Acceleration of the Cathodic Kinetics on Aluminum Alloys by Aluminum Ions

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The effect of Al\(^{3+}\) on the cathodic kinetics of Al alloys as well as Pt and SS316L has been investigated by a number of electrochemical techniques. It has been observed that the addition of Al\(^{3+}\) into NaCl solution can significantly increase the diffusion limited cathodic kinetics of Al alloys, and this increase is proportional to the [Al\(^{3+}\)]. The same phenomenon was also observed on Pt and SS316L, which indicates that this enhancement in cathodic kinetics is not related to the surface structure of Al alloy, and it is the HER diffusion-limited kinetics that are increased rather than ORR kinetics as a result. Based on electrochemical studies on Pt, it is proposed that although the addition of Al\(^{3+}\) can lead to the precipitation of an oxide/hydroxide film on Pt there is a greatly enhanced proton diffusion which overwhelms the barrier effect of the precipitate film, leading to substantially increased cathodic kinetics. The results are interpreted in terms of an extension of the Grotthuss Theory in which Al\(^{3+}\) can facilitate transport of the proton.

High strength aluminum alloys (Al alloys) have received wide application in the aerospace and automotive industries for decades. However, these alloys are prone to localized corrosion due to their highly heterogeneous microstructures, with susceptibility to pitting and crevice corrosion, intergranular corrosion, exfoliation corrosion, and environmental assisted cracking, depending upon the alloy composition and temper. These localized corrosion modes are detrimental to the Al-alloy based structures, and there has been a great number of experimental studies performed aimed at understanding the mechanism of cathodic kinetics, as well as development of pertinent test protocols to better quantify these phenomena. Among these experimental protocols, accelerated corrosion testing methods are designed to create corrosion morphologies that mimic those observed in service and to evaluate the interactions between exposure environment and the degree of localized corrosion in a timely fashion. For exfoliation corrosion, the available accelerated testing protocols include ASTM G34 (EXCO), ASTM G85, and ANClT. For ANClT, the available accelerated testing protocols include ASTM G34 (EXCO), ASTM G85, and ANClT. For ANClT, the enhancement of cathodic kinetics and corrosion behavior of Al alloys as well as Pt and stainless steel 316L, in order to identify the underlying mechanism of cathodic kinetics enhancement by Al\(^{3+}\).

Experimental

Materials preparation.—Three types of Al alloys: AA2024-T351, AA5083-H131 and AA7050-T451, all of which were obtained from ALCOA (Pittsburgh, PA), as well as SS316L (McMaster-Carr Supply Company, Elmhurst IL) were cut into 1" × 1" test coupons. A platinum rotating disk electrode (Pt Research Instrumentation, Inc., Durham, NC) with a diameter to 0.5 cm was used for the RDE test. The nominal compositions of the three types of Al alloys are listed in Table I. In addition to the regular Al alloy samples for electrochemical tests, sensitized AA5083-H131, DoS = 50 mg/cm\(^2\) specimen were mounted in the epoxy and used for immersion exposure tests. All of these specimens were polished to a surface finish of 1200 grit with SiC paper, and subsequently degreased with ethanol followed by deionized water, prior to experiment.

Table I. Nominal Composition of AA7050-T7451, AA5083-H131 and AA2024-T351 (All values in weight percent).

| Si  | Fe  | Cu  | Mn  | Mg  | Cr  | Zn  | Ti  | Zr  | Al  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.12| 0.15| 2.60| 0.10| 2.60| 0.04| 6.70| 0.06| 0.15| balance |
| 0.10| 0.22| 0.05| 0.70| 4.40| 0.08| 0.02| 0.02| N/A | balance |
| 0.093| 0.18| 4.50| 0.62| 1.30| 0.01| 0.10| 0.018| 0.003| balance |

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Electrochemical tests.—A three-electrode electrochemical cell was used with the alloy test specimens as the working electrode (WE) with an exposure area of 1 cm² (except that Pt disc electrode had surface area = 0.2 cm²), a saturated calomel reference electrode (SCE) as reference electrode (RE), and a platinum-niobium mesh as the counter electrode (CE). A Bio-Logic SP-200 (Bio-Logic SAS, Claux, France) potentiostat was utilized with EC-Lab (Version 11.01) software to perform all of the electrochemical measurements. The details of each electrochemical technique will be described in below.

