Potentiodynamic polarization curves of AA7075 at high scan rates interpreted using the high field model

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The drastic distortion of potentiodynamic polarization curves measured at high potential scan rates prevents the extraction of accurate kinetic parameters. In this work, we start by measuring potentiodynamic polarization curves of AA7075 at scan rates ranging from 0.167 mV·s⁻¹ to 100 mV·s⁻¹, in an acidic 0.62 M NaH₂PO₄ solution and a near-neutral 3.5 wt% NaCl solution. Changes in potentiodynamic polarization curves are observed not only at different scan rates and electrolytes but also between replicated experiments. Contrary to what was reported in previous studies, the disturbance of charging current associated with high scan rates does not satisfactorily explain the potentiodynamic polarization shape. Instead, the high field model that incorporates the kinetics of anodic oxide growth successfully captures the features of experimental potentiodynamic polarization curves. Compared to Tafel’s theory, the high field model explains remarkably the changing kinetics with scan rates, electrolytes, and the variance between measurements performed at different sites.

RESULTS AND DISCUSSION

Complex trends emerge from PDP at high scan rates

The experimental PDP curves of AA7075 in 0.62 M NaH₂PO₄ and 3.5 wt% NaCl are presented in Fig. 1. Prior to the PDP measurement, the sample was at OCP until steady-state is reached: ~20 min for OCP to stabilize at ~0.82 V vs. SCE in 0.62 M NaH₂PO₄ and ~5 min for OCP to stabilize at ~0.78 V vs. SCE in 3.5 wt% NaCl. Before starting the potential scan in the positive direction, a potential of ~0.25 V vs. OCP was then applied for 20 s...
to reduce the transient effects such as charging current and diffusion of O₂.

In 0.62 M NaH₂PO₄, the  \( E_{\text{corr}} \) and corrosion current density (\( j_{\text{corr}} \)) measured at 0.167 mV·s⁻¹ (black line in Fig. 1a) are \(-0.77 \) V vs. SCE and 9.8 \( \mu\)A·cm⁻², respectively, which is in agreement with values from the literature. Under acid conditions (pH of 3.6), HER is the dominant cathodic reaction. At the anodic branch, the current steadily increases until it reaches a current plateau, the critical passivation current, where corrosion proceeds uniformly. At scan rates of 5, 25, and 100 mV·s⁻¹ (red, blue, and green lines in Fig. 1a), the  \( E_{\text{corr}}^{\text{app}} \) all shift to a similar potential value, \( \sim -0.848 \) V vs. SCE comparatively to \(-0.77 \) V vs. SCE at 0.167 mV·s⁻¹. Moreover, the anodic branch current magnitude increases with increasing scan rates. The differences from the high scan rates PDP translate into different values of  \( E_{\text{corr}} \) and  \( j_{\text{corr}} \) for each scan rate (Supplementary Table 2). Thus, the ‘apparent’ superscript is used here to distinguish between the  \( E_{\text{corr}}^{\text{app}} \) and  \( j_{\text{corr}}^{\text{app}} \) obtained at 0.167 mV·s⁻¹ from the ones obtained at higher scan rate.

