on the role of aluminum hydride (AlH$_3$) as a reaction intermediate, as suggested by the recent detection of AlH$_3$ formation during open-circuit dissolution. Potential step experiments at pH 11.75 revealed that the potential at the metal–surface film interface was close to the Nernst potential of AlH$_3$ oxidation. This finding suggested a reaction mechanism in which an interfacial AlH$_3$ layer is formed continuously by reaction of cathodically formed H with Al, and is then oxidized to the dissolution product, aluminate [Al(OH)$_4$]$^-$ ions. However, potential step experiments at pH 11 did not indicate the presence of interfacial AlH$_3$, instead, the metal–film interface was close to the equilibrium potential of Al oxidation. Analysis of the CV indicated an abrupt transition in dissolution behavior between the two pH values, from a relatively rapid dissolution controlled by diffusion and film conduction in highly alkaline solutions, to a slow dissolution at a lower pH controlled by a highly resistive surface film. The formation of interfacial AlH$_3$ occurs readily at the higher pH, but is suppressed as the pH approaches neutrality.

The electrochemical dissolution of aluminum and its alloys in alkaline solutions is technologically relevant as the anode reaction in aluminum–air batteries. This interest in batteries has led to a number of mechanistic studies of the dissolution process. In moderately basic solutions, the rate of anodic dissolution may be controlled by the combination of electrode kinetics, mass transport, or conduction through a surface film. The dissolution reaction mechanism in concentrated KOH solutions was investigated by Macdonald et al. using electrochemical impedance spectroscopy. They determined that the metal corrodes by a reaction pathway in which OH$^-$ ions are added sequentially to Al atoms, until the stable aluminate ion, Al(OH)$_4^-$, is formed. A different view of the mechanism is suggested by a study by Perrault, which indicated that the oxidation of aluminum hydride, AlH$_3$, may be involved in the dissolution. He showed that the open-circuit potential of Al in alkaline solutions corresponds closely to the Nernst potential for hydride oxidation. In support of the possible role of hydride, Despić and co-workers observed that polarization at cathodic potentials generates a product with an oxidation potential close to that of aluminum hydride.

In a recent secondary ion mass spectrometry investigation, we showed that submicrometer AlH$_3$ particles are formed as a product of open-circuit Al dissolution in 1 M NaOH solution at room temperature. Potential measurements indicated that the dissolution potential was close to the Nernst potential for oxidation of the hydride. It was proposed that AlH$_3$ is continuously created through the etching of Al by cathodically generated hydrogen atoms.

$$H_2O + e^- \rightarrow OH^- + H \quad [1]$$
$$Al + 3H \rightarrow AlH_3 \quad [2]$$

Evidence for Reaction 2 has been found in a number of vacuum studies of H interactions with clean Al surfaces. The hydride then oxidized according to the reaction identified by Perrault:

$$AlH_3 + 7 OH^-(aq) \rightarrow Al(OH)_4^- + 3H_2O(aq) + 6e^- \quad [3]$$

In this mechanism Reaction 3 is close to equilibrium, and so its Nernst potential determines the open-circuit potential during dissolution. The overall open-circuit reaction formulated by the combination of these reactions accounts for the observed formation of AlH$_3$.

$$2Al + OH^- + 3H_2O \rightarrow Al(OH)_4^- + AlH_3 \quad [4]$$

The present paper examines whether the electrochemical behavior of anodic Al dissolution in alkaline solutions supports the participation of AlH$_3$ as a reaction intermediate. Results of cyclic voltammetry (CV) and potential step experiments are interpreted using models for the Al electrode based on the proposed mechanism. In particular, because AlH$_3$ formation by Eq. 2 should occur at the Al surface, the hydride is assumed to be present as a layer of unknown thickness in contact with the metal. The hydride may also be covered by a precipitated Al(OH)$_3$ overlayer, in view of some evidence for such a layer during alkaline dissolution. Indeed, there is a substantial driving force for Al(OH)$_3$ formation, because the open-circuit potential is about 0.5 V positive to the Nernst potential of Al oxidation. The present experiments sought to identify the potential at the interface of the metal and this surface film, and to determine whether it corresponds to the Nernst potential for the oxidation of aluminum hydride.