Table II. pH of each test solution.

| Solution          | pH   |
|------------------|------|
| 0.6M NaCl         | 5.60 |
| 0.57M NaCl+0.01M AlCl₃ | 3.57 |
| 0.45M NaCl+0.05M AlCl₃ | 3.20 |
| 0.3M NaCl+0.1M AlCl₃  | 3.01 |
| 0.2M AlCl₃       | 2.87 |

Potentiodynamic polarization measurements.—Cathodic polarization measurements were performed on AA7050-T451, AA5083-H131, AA2024-T351 and SS316L at a scan rate of 0.2 mV/s after 1 hr of open circuit potential (OCP) measurement, starting from OCP to −1.5 V vs. SCE in five different solutions: (1) 0.6 M NaCl, (2) 0.57 M NaCl+0.01 M AlCl₃, (3) 0.45 M NaCl+0.05 M AlCl₃, (4) 0.3 M NaCl+0.1 M AlCl₃, and (5) 0.2 M AlCl₃. The pH of each solution was measured by Fisherbrand Accumet XL200 pH/Conductivity Benchtop Meter (Hampton, NH) and listed in Table II. Two additional test solutions with a basis of 0.6 M NaCl with the pH adjusted by HCl were prepared to compare to solutions 2 and 4 at the same pH: 0.6 M NaCl with pH = 3.57 and 0.6 M NaCl with pH = 3.01. The purpose of performing cathodic polarization from OCP is to avoid the effects of prior anodic dissolution on the surface structure if the scan was to be started above OCP, and only focus on the cathodic characteristics of as-polished samples. To determine the dependence of the polarization resistance (R_p) and corrosion potential (E_cor) on the [Al³⁺], full polarization measurements were performed on all Al alloy samples with a scan rate of 0.2 mV/s, which started at 0.3 V below OCP and ended at −0.6 V vs. SCE.

Electrochemical impedance spectroscopy (EIS).—A typical electrochemical impedance spectrum was acquired over the frequency range from 10 kHz to 10 mHz at 10 points per decade with a 10 mV AC amplitude around OCP after 1 hr immersion time. AA7050-T7451 specimen were immersed in solutions 1−5 as described above to study the effect of Al³⁺ concentration on interfacial electrochemical parameters. All the EIS data was fitted by the EC-Lab software.

Rotating disc electrode measurements.—A Pine Instrument ASR rotator (Pine Research Instrumentation, Inc., Durham, NC) was used with a Pt WE. Two types of experiments with RDE configurations were performed: (1) after 10 min stabilization, direct RDE cathodic polarization measurements from −0.20 V vs. SCE to −1.10 V vs. SCE with a scan rate of 0.20 mV/s and rotation speeds of 100, 200, 500, and 1,000 rpm, in 0.3 M NaCl+0.1M AlCl₃ and 0.6 M NaCl (pH = 3.01), respectively; (2) RDE cathodic polarization measurements starting from OCP to −1.00 V vs. SCE after 1 hr OCP measurement in 0.6 M NaCl, 0.6 M NaCl (pH = 3.01) and 0.3 M NaCl+0.1 M AlCl₃ (all three solutions were in a quiescent condition). One additional test in N₂-purged environment was conducted in the last solution.

SEM/EDS characterization.—A Pt surface was characterized after cathodic polarization in Al³⁺-containing solution by FEI QUANTA 200 scanning electron microscopes (SEM) with an energy dispersive spectroscopy (EDS) detector (Hillsboro, OR).

Results

A description of the corrosion kinetics of Al alloys in the absence and presence of Al³⁺, as well as the dependence of mass-transfer limited cathodic kinetics and corrosion resistance of Al alloys on the Al³⁺ concentration will be presented here. Most of the results presented are for AA7050-T451.

Mass transfer limited cathodic kinetics and polarization resistance of Al alloys as a function of [Al³⁺].—Typical cathodic polarization curves of AA7050-T7451 in pure 0.6 M NaCl and NaCl+AlCl₃ with different [Al³⁺] and fixed [Cl⁻] = 0.6 M are displayed in Figure 1a. Before introducing Al³⁺, the cathodic limiting current density (i_lim) of AA7050 was ORR-controlled in neutral 0.6 M NaCl (on the order of 1E-06 A/cm²) and smaller than a typical i_lim of SS/Pt in the same solution (on the order of 1E-05 A/cm²).

Once [Al³⁺] was added to the NaCl, i_lim increased significantly, and i_lim increased steadily as [Al³⁺] increased. A comparison of i_lim chosen at a reference potential −1.00 V vs. SCE as a function of [Al³⁺] is shown in Figure 1b. A sharp jump in i_lim (~6x) when 0.01 M [Al³⁺] was added to the NaCl was evident. A comparison of i_lim chosen at a reference potential −1.00 V vs. SCE as a function of [Al³⁺] is shown in Figure 1b. A sharp jump in i_lim (~6x) when 0.01 M [Al³⁺] was added to the NaCl was evident.