In 3.5 wt% NaCl, at pH 7, the  \( E_{\text{corr}} \) and  \( j_{\text{corr}} \) measured at 0.167 mV·s⁻¹ (black line in Fig. 1b) are \(-0.78 \) V vs. SCE and 1.60 \( \mu\)A·cm⁻², respectively, which is in agreement with values from the literature. Both the value of  \( j_{\text{corr}} \) and the magnitude of all currents before the onset of pitting are smaller in NaCl compared with those measured in acidic NaH₂PO₄. This observation can be attributed to a less reactive environment for the cathodic reaction and a slower oxide dissolution rate in the neutral solution. The anodic branch does not present the typical passive behavior, and  \( E_{\text{corr}} \) is close to  \( E_{\text{pit}} \) at 0.77 V vs. SCE at 0.167 mV·s⁻¹. The inconsistency in measured \( E_{\text{corr}} \) for AA7075 is due to the etching of the oxide into a porous structure. The difference in reported values for AA7075 can range from 10 to 3500 \( \mu\)F·cm⁻². This inconsistency in measured \( E_{\text{corr}} \) for an oxide-covered metal can be attributed in part to interference from corrosion occurring at the metal/oxide/electrolyte interface. \( E_{\text{pit}} \) is most often measured by EIS where the chosen equivalent circuit has a major impact in evaluating \( E_{\text{pit}} \), but the choice of the equivalent circuit and its physical interpretation remain a contentious subject among corrosion specialists. Moreover, corrosion of the metal matrix can lead to changes in real surface area due to the etching of the oxide into a porous structure, causing the value of \( E_{\text{corr}} \) to change during the measurements.

At higher scan rates, a qualitative evaluation of the corrosion process can be drawn from the shifts of the corrosion potential and pitting potential, but due to the drastic distortions observed in the Tafel plots, the extracted apparent Tafel parameters cannot be used quantitatively (Supplementary Table 2). For a specific electrolyte solution, the intrinsic corrosion metrics should not change with scan rates, meaning that the Tafel fit is also capturing processes that accompany a change in scan rate.

### The Inability of Capacitive Current to Describe High Scan Rates PDP

The PDP current density (\( j_{\text{pdp}} \)) can be expressed as a convolution of the current originating from faradaic and capacitive processes.

\[
j_{\text{pdp}} = j_f + j_{\text{cap}}
\]

(1)

Where \( j_{\text{pdp}} \) is the PDP current density,  \( j_f \) is the faradaic current density, and  \( j_{\text{cap}} \) is the capacitive current density.

Based on Eq. (2),  \( j_{\text{cap}} \) increases with the scan rate and could potentially explain the PDP trends observed at higher scan rates in Fig. 1.

\[
j_{\text{cap}} = C(t) \frac{\partial V}{\partial t}
\]

(2)

Where \( C(t) \) is the capacitance and  \( \frac{\partial V}{\partial t} \) is the potential scan rate.

In order to evaluate the effect of  \( j_{\text{cap}} \) on high scan rates PDP, the PDP curves at scan rates of 5, 25, and 100 mV·s⁻¹ were simulated by calculating  \( j_{\text{pdp}} \) using Eq. (1). The measured PDP current at 0.167 mV·s⁻¹ was used as an approximation for  \( j_f \) (condition where  \( j_{\text{cap}} \to 0 \)), while  \( j_{\text{cap}} \) was calculated from Eq. (2). However, determining  \( C(t) \) is not an easy task as evidenced by the large discrepancy in reported values for AA7075 which can range from 10 to 3500 \( \mu\)F·cm⁻². The inconsistency in measured \( C(t) \) for an oxide-covered metal can be attributed in part to interference from corrosion occurring at the metal/oxide/electrolyte interface. \( C(t) \) is most often measured by EIS where the chosen equivalent circuit has a major impact in evaluating \( C(t) \), but the choice of the equivalent circuit and its physical interpretation remain a contentious subject among corrosion specialists. Moreover, corrosion of the metal matrix can lead to changes in real surface area due to the etching of the oxide into a porous structure, causing the value of  \( C(t) \) to change during the measurements.