**Experimental**

CV and potential step experiments were carried out in 0.1 M Na$_2$SO$_4$ solutions adjusted to the pH of either 11 or 11.75. These pH values were selected for the following reasons. First, they lie within the pH range in which the open-circuit potential is close to the Nernst potential of hydride oxidation (Eq. 3), suggesting the possible presence of interfacial hydride. Second, at these pH values currents due to cathodic reactions are not significant above the open-circuit potential, thus facilitating interpretation of the current measurements in terms of anodic processes. Finally, this pH range embodies the transition between the rapid dissolution of Al found in alkaline solutions and its passive behavior in neutral solutions. Thus, the results allow us to suggest whether the AlH$_3$ mechanism might be relevant to either or both of these regimes of the Al electrode.

The Al samples were 110 μm thick foils of 99.99% purity (Toyo). The foil was provided in the as-annealed condition, and its grain size was roughly 100 μm. No evidence for grain boundary attack was found during a microscopic examination of the samples after alkaline treatments.

Solutions for all experiments were prepared using reagent grade chemicals and Nanopure water. Prior to voltammetry, the samples were treated by electropolishing and caustic etching. Electropolishing was carried out in a solution of 20% HClO$_4$ in ethanol at 5°C and 30 V for 5 min. The samples were then washed in deionized water and mounted in a glass electrochemical cell used for both alkaline treatment and voltammetry. The exposed sample area in the cell was 1.77 cm$^2$. The edge of the electropol-
ished area was deliberately covered because of indications that preferential dissolution had occurred in this region. Alkaline etching was at open circuit in 1 M NaOH solution for a period of 1 min at 21°C.

After alkaline treatment, the cell solution was replaced with 0.1 M Na₂SO₄, with its pH adjusted to either 11 or 11.75 by the addition of NaOH crystals. A potentiostat was used to apply electrochemical polarization, using a Pt wire counter electrode and a Ag/AgCl reference electrode. The cited potentials are expressed relative to Ag/AgCl unless otherwise specified. Because the currents measured during CV were found to be temperature-sensitive, the temperature was controlled at 21°C. The solutions were typically air-saturated, but in some experiments deaeration was accomplished by nitrogen sparging for 60 min. Two types of electrochemical experiments were carried out, CV and potential step experiments. CV experiments were initiated by scanning in the anodic direction from a potential near open circuit. In the potential step experiments, the Al electrode was first held at a constant potential above open circuit for 5 min, in order to obtain a steady-state passive current density. Then, a sequence of positive 0.1 V potential steps at 10 ms intervals was executed, and the resulting current transients recorded. As described in detail below, current-potential plots were obtained from these data which revealed characteristics of conduction in the surface film, and indicated the potential at the metal–film interface.

The cell ohmic resistance, which was required for analysis of both CV and potential step experiments, was obtained by anodically etching aluminum foils in 1 M HCl solution, in the same cell.²⁰ The etching current density was shown to be controlled by the cell ohmic resistance. The cell resistance during etching was multiplied by the ratio of the conductivity of 0.1 M Na₂SO₄ to that of 1 M HCl, to obtain the cell resistance applicable to the present experiments. The resistance was found to be 300 Ω cm².

Results and Discussion

CV.— Figure 1 shows four CV experiments at scan rates between 0.5 and 4 mV/s, in air-saturated pH 11.75 solution. Deaeration by nitrogen sparging was found to suppress cathodic currents, but had no significant effect on currents in the anodic potential region, the main focus of attention. Each positive scan in Fig. 1 displayed a broad current density maximum between 150 and 300 μA/cm², which increased with scan rate. Both the peak shape and the effect of the scan rate are qualitatively consistent with at least partial diffusion control of the anodic reaction rate.²¹ The influence of diffusion was explicitly demonstrated in an experiment in which the bubble stream from a nitrogen sparger was positioned near the Al surface (Fig. 2). The sudden initiation of stirring by bubbles caused the current nearly to double within a time of 4 s, clearly indicating a sensitivity to mass transport. The same conclusion was reached by Heusler and Allgaier in their rotating-disk electrode study of Al dissolution at comparable pH values.²² However, the anodic peak currents in Fig. 1 increase more slowly with scan rate than the one-half power dependence expected for pure diffusion control, and the peak potentials shift in the positive direction at higher scan rates. This behavior may be attributed to the additional influence of electrode kinetics and/or surface film conduction.²³ Therefore, quantitative characterization of conduction and kinetics, with the help of the potential step experiments, was necessary for the interfacial potential to be determined.