Figure 1. a) Comparison of cathodic polarization curves of AA7050 as a function of [Al³⁺]; b) i_lim vs. [Al³⁺] at a reference potential −1.00 V vs. SCE.
introduced into pure NaCl solution followed by a steady increase in \( i_{\text{lim}} \) with increasing \([\text{Al}^{3+}]\), albeit at a slower rate between 0.05 and 0.1 M, until a maximum was reached at 0.2 M \([\text{Al}^{3+}]\), at which \( i_{\text{lim}} \) was approximately 9 times higher than 0.6 M NaCl. It is obvious that the addition of \([\text{Al}^{3+}]\) can significantly enhance mass transfer limited cathodic kinetics of AA7050. To determine if the effect of \([\text{Al}^{3+}]\) also takes place in the other Al alloys, cathodic polarization curves of AA7050-T7451, AA5083-H131 and AA2024-T3 in 0.6 M NaCl and also takes place in the other Al alloys, cathodic polarization curves of AA2024 + AlCl3 were generated and are compared in Fig. 2. It is clearly seen that, with addition of \([\text{Al}^{3+}]\) into NaCl solution, \( i_{\text{lim}} \) was significantly enhanced for all three Al alloys, and the order of the increased \( i_{\text{lim}} \) being AA2024 > AA7050 > AA5083 in both solutions in the presence and absence of \([\text{Al}^{3+}]\). The fact that AA2024 had highest \( i_{\text{lim}} \) can be attributed to its high Cu content which allows increased mass-transfer limited cathodic kinetics.

It is known that \([\text{Al}^{3+}]\) can be hydrated with six water molecules to form complex ion \( \text{Al(H}_2\text{O)}_{6}\text{Al}^{3+} \) in neutral solutions.29 This complex ion can undergo a series of complicated hydrolysis reaction, with the resultant product: \[
\text{Al}(\text{H}_2\text{O})_{6}\text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_{3}^{2+} + \text{H}_2\text{O} + p\text{K}_1 = 4.96 \quad [1]
\]
The hydrolysis of hydrated \([\text{Al}^{3+}]\) results in an acidic pH. To distinguish the enhanced cathodic kinetics of Al alloys by adding \([\text{Al}^{3+}]\) from that due to a lowered pH, a comparison of cathodic kinetics of AA7050 in 0.6 M NaCl \((pH = 5.60)\), 0.6 M NaCl \((pH = 5.01)\), and 0.3 M NaCl + 0.1 M AlCl3 \((pH = 3.01)\) is displayed in Fig. 3. Using the value at \(-1.00 \text{ V}_{\text{SCE}}\) again for reference potential, the \( i_{\text{lim}} \) for the \([\text{Al}^{3+}]\)-containing solution was about twice that for 0.6 M NaCl at the same pH, indicating the increase in \( i_{\text{lim}} \) was not solely caused by low pH due to hydrolysis of \([\text{Al}^{3+}]\).

As for the effect of \([\text{Al}^{3+}]\) on the polarization resistance, a comparison of full polarization curves of AA7050 as a function of \([\text{Al}^{3+}]\) is shown in Fig. 2a. \( R_p \), \( E_{\text{corr}} \) and \( i_{\text{corr}} \) (calculated by the EC-lab software) for each solution in Fig. 2a are listed in Table III. It can be seen that \( R_p \) fell dramatically from 1.98E+04 \( \Omega \cdot \text{cm}^2 \) to 3.79E+03 \( \Omega \cdot \text{cm}^2 \) upon the addition of 0.01 M \([\text{Al}^{3+}]\), with a continued gradual decrease as \([\text{Al}^{3+}]\) increased until reaching a minimum in 0.2 M AlCl3 with a value of only about 11% of that in pure 0.6 M NaCl. The \( i_{\text{corr}} \) values showed the reversal trend due to its reciprocal relation with \( R_p \), starting from 7.15E-07 A/cm^2 to 1.21E-05 A/cm^2 with increasing \([\text{Al}^{3+}]\). Interestingly, \( E_{\text{corr}} \) first dropped from \(-0.74 \text{ V}_{\text{SCE}}\) to \(-0.94 \text{ V}_{\text{SCE}}\) upon the addition of 0.01 M \([\text{Al}^{3+}]\) into the NaCl solution, and then rose with increasing \([\text{Al}^{3+}]\). This behavior can be explained by Fig. 2b. When the solution changes from 1 to 2, application of Mixed Potential Theory demonstrates that the enhancement of the anodic/dissolution kinetics of AA7050 due to addition of \([\text{Al}^{3+}]\) decreased solution pH and dominated the change in the anodic kinetics, thus the resultant \( E_{\text{corr}} \) moved in negative direction and the \( i_{\text{corr}} \) value increased. However, the mass transfer limited cathodic kinetics significantly increased as \([\text{Al}^{3+}]\) increased further from solution 2 to 5, such that changes in the cathodic kinetics became more dominant than those in the anodic kinetics, with the resultant \( E_{\text{corr}} \) moving in the positive direction and the \( i_{\text{corr}} \) value increasing. This behavior also implies that a significant \([\text{Al}^{3+}]\) (\(\sim0.05\) M) is needed in order to maintain a high corrosion rate of Al alloys controlled by enhanced cathodic kinetics.