Since we are solely interested in evaluating  \( C(t) \) for AA7075 and not the corrosion kinetics, the EIS measurements were restricted to the higher frequency region (10¹ to 1 Hz) where the capacitive process dominates. The oxide/electrolyte interface is modeled using a solution resistance (\( R_s \)) for the electrolyte and a constant phase element (CPE) in parallel with a polarization resistance (\( R_p \)) to represent the non-ideal capacitive behavior of the oxide film (Fig. 2a). Here, the CPE is defined as a combination of the electrochemical double layer (\( C_{dl} \)) and oxide (\( C_{ox} \)) in series, where the total capacitance is often defined by Eq. (3).

\[
\frac{1}{C(t)} = \frac{1}{C_{dl}} + \frac{1}{C_{ox}}
\]

(3)

According to Gharbi et al., Eq. (3) is not accurate for CPE and is only valid at very high frequency or scan rate, where  \( C(t) \) would be dominated by \( C_{ox} \). At frequency, within the range of typical PDP (1 mVs⁻¹ to 100 mVs⁻¹) the measured  \( C(t) \) would be more

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**Fig. 1** Experimental PDP of AA7075 at scan rates of 0.167, 5, 25, 100 mVs⁻¹. PDP measured in (a) 0.62 M NaH₂PO₄ and (b) 3.5 wt% NaCl solution. The data with a 95% confidence interval is presented in the SI (Supplementary Fig. 1).
reflective of $C_{dl}$. This would explain the frequency dependence observed for $C(t)$ on pure aluminum, where they measured a change in $C(t)$ from $35 \mu F \cdot cm^{-2}$ at scan rate of $1 \text{mV} \cdot \text{s}^{-1}$ to $15 \mu F \cdot cm^{-2}$ at scan rate of $2000 \text{mV} \cdot \text{s}^{-1}$. Thus, $C(t)$ was extracted using the Brug equation (Eq. (4)), since it is suited to describe processes with a surface time-constants distribution\textsuperscript{56,57}.

$$C = Q^{1/\alpha} \left( \frac{R_pR_s}{R_p + R_s} \right)^{1-\alpha/\alpha} \quad \text{(4)}$$

Where $\alpha$ and $Q$ are CPE parameters, $R_p$ is the polarization resistance and $R_s$ is the solution resistance. Also, to account for any change in $C(t)$ during the measurement of PDP, EIS measurements were performed at multiple potentials and after conditioning of the sample by PDP at $5 \text{mV} \cdot \text{s}^{-1}$ and $100 \text{mV} \cdot \text{s}^{-1}$ (Fig. 2b, c). The $\alpha$ for all spectra were above 0.85 (Supplementary Tables 3, 4) and based on Fig. 3, the extracted $C(t)$ is different between both electrolytes but does not vary significantly as a function of the applied potential or the sample conditioning.

The addition of $j_{cap}$ can partially explain some of the changes observed in high scan rates PDPs (Fig. 4) such as the shift of the $E_{corr}^{app}$, but it does not correctly predict the overall shape of the curves for any scan rates and electrolytes. For example, in $0.62 \text{ M NaH}_2\text{PO}_4$ with a $C(t)$ of $300 \mu F \cdot cm^{-2}$ (blue line in Fig. 4a), the addition of capacitive current predicts correctly the $E_{corr}^{app}$ shift for the PDP performed at a $100 \text{mV} \cdot \text{s}^{-1}$. However, it fails to do so for slower scan rates, even when accounting for increasing $C(t)$ at slower scan rates. It also fails to fit the anodic branch and to explain any other observed trend, like the overlap of both the cathodic branches and $E_{corr}^{app}$ observed for scan rates of 5, 25, and $100 \text{mV} \cdot \text{s}^{-1}$ (Fig. 1a).

A gap, similar to that seen for the anodic branches, would be expected based on the $j_{cap}$ calculated from Eq. (2) with a constant $C(t)$. Similarly, attempts to fit the PDP curves obtained in 3.5 wt% NaCl are unsuccessful (Fig. 4b), even if we disregard the pitting occurring after $E_{corr}$ that is not directly related to the capacitive current. Here $C(t)$ would need to vary drastically, up to 1 or 2

**Fig. 2** EIS spectra of AA7075 in $0.62 \text{ M NaH}_2\text{PO}_4$ and 3.5 wt% NaCl solution. The frequency range of all measurements is from $10^5$ Hz to 1 Hz. a The equivalent circuit used to fit the data. b Nyquist plot as a function of the applied potential. c Nyquist plot as a function of surface conditioning.