CV results in pH 11 Na₂SO₄ solution are shown in Fig. 3. Upon initiation of the scans, the anodic current density increased rapidly to peaks at about 90 μA/cm², and subsequently decayed to much lower current densities of 20–30 μA/cm². The current density in the second positive scan (dashed lines) remained below 20 μA/cm². Aside from the initial anodic peaks, the anodic currents at pH 11 were much lower than those at pH 11.75. The high sensitivity to pH is not surprising, as the open-circuit corrosion rate decreases by an order of magnitude as the pH is reduced from 12 to 11.²⁴ In contrast to the results at pH 11.75 (Fig. 1), the peak currents in Fig. 3 did not depend on the scan rate. Indeed, as Fig. 4 demonstrates, the anodic current peaks and decays depended only on the elapsed time during the scan, and were independent of potential. Evidently, these transients resulted from time-dependent processes accompanying the start of the experiment, after the Al samples were
transferred from the 1 M NaOH pretreatment bath (pH 13.5) to the pH 11 Na₂SO₄ solution. The modeling results presented below will help to clarify the nature of these processes.

After the initial decays, the currents in the first positive sweep approached constant values. The positive scans during the second CV cycles exhibited no initial anodic peaks, and instead showed anodic plateaus below 20 μA/cm². A similar CV response was demonstrated previously in the neutral pH range by Isaacs, White, and their co-workers.²²⁻²⁵ They showed that the anodic plateaus were due to currents controlled by ionic conduction through a highly resistive surface film exhibiting high-field conduction. Evidently, over the narrow pH range from 11.75 to 11, there is an abrupt transition from diffusion-sensitive dissolution rates, characteristic of alkaline solutions, to passive behavior dominated by a resistive surface film, as typically found in neutral solutions.

Potential step experiments.—Potential step experiments were carried out to determine the potential at the metal/film interface, through analysis of the potential drop through the surface film. The procedure of these experiments was first developed by Hurlen and Haug.²⁰ As described in the Experimental section, the Al electrode was first held at a constant potential above open circuit, in order to establish a steady-state passive current density. At steady state, the surface film thickness (δss) was given by

$$E_{\text{ss}} = E_{\text{init}} + \delta_{\text{ss}} \frac{B}{\ln \left( \frac{i_{\text{ss}}}{i_{\text{ss}}} \right)}$$

where $E_{\text{init}}$ is the initial applied potential, $E_{\text{ss}}$ is the potential at the metal/film interface, and the second term on the right represents the potential drop through a high-field conducting surface film, in which the current increases exponentially with electric field. In this term, $i_{\text{ss}}$ is the approximately potential-independent steady-state passive current density; $i_{\text{ss}}$ and $B$ are the pre-exponential current density and field coefficient in the high-field conduction rate equation.

After the potential hold at $E_{\text{init}}$, a sequence of 0.1 V potential steps was applied at 10 ms intervals, resulting in a transient current response like the example shown in Fig. 5. Each voltage step was immediately followed by an exponential current decay. This transient decay is attributed to capacitive charging, because the decay time of about 10 ms is consistent with the capacitive time constant of 3 ms estimated from the cell resistance of 300 Ω cm² and a typical capacitance of 10 μF/cm² for Al.²⁷ After the capacitive transient, the current continued to decay more slowly, due primarily to anodic film growth. However, calculations based on Faraday’s law indicated that no significant film growth would have occurred during the 40 ms time interval of the step sequence. Also, this time interval is too short for diffusion to produce significant changes in the solution composition near the Al surface. Therefore, the current at 10 ms after each step ($i_{\text{step}}$) represented the conduction current density passed through the initial steady-state film thickness $\delta_{\text{ss}}$

$$i_{\text{step}} = i_{\text{ss}} \exp \left( \frac{B(E_{\text{step}} - E_{\text{ss}})}{\delta_{\text{ss}}} \right)$$

where $E_{\text{step}}$ is the applied potential during the step, after correction for cell ohmic resistance. Figures 6 and 7 show that, at both pH values, $i_{\text{step}}$ varies exponentially with $E_{\text{step}}$ as expected from Eq. 6. Also, the figures indicate that the slope of $\ln i_{\text{step}}/dE_{\text{step}}$ decreases with increasing values of the initial potential $E_{\text{init}}$. This trend is attributable to the increasing steady-state film thickness with $E_{\text{init}}$, according to Eq. 5, and is evidence that the exponential current–potential relations in Fig. 6 and 7 are controlled by conduction rather than electrochemical kinetics.