**EIS analyses**—In order to better understand the electrochemical mechanism of the effect of \([\text{Al}^{3+}]\) on the corrosion behavior of Al alloys and evaluate passive oxide film quality as a function of \([\text{Al}^{3+}]\), EIS analyses were performed on AA7050-T7451. Fig. 5 shows the corresponding Nyquist plots for the different solutions. It is clearly seen that an inductive loop appears in the low frequency regime in \([\text{Al}^{3+}]\)-containing solution, and as a result, two types of equivalent circuit models were used as shown in Fig. 6. The equivalent circuit model in Fig. 6a was used to fit data in 0.6 M NaCl, and that in Fig. 6b was used for the NaCl+AlCl3 solutions to take in account the inductive loop, which might be caused relaxation of absorbed intermediate in the oxide film during HER.30–33 Also, a Warburg impedance element was used in both models to account for mass transfer of protons to the oxide/electrode interface in the low frequency regime. At high frequencies, both models have CPE behavior attributed to the passive oxide film, in order to estimate the effective capacitance values from the CPE following the method developed by Hirschorn et al.34,35 They showed the mathematical relation between the constant phase element (CPE) and the effective capacitance for oxide film thickness to be

\[
C_{\text{eff}} = \frac{gQ(p_e\varepsilon_0)^{1-a}}{\omega}
\]

Where \(C_{\text{eff}}\) is the effective capacitance, \(\varepsilon_0\) is the film resistivity, \(\varepsilon\) is the dielectric constant for the film, \(\varepsilon_0\) is the vacuum permittivity \((8.852E-12 \text{ F/m})\), and \(g\) is a dimensionless number which is a function of

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**Table III. A list of Fitted Electrochemical Parameters for AA7050 as a function of [Al3+] in solutions.**

| Solution | \(R_p\) (\(\Omega \cdot \text{cm}^2\)) | \(E_{\text{corr}}\) (\(\text{V}_{\text{SCE}}\)) | \(i_{\text{corr}}\) (A/cm^2) |
|----------|-------------------------------|-----------------|---------------------|
| a        | 0.6M NaCl                      | 1.98E+04        | -0.74               | 7.15E-07            |
| b        | 0.57M NaCl+0.01M AlCl3        | 2.93E+03        | -0.74               | 4.09E-06            |
| c        | 0.45M NaCl+0.05M AlCl3        | 2.81E+03        | -0.85               | 9.30E-06            |
| d        | 0.3M NaCl+0.1M AlCl3          | 1.62E+03        | -0.82               | 1.21E-05            |
| e        | 0.2M AlCl3                    | 2.16E+03        | -0.82               | 1.21E-05            |

*Figure 2.* Comparisons of cathodic kinetics of AA7050, AA5083 and AA2024 in 0.6M NaCl and 0.3M NaCl+0.1M AlCl3.

*Figure 3.* A comparison of cathodic kinetics of AA7050 in 0.6M NaCl (pH = 5.60), 0.6M NaCl (pH = 3.01), and 0.3M NaCl + 0.1M AlCl3 (pH = 3.01).
α : $g = 1 + 2.88(1 - \alpha)^2$.\textsuperscript{375} For $\rho_t$ and $\varepsilon$, it is assumed that the oxide film is mainly alumina with film resistivity $= 1.00E+012 \text{ohtm}\cdot\text{m}$\textsuperscript{36} and $\varepsilon = 9.37$. All of the fitted EIS parameters are listed in Table IV. Based on these fitted parameters, two factors can be evaluated: the $R_{\text{film}}C_{\text{film,eff}}$ product to evaluate oxide film quality, and $R_{\text{total}} = R_{\text{film}} + R_{\text{ct}} + R_{\text{Loop}}$ to evaluate total corrosion resistance. The reason the RC product can be used to evaluate oxide film quality is that: $R_{\text{film}} = \rho_{\text{film}} A_{\text{film}}$, so $R_{\text{film}}C_{\text{film,eff}} = \rho_{\text{film}} A_{\text{film}}$ is only a function of film resistivity assuming the dielectric constant is unchanged. Fig. 7 shows the dependence of $R_{\text{film}}C_{\text{film,eff}}$ as well as $R_{\text{total}}$ on $[\text{Al}^{3+}]$. The $R_{\text{film}}C_{\text{film,eff}}$ product declined dramatically with small additions of $\text{Al}^{3+}$, which might be attributed to hydration of oxide film under anodic control when $\text{Al}^{3+}$ was introduced into NaCl. Higher $\text{Al}^{3+}$ concentrations led to small increases in $R_{\text{film}}C_{\text{film,eff}}$, possibly due to the accumulation of aluminum oxide/hydroxide on the alloy surface with increased $\text{Al}^{3+}$ concentration. The total resistance decreased with increasing $\text{Al}^{3+}$ concentration with the largest decrease occurring at the smallest $\text{Al}^{3+}$ concentrations, echoing the tendency of polarization resistance calculated previously, indicating that the Al alloy is more prone to localized corrosion with increasing $[\text{Al}^{3+}]$.