**Fig. 3** The capacitance of AA7075 measured by electrochemical impedance spectroscopy (EIS). The capacitance of AA7075 extracted by the Brug equation as a function of (a) applied potential and (b) sample conditioning (measurements performed at OCP). The error bars represent a 95% confidence interval. Each measurement was done on a fresh spot.
orders of magnitude, as a function of the electrolyte, the potential, and the scan rates, to account for all the observed trends in PDPs at high scan rates. However, such an extensive increase in $C(t)$ is not supported by our EIS measurements (Fig. 3). Thus, the capacitive current alone cannot explain the complex trends observed at different scan rates in both electrolytes, which is surprising since it has often been alluded to be the main contributor to PDP distortion$^{20,25}$.

**Defining Scan Rate Dependent Processes for Modeling High Scan Rates PDP**

Since the addition of capacitive current failed to predict the trends observed in PDP at higher scan rates, we now investigate the current originating from the growth of the oxide layer as described by the high field model. For reactive materials like aluminum alloys, classified as ‘valve metals’, the corrosion process is inhibited by the spontaneous formation of an insulating oxide film in ambient conditions$^{32,58}$. Radiotracer and secondary ion mass spectrometry$^{59–62}$ experiments confirmed that the oxide layer grows at the metal/oxide interface by the migration of $\text{OH}^-/\text{O}_2^-$ species (Fig. 5a), and at the oxide/electrolyte interface by the migration of $\text{Al}^{3+}$ (Fig. 5b). Equations (5) to (7) summarize the passivation process under such conditions. However, direct dissolution of Al can still occur via field-assisted ejection of $\text{Al}^{3+}$ species in solution$^{53,64}$ (Fig. 5c).

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \]  
(5)  
\[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{O}_2^- \]  
(6)  
\[ 2\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ \]  
(7)

In the high field model, the migration of ionic species across the oxide film is considered the rate-limiting step for the metal oxidation rather than charge transfer. Mott and Cabrera derived the current expression, by defining the potential drop within the oxide film as the main driving force for the migration of ions$^{65}$.

\[ j_{hf} = A \exp[\beta_\eta E] \]  
(8)  
\[ E = \eta \]  
(9)  
\[ \frac{\partial}{\partial t} \]  
\[ \eta = E_{\text{app}} - E_{\text{Al}_2\text{O}_3} \]  
(10)
Where $j_{hf}$ is the anodic current density derived under the high field model, $A$ and $\beta_a$ are kinetic parameters that describe the mobility of ions in the oxide, $E$ is the magnitude of the electric field, $d$ is the oxide film thickness, $\eta$ is the overpotential, $E_{app}$ is the applied potential, and $E_{Al_2O_3}$ is the equilibrium potential for the formation of $Al_2O_3$ described by Eq. (7).

The $j_{hf}$ can be converted into an oxide film growth rate from Faraday’s electrolysis law. A passivation efficiency factor ($\epsilon_p$) was introduced by Lee et al.64 to differentiate between the $j_{hf}$ fraction that contributes to oxide growth and direct dissolution of Al.

where $\epsilon_p$ is the passivation efficiency ($1 = 100\%$ passivation efficiency), $M$ is the molar mass of $Al_2O_3$, $\rho$ is the density of $Al_2O_3$, $n$ is the number of electrons transferred, and $F$ is the Faraday’s constant.

The oxide film growth is also balanced by the chemical dissolution of $Al_2O_3$ in solution29,33 (Fig. 5d), where the dissolution rate is known to be enhanced in acidic/alkaline conditions64,66,67.

\[
\frac{\partial d}{\partial t} = -\frac{M}{\rho} R_{diss}
\]

Where $R_{diss}$ is the dissolution rate of $Al_2O_3$.

To determine the electric field magnitude, which depends on the overpotential and the oxide film