According to Eq. 6, the inverse slopes in Fig. 6 and 7, $dE_{\text{step}}/d \ln i_{\text{step}}$ are directly related to the steady-state film thickness $\delta_{\text{ss}}$. From Eq. 5, the inverse slope is expected to depend linearly on the initial applied potential.
proposed reaction scheme involving AlH₃ as an intermediate: evi-
vised to aluminum oxide or hydroxide. This result supports the
or oxide.
the film composition at the interface is close to aluminum hydroxide
OH
/ H₂O₈₄⁹ oxidation of Al to Al₂O₃, −2.32 V. 19 We conclude that
Hi
finds to be −2.34 V, nearly identical to the Nernst potential for the
Hi
oxidation to determine the interfacial potential, a high fraction of the
Hi
processes control the dissolution rate at the two tested pH values.
According to the discussion of the CV experiments, different
Hi
models were formulated to simulate the CV at the two pH values. Both models considered only anodic electro-
Hi
chemical reactions, and were not intended to apply below the open-
circuit potential.

Mathematical Models
According to the discussion of the CV experiments, different
processes control the dissolution rate at the two tested pH values.
The current at pH 11.75 is influenced by solution phase diffusion
and film conduction, while the film conduction resistance dominates
at pH 11. Different models were formulated to simulate the CV at
the two pH values. Both models considered only anodic electro-
chemical reactions, and were not intended to apply below the open-
circuit potential.

Model for dissolution at pH 11.75.— In this model, we assume
that the potential at the metal–film interface is close to the Nernst
potential of the anodic hydride oxidation reaction (Eq. 3). The poten-
tial is given by

\[ E = E_{\text{AlH}_3}^\circ - 2.303 \frac{RT}{F} \log \left( \frac{y_{\text{AlH}_3}}{y_{\text{H}^+} y_{\text{OH}^-}} \right) + \phi + iR_s \]  

where \( E \) is the measured potential relative to the standard hydrogen
electrode (NHE), and the standard potential \( E_{\text{AlH}_3}^\circ \) represents

\[ E_{\text{AlH}_3}^\circ = \frac{1}{6F} [3\mu_{\text{Al(OH)_3}^\circ} - 3\mu_{\text{H}_2\text{O}} - \mu_{\text{Al(OH)}_4}^\circ] \]  

Using the AlH₃ standard chemical potential of 25 kcal/mol cited by
Perrault, \( E_{\text{AlH}_3}^\circ \) is found to be −0.957 V vs NHE. The second term on
the right of Eq. 8 corrects for the bulk pH (pHₐ), the third term is the
concentration overpotential, and the remaining terms are the potential
drops through the surface film (\( \phi \)) and across the cell ohmic
resistance (\( iR_s \)). In the concentration overpotential, \( \gamma_{\text{OH}^-} \), and \( \gamma_{\text{Al}} \), are
dimensionless concentrations of hydroxide and aluminate ions close
to the electrode surface. \( \gamma_{\text{OH}^-} \) is defined according to

\[ \gamma_{\text{OH}^-} = \frac{[\text{OH}^-]}{[\text{OH}^\circ]} b, \]  

where \( [\text{OH}^-] \) and \( [\text{OH}^\circ] \) are the surface and
bulk OH⁻ concentrations. \( \gamma_{\text{Al}} \) is the concentration of aluminate ions and

\[ \gamma_{\text{Al}} = \frac{[\text{Al(OH)₃}^\circ]}{[\text{Al(OH)₄}^\circ]} \text{Al(OH)₄}^\circ \], \text{Al(OH)₃}^\circ \text{Al(OH)₃}^\circ \]  