**Full immersion exposure test for sensitized AA5083-H131 in $\text{Al}^{3+}$-containing solution.**—Fig. 8 shows the optical micrographs of cross-sections of sensitized AA5083-H131 samples after exposure to solutions containing $1 \text{M Cl}^-$ and $0.05 \text{M K}_2\text{S}_2\text{O}_8$ (with varying $\text{Al}^{3+}$ ion concentration and $\text{pH} = 3$). Qualitatively, the micrographs show an increase in corrosion damage with an increase in the $\text{Al}^{3+}$ ions in solution. ImageJ software\textsuperscript{38} was used to analyze the images to quantitatively evaluate the difference between the corrosion damage obtained in each case. The images were converted into 8-bit and processed for binary (black and white) color composition. Table V shows the results from ImageJ analysis. As evident qualitatively, the analysis confirmed that overall damage increased with an increase in Al ion concentration in solution.

**The effect of $\text{Al}^{3+}$ on cathodic kinetics of Pt and SS.**—Several previous studies have investigated the effect of cathodic polarization on the corrosion of pure Al. Lin and Hebert\textsuperscript{39,40} found that the hydrated oxide film transformed into hydroxide and became an ohmic conductor with high conductivity upon polarization to a cathodic potential $\sim -1.70 \text{V}_{\text{SCE}}$, resulting in higher cathodic charge and enhanced corrosion rate. Moon and Pyun\textsuperscript{41,42} studied the electrochemical behavior of Al after prior cathodic polarization, showing that the observed enhanced corrosion rate was caused by the dissolution of native oxide film due to the prior cathodic polarization (and alkalinization of the surface). However, both of these studies indicate that cathodic
Table IV. Fitted EIS parameters as a function of [Al$^{3+}$] for AA7050 ($R_{s}$: solution resistance, $Q_{film}$: CPE for the surface oxide film, $\alpha_{film}$: exponent parameter for $Q_{film}$, $C_{film,eff}$: effective film capacitance, $R_{film}$: film resistance, $L_{loop}$: inductive loop pertinent to surface film, $R_{loop}$: resistance parallel to the inductive loop, $Q_{dl}$: double layer capacitance, $\alpha_{dl}$: exponent parameter for $Q_{dl}$, $R_{ct}$: charge transfer resistance, $W$: Warburg impedance).

| Solvent                  | 0.6M NaCl | +0.01M AlCl$_3$ | +0.05M AlCl$_3$ | +0.1M AlCl$_3$ | 0.2M AlCl$_3$ |
|--------------------------|-----------|-----------------|-----------------|----------------|---------------|
| $R_{s}$ ($\Omega \cdot$ cm$^2$) | 1.86E+01  | 1.85E+01        | 2.01E+01        | 1.90E+01       | 2.60E+01      |
| $Q_{film}$ ($S \cdot \epsilon^2$) | 2.685E-05 | 1.01E-05        | 3.40E-05        | 5.00E-05       | 6.75E-05      |
| $\alpha_{film}$          | 0.90      | 0.95            | 0.93            | 0.92           | 0.93          |
| $C_{film,eff}$ (F$^{-1} \cdot$ cm$^{-2}$) | 3.80E-05  | 1.22E-05        | 4.30E-05        | 6.62E-05       | 8.60E-05      |
| $R_{film}$ ($\Omega \cdot$ cm$^2$) | 4.04E+03  | 2.76E+03        | 1.52E+03        | 8.40E+02       | 7.13E+02      |
| $L_{loop}$ (H)            | N/A       | 1.65E+02        | 2.10E+02        | 3.30E+02       | 3.00E+03      |
| $R_{loop}$ ($\Omega \cdot$ cm$^2$) | N/A       | 1.21E+02        | 2.51E+02        | 4.59E+02       | 2.65E+02      |
| $Q_{dl}$ ($S \cdot \epsilon^2$) | 5.51E-06  | 1.05E-02        | 8.00E-03        | 6.70E-03       | 5.98E-03      |
| $\alpha_{dl}$            | 0.83      | 0.99            | 0.75            | 0.70           | 0.69          |
| $R_{ct}$ ($\Omega \cdot$ cm$^2$) | 1.57E+04  | 1.22E+03        | 1.12E+03        | 1.00E+03       | 6.01E+02      |
| $W$ ($S \cdot \epsilon^2 \cdot$ cm$^{-2}$) | 1.20E+03  | 1.60E+02        | 1.20E+02        | 1.15E+02       | 1.20E+02      |

Figure 7. a) $R_{film}C_{film,eff}$ product vs. [Al$^{3+}$] and b) $R_{total}$ vs. [Al$^{3+}$] for AA7050 from EIS analysis.

charge changed the property of oxide film which in turn accelerated the corrosion rate. Here, we show that the enhanced cathodic kinetics or corrosion rate is not limited to the Al alloy system, but can be also extended to the other metals and alloys, of which Pt and SS were utilized as two examples in this study.

Cathodic polarization curves of SS316L in three different solutions are shown in Fig. 9a. Similar to the phenomenon observed with the Al alloys, SS316L showed enhanced mass transfer limited cathodic kinetics in the presence of Al$^{3+}$ compared to that in 0.6M NaCl with natural pH, and 0.6M NaCl adjusted to the same pH, proving again that this enhancement was contributed to the Al$^{3+}$ ion, not only the low solution pH due to hydrolysis of Al$^{3+}$. However, it is still difficult to distinguish the ORR limiting current density from HER one. Another group of cathodic polarization curves of Pt in the same three solutions as used in the SS 316L tests, plus one additional test of 0.3M NaCl+0.1 M AlCl$_3$ in deaerated solution, are displayed in Fig. 9b. Because the $i_{lim}$ in 0.6 M NaCl (pH = 5.60) for Pt is attributed to ORR only, this curve can be utilized to distinguish the HER diffusion limited potential region from that of ORR in both 0.6M NaCl pH = 3.01, and 0.3 M NaCl+0.1M AlCl$_3$ quiescent solutions. Such an analysis led to an assignment of 0.20 V$\text{SCE}$~−~0.30 V$\text{SCE}$ for ORR diffusion limited kinetics, and ~0.50 V$\text{SCE}$~−~0.90 V$\text{SCE}$ for HER diffusion limited kinetics. It is clearly seen that the $i_{lim}$ pertinent to ORR in both 0.6M NaCl (pH = 3.01) and 0.3M NaCl+0.1 M AlCl$_3$ solutions were almost identical to that in 0.6 M NaCl with natural pH, proving that Al$^{3+}$ has negligible effects on ORR related diffusional cathodic kinetics. By comparing $i_{lim}$ in quiescent and deaerated 0.3 M NaCl+0.1 M

Figure 8. AA5083-H131 optical microscopic image of the LS cross section after 100 hours of open circuit exposure in 1M Cl$^{-}$ + 0.05M K$_2$S$_2$O$_8$ solution (pH 3). Horizontal direction corresponds to S and vertical direction corresponds to L.

Table V. IGC damage measured using ImageJ analysis for the exposures shown in Fig. 8. The total damage reported here corresponds to anodic dissolution of both the grain boundaries and the matrix.

| 100-hr full immersion exposure in solution (pH) | Damage ($\mu$m$^2$) |
|-----------------------------------------------|---------------------|
| 1M NaCl                                       | 5.49E+04            |
| 0.93M NaCl+0.022 M AlCl$_3$                   | 7.79E+04            |
| 0.85M NaCl+0.050 M AlCl$_3$                   | 8.69E+04            |
| 0.70M NaCl+0.100 M AlCl$_3$                   | 1.28E+05            |

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AlCl$_3$ solutions, one can see that $i_{\text{lim}}$ in deaerated solution was only about 40% of that in quiescent solution, because the reduced ORR-related current density resulted in a lower total current density due to deaeration, whereas $i_{\text{lim}}$ pertinent to HER was still about 40 times higher than that in 0.6 M NaCl with same pH, proving that Al$^{3+}$ is the dominant factor contributing significant enhancement in HER diffusional cathodic kinetics. This finding also implies that the interaction between Al$^{3+}$ and the native oxide film on the Al alloy surface is not the only contributing factor to the enhancement of cathodic kinetics, but the change in solution property must occur when introducing Al$^{3+}$ into NaCl system.