is the surface concentration of aluminate ions and

\[ \gamma_{\text{Al}}^\circ \] represents the concentration of aluminate ions in equi-
librium with solid Al(OH)₃ at the bulk solution pH. \( \gamma_{\text{Al}}^\circ \) depends on the bulk pH according to

\[ [\text{Al(OH)₄}^\circ] = \gamma_{\text{Al}}^\circ [\text{OH}^-] \]  

where \( \gamma_{\text{Al}}^\circ \) is the equilibrium constant of Al(OH)₃ formation. The potential
drop in the film was obtained from the results of potential
step experiments at the initial potential of −1.7 V

\[ \phi = \frac{1}{b} \ln \left( \frac{i}{i_{\text{eo}}} \right) \]  

where the parameters \( b \) and \( i_{\text{eo}} \) were taken from the slope and inter-
cept of the regression fit in Fig. 6 at −1.7 V.

The near-surface concentrations of OH⁻ or Al(OH)₄⁻ ions in Eq.
8 were obtained by solving the diffusion equations for these species

\[ \frac{\partial y_{\text{OH}^-}}{\partial \tau} = \frac{D_{\text{OH}^-}}{\partial z} \]  

where \( i \) can be OH⁻ or Al(OH)₃⁻. The concentration of Na₂SO₄
supporting electrolyte was considered to be high enough so that
the migration flux in the diffusion layer could be neglected relative to
the diffusion flux. The boundary conditions at the electrode surface
are

\[ \frac{\partial y_{\text{OH}^-}}{\partial z} \bigg|_{z=0} = \frac{4i}{3F \text{D}_{\text{OH}^-}} \]  

Figure 7. Examples of current–potential characteristics, obtained from se-
quential steady-state potentials at pH 11. Results are shown for various
applied steady-state potentials prior to the potential steps.

\[ \frac{dE_{\text{step}}}{d \ln i_{\text{step}}} = \frac{E_{\text{final}} - E_{\text{init}}}{\ln \frac{i_{\text{final}}}{i_{\text{init}}}} \]  

In Fig. 8, the inverse slopes from all the potential step experiments
at pH 11 and 11.75 are plotted against the initial applied potential.
The data were well approximated by different linear potential de-
pendences at the two pH values. Equation 7 indicates that the ex-
trapolations of the regression lines to the potential axis should pro-
vide estimates of the interfacial potential \( E_{\text{init}} \). At pH 11, \( E_{\text{init}} \) was
found to be −2.34 V, nearly identical to the Nernst potential for the
oxidation of Al to Al₂O₃, −2.32 V. We conclude that the film com-
position at the interface is close to aluminum hydroxide or oxide. \( E_{\text{init}} \) at pH 11.75 was −1.92 V vs Ag/AgCl, a value close
to the Nernst potential of Al₂O₃ oxidation, −1.82 V. For hydride
oxidation to determine the interfacial potential, a high fraction of the
metal/film interface should be in direct contact with AlH₃ as op-
posed to aluminum oxide or hydroxide. This result supports the
proposed reaction scheme involving AlH₃ as an intermediate: evi-
dently, aluminum hydride is formed continuously by the reaction of
Al with cathodically generated H (Eq. 1 and 2), even under anodic
polarization. It is concluded that the interface composition during anodic polarization differs qualitatively between these two closely
separated pH values. The results do not preclude the possibility that
the entire film may be composed of AlH₃. In the next section, these
interface compositions are used as a basis for modeling the CV
experiments.

Figure 8. Reciprocal slopes of current–potential characteristics at pH 11 and
11.75, plotted against the applied steady-state potential prior to potential
steps. Lines are linear regressions of the data. The zero-current intercepts of
the regression lines are −2.32 V (pH 11) and −1.92 V (pH 11.75).
Further, since the kinetics of metal ion transfer is relatively equivalent to the
boundary conditions in the bulk solution, i.e., as $\zeta$ approaches
infinity, are $\gamma_{OH} = 1$ and $\gamma_A = 0$. Equations 11-13 were solved
numerically. The diffusivities $D_{OH}$ and $D_A$ were $5.3 \times 10^{-5}$ and $8.4$
$\times 10^{-5}$ cm$^2$/s, respectively. The equilibrium constant $K_a$ was
0.05.35 The values of all model parameters were known from the
potential step experiments or other sources.

Model for dissolution at pH 11.— According to the results of
the potential step experiments, this model assumes that the reaction
at the metal/film interface is the direct oxidation of Al. The potential
at this interface is the Nernst potential of the Al oxidation reaction,
and the current is controlled by high-field conduction in the surface
film. The concentration overpotential and ohmic drop are neglected
because the large conduction resistance leads to low current densi-
ties of tens of $\mu$A/cm$^2$. With these assumptions, the electrode
potential may be related to the Nernst potential for the oxidation of Al

$$E = E_{\text{Al}}^o + 2.303 \frac{RT}{F} \text{pH}_0 + \phi$$

where the standard potential $E_{\text{Al}}^o$ is

$$E_{\text{Al}}^o = \frac{1}{3} \frac{3}{2} \mu_{H^+} - 3 \mu_{O^{2-}} - \mu_{Al} + \mu_{AlO_2^-}$$

which has the value $-1.50$ V vs NHE.35 The model assumes that
the film composition is $Al_2O_3$ because the conduction parameters of
the oxide are known from studies of anodic films.30

The current through the film/solution interface is carried by ion-
transfer processes, whereby $OH^-$ or $H_2O$ in solution react to form
$O^{2-}$ ions in the film, and $Al^{3+}$ ions in the film are ejected to form
$Al(OH)^{2+}$ ions in solution. It is necessary to characterize these
processes, because $O^{2-}$ transfer leads to film growth or dissolution,
which affects the conduction resistance. In view of the very low
current densities in Fig. 3, along with the typically facile kinetics of
oxygen transfer,31 the potential drop at the film/solution interface is
assumed to be close to equilibrium with respect to the $O^{2-}$ transfer
process. Further, since the kinetics of metal ion transfer is relatively
sluggish, this constant interfacial potential drop implies that the
metal ion transfer current density is approximately fixed at a value
$i_{\text{co}}$. The rate of film growth or dissolution during the CV experiment
then can be written as

$$\frac{dx}{dt} = \frac{(i - i_{\text{co}}) \Omega_{\text{Al}}}{6F}$$

where $\Omega$ is the film thickness and $\Omega_{\text{Al}}$ is the molar volume of the
oxide. The quantity $i - i_{\text{co}}$ represents the portion of the current
density passing the film/solution interface which leads to the formation
of $O^{2-}$ ions in the film. The conduction current density $i$ is related to
the electric field in the film by the high-field conduction law, $i = i_{\text{co}} \exp(B\phi/\delta)$. A differential equation for $i(t)$ was obtained by
substituting for $\delta$ into Eq. 16 from the high-field conduction
equation.

$$\frac{di}{dt} = -iv \ln(i/i_{\text{co}}) \left[ 1 - \ln(i/i_{\text{co}}) \Omega_{\text{Al}}(i - i_{\text{co}}) \right]$$

where $v$ is the voltage scan rate $dE/dt$ during CV. The parameters
$i_{\text{co}}$, $B$, and $\Omega_{\text{Al}}$ were assigned values characteristic of anodic oxide
films: $2.0 \times 10^{-15}$ A/cm$^2$, $3.44 \times 10^{-8}$ cm$^2$/V, and $32.9$ cm$^3$/mol,
respectively.

The present CV model is mathematically the same as previous
models for the CV of aluminum in neutral pH.22,25 Both prior models
incorporate high-field conduction, as is done here, along with an
expression for the “oxide dissolution rate” which is related to the
present metal ion dissolution current density $i_{\text{co}}$. For example, $i_{\text{co}}$
is equivalent to $R_{\text{oh}}/nF$ in Ref. 22, in which $R_{\text{oh}}$ is the oxide
dissolution rate. While the resulting models are equivalent, the present
formulation is fundamentally more valid, because it incorporates the
view that metal and oxygen ions in the film transfer individually to
and from the aqueous solution. Requiring $Al_2O_3$ to dissolve as a
stoichiometric entity, as in the prior models, implies that no current
is passed at the film/solution interface, and therefore violates the
continuity of the interface and conduction current.