It was also observed that a very thin, white film was formed after cathodic polarization of SS/Pt in Al$^{3+}$-containing solution, and SEM/EDS was then utilized to look at the film morphology and composition. Typical SEM and EDS images of Pt after cathodic polarization in 0.3 M NaCl+0.1 M AlCl$_3$ are displayed in Fig. 10. In the SEM

![Figure 9](image1.png)

**Figure 9.** Comparison of cathodic polarization curves of a) SS316L, and b) Pt in 0.6 M NaCl (natural pH), 0.6 M NaCl (pH = 3.01), and 0.3 M NaCl+0.1 M AlCl$_3$ (pH = 3.01, additional test in deaerated solution for Pt).

![Figure 10](image2.png)

**Figure 10.** a) SEM image, b) overlaid EDS map, c) EDS O elemental map, and d) EDS Al elemental map of film covered on the Pt surface after cathodic polarization in 0.3M NaCl+0.1M AlCl$_3$ solution.
image, the film consists of loosely packed, irregularly shaped flakes, and the composition of film consists of Al and O, implying some type of aluminum oxide/hydroxide was formed on the Pt surface. Lin and Hebert39 found that aluminum hydroxide can exist on the Al surface even in an acidic environment (0.1 M HCl). However, the detailed composition and chemical structure of this film is beyond the study scope in this work.

**Discussion**

According to Fick’s 1st Law, the theoretical diffusion limited current density assuming one dimensional diffusion can be expressed as

\[
i_{\text{lim, theoretical}} = \frac{nFD(C_{\text{bulk}} - C_{\text{surface}})}{\delta}
\]

where \(n\) is the number of transferred during electrochemical reaction, \(D\) is the diffusivity of reacting species, \(C_{\text{bulk}}\) and \(C_{\text{surface}}\) are the concentration of reacting species at the bulk solution and electrode surface respectively, and \(\delta\) is the diffusion layer thickness. In this section, a deconstruction of Eq. 3 will be performed to target the dominant parameter controlling the increased HER related diffusion current density.

**Formation of aluminum oxide/hydroxide film on the surface as diffusional barrier to HER.**—A thin white film was formed on the Pt surface after cathodic polarization in Al\(^{3+}\) solution as indicated previously. To discern the role of this film in mass transfer limited cathodic kinetics, continuous cathodic polarization measurement was performed on Pt in 0.3 M NaCl+0.1 M AlCl\(_3\), in which after one scan, Pt was allowed to rest in the test solution for 5 mins, and then a following scan from the OCP to the final potential was conducted. This procedure was repeated three times. The measured cathodic polarization scans are shown in Fig. 11. After the formation of aluminum oxide/hydroxide film on the surface during the 1st scan, the \(i_{\text{lim}}\) in both the ORR region and the HER region were decreased, which indicates that the formed film is diffusion barrier to both ORR and HER. According to Eq. 3, the effective diffusion layer thickness is \(\delta = \delta_{\text{natural convection}} + \delta_{\text{film}}\), where \(\delta_{\text{natural convection}}\) is the critical natural convection boundary layer thickness in quiescent solution, and \(\delta_{\text{film}}\) is the film thickness. Once the film formed on the surface, the diffusion layer thickness increased from \(\delta_{\text{natural convection}}\) to \(\delta_{\text{natural convection}} + \delta_{\text{film}}\), resulting in a lower limiting current density. However, both \(i_{\text{lim, ORR}}\) and \(i_{\text{lim, HER}}\) were almost the same in 2nd and 3rd scan, which implies that the film covered Pt surface might not be a good substrate for future film deposition such that the accumulation of film thickness was negligible after the 1st scan.

**Mechanism of enhanced diffusivity of proton (Grotthuss mechanism).**—To investigate the diffusivity of the proton in the Al\(^{3+}\) solution and compare it with that in purely acidified NaCl solution, RDE tests were performed on Pt in both 0.6 M NaCl pH = 3.01 and 0.3 M NaCl+0.1 M AlCl\(_3\) (pH = 3.01) with rotation speeds of 100, 200, 500 and 1000 rpm (Fig. 12). It can be clearly observed that addition of Al\(^{3+}\) did not alter ORR diffusional cathodic kinetics but increased the HER diffusional cathodic kinetics as rotation speed increased. To exclude the effect of charge-transfer limited kinetics from the total cathodic kinetics, Koutecký–Levich (K-L) analysis44 was applied which can be expressed as

\[
\frac{1}{i} = \frac{1}{i_{\text{total cathodic}}} + \frac{1}{i_{\text{lim}}} = \frac{1}{i_{\text{ct}}} + \frac{1}{B_L(C_H^+)^{0.5}}
\]