When Eq. 17 was integrated with $i_{\text{co}}$ taken to be constant, the predicted
CV results displayed anodic current plateaus similar to those in the earlier models, but the anodic current peaks in the first scan of experimental CVs (Fig. 3 and 4) were absent. Anodic peaks
in the simulated CV could be obtained when a transient decay of $i_{\text{co}}$
was introduced

$$i_{\text{co}} = i_{\text{co}}^i + (i_{\text{co}}^f - i_{\text{co}}^i) \exp\left(-\frac{t}{t_i}\right)$$

Here, $i_{\text{co}}^i$ and $i_{\text{co}}^f$ are the initial and final values of $i_{\text{co}}$, and $t_i$ is the
time constant associated with its decay. The time dependence of $i_{\text{co}}$
may derive from the sensitivity of the kinetics of metal ion transfer
to the chemical composition of the oxide surface, which in turn
depends on the solution pH. The decay in Eq. 18 would be caused
by the relaxation of the oxide surface from its initial state in the 1 M
NaOH pretreatment solution, to its final condition in the pH 11 solution
used in CV experiments. The pH-dependent surface composition
may reflect a change of the overall film composition from $AlH_4$ in 1 M NaOH to aluminum oxide or hydroxide at pH 11.

Comparison of experimental results with model calculations.— In Fig. 9, predic-
tions of the CV model based on $AlH_4$ oxidation at the metal/film interface (Eq. 8-13) are compared with the experimental results at pH 11.75. Particularly in view of the absence of adjustable fitting parameters, the figure demonstrates an
excellent agreement between the shapes of predicted and experi-
mental CV waveforms. The deviation near the open-circuit potential was
expected, because cathodic reactions were not included in the
model. The discrepancy of anodic peak currents and potentials at
higher scan rates may also relate to simplifications inherent in the
model. In particular, Fig. 6 indicates that the surface film thickness
depends on potential, while the model assumes a constant conduc-
tion resistance. Film growth and dissolution were not included be-
cause the film/solution interface kinetics is unknown. Nonetheless,
the overall very good agreement exhibited in Fig. 8 is additional
evidence that the interfacial potential is controlled by the $AlH_4$
oxidation reaction.

The calculations from the $Al$ oxidation model (Eq. 17 and 18) are
compared to experimental CV in Fig. 10 and 11. Figure 10 shows the
first CV cycle and Fig. 11 the second. In order to fit the model to
the experiment, the initial film thickness was set to 1.7 nm, and $i_{\text{co}}$

Figure 9. Comparison of experimental (solid lines) and simulated (dashed lines) CV responses at pH 11.75, at various scan rates.
field conduction in the surface film controls the anodic current. Agreement with experimental CV supports the concept that high
with scan rate as in the experimental CV. The overall excellent agreement supports the view that these features are caused by a
time-dependent volume defect formation in the metal, as observed in alkaline solutions.19 In view of the present results, it is possible that the film at pH 11.75 and higher consists primarily of aluminum hydride. The interfacial hydride layer may assist the high rates of hydrogen absorption and open-volume defect formation in the metal, as observed in alkaline solutions.

Conclusions

The mechanism of Al dissolution in alkaline solutions was investigated by analysis of CV and potential step experiments. An abrupt transition of the surface film properties and dissolution mechanism was demonstrated in the pH range from 11 to 11.75. At pH 11, the behavior of the Al electrode is similar to that in neutral pH solutions, controlled by the anodic formation of a surface film with a high ionic conduction resistance. The potential at the metal/film interface indicates that the primary anodic reaction is Al oxidation. At pH 11.75, the surface film resistance is significantly reduced, and the consequently much larger dissolution current is strongly influenced by mass transport and ohmic resistance. Anodic metal dissolution is mediated by the formation and oxidation of interfacial aluminum hydride. The presence of interfacial AlH$_x$ during anodic polarization at pH 11.75 suggests that water transport to the metal/film interface is fast enough so that hydride can form before Al$^{3+}$ ions can be transported away from the interface. The film structure and possibly composition is apparently quite different between the two pH values: the film at pH 11.75 seems to possess an appreciably lower conduction resistance and higher water permeability than the film at pH 11. These structural differences may correlate with the high sensitivity of oxide solubility to pH in this range.19 In view of the

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