where \(i_{\text{total cathodic}}\) is the total cathodic current density, \(i_{\text{lim}}\) is the true mass-transfer limited current density, \(i_{\text{ct}}\) is the charge-transfer limited kinetics, \(B_L\) is Levich constant, and \(\omega\) is the rotation speed of the RDE. An example of K-L plots at potential = −0.7, −0.8 and −0.9 V\(_{\text{SCE}}\) in Al\(^{3+}\) solution is displayed in Fig. 13a. From this figure, one can obtain the values of \(i_{\text{ct}}\) at each potential and then calculate the average \(i_{\text{lim}}\) at each rotation speed based on three different potentials. As a result, modified Levich analyses can be obtained in NaCl, and NaCl+AlCl\(_3\) solutions respectively (shown in Fig. 13b). The calculated slopes for two solutions are: 1.78E-04 for 0.6 M NaCl (pH = 3.01), and 4.05E-03 for 0.3 M NaCl+0.1 M AlCl\(_3\). According to Levich equation:

\[
i_{\text{lim}} = 0.620 \cdot nFD_{H^+}^{2/3} \cdot \nu^{1/6} \cdot C_{H^+}^{1/2} \cdot \omega^{-0.5}
\]

where \(D_{H^+}\) is the diffusivity of proton at 25°C, \(\nu\) is the kinematic viscosity of solution, \(C_{H^+}\) is the bulk concentration of proton assuming fast HER at the electrode/electrolyte interface such that \(C_{\text{surface, H}}\) is zero, and \(\omega\) is the rotation speed of the RDE. Assuming two solutions have the same \(\nu\) and \(C_{H^+}\), the ratio of the slopes of the two Leitwich expressions is equal to

\[
\left[ \frac{D_{H^+} (\text{Al}^{3+})}{D_{H^+} (\text{no Al}^{3+})} \right]^{2/3} = \frac{4.05E - 3}{1.78E - 4}
\]

Hence \(D_{H^+} (\text{Al}^{3+}) / D_{H^+} (\text{no Al}^{3+})\) is about 108, which means diffusivity in Al\(^{3+}\) containing solution was two orders of magnitude larger than pure NaCl solution under the same pH value. To roughly estimate the value of proton diffusivity in Al\(^{3+}\) solution, one can start from calculating \(D_{H^+}\) in acidified NaCl: assuming that the viscosity.
of 0.6M NaCl (pH = 3.01) is equivalent to that of neutral 0.6M NaCl solution (9.20E-07 m2/s), and considering that the Levich equation has a slope = 0.620 · nFΔHf \(2/3\) \(\nu^{-1/2}C_H^+\), one can calculate the proton diffusivity in acidified 0.6 M NaCl without any dissolved aluminum ions to be \(\sim 5.03E-09\) m2/s. Then, based on the Eq. 6, the estimated \(D_H^+ (0.1M Al^{3+})\) would be \(\sim 5.43E-07\) m2/s.

A mechanism based on Grothuss Theory\(^{45,46}\) is proposed to explain the large increased proton diffusivity in Al\(^{3+}\)-containing solutions. In this theory, proton transport occurs along chains of hydrogen bonds in water involving hopping or tunneling of the proton from one molecule to the next. In pure acidified NaCl solution, the transport of proton can be illustrated in Fig. 14a. Protons from the bulk solution, move along the proton chains in water system, and reach the electrode surface to undergo reduction. The Grothuss Theory can also be applied along the proton chains in water system, and reach the electrode surface to undergo reduction. This mechanism can facilitate transport of the proton, even though a precipitated oxide/hydroxide film on Pt which one might expect to act as a diffusional barrier to HER.

The effect of Al\(^{3+}\) on the cathodic kinetics of Al alloys has been explored. It has been found that the addition of Al\(^{3+}\) into NaCl solutions can significantly increase the diffusion limited cathodic kinetics of Al alloys, and this increase is proportional to the [Al\(^{3+}\)]\(^{1}\). The same phenomenon was also observed on Pt and SS316L, which indicates that this enhancement in cathodic kinetics is not related to the surface structure of Al alloy, and HER diffusion limited kinetics are increased rather than ORR kinetics as a result. Based on electrochemical studies on Pt, it is proposed that, a mechanism similar to that described by the Grothuss Theory is operative in which Al\(^{3+}\) can facilitate transport of the proton, even through a precipitated oxide/hydroxide film on Pt which one might expect to act as a diffusional barrier to HER during cathodic polarization. This enhanced proton diffusivity due to Al\(^{3+}\) overwhelms the barrier effect of precipitate film, and then significantly increases cathodic limiting current density.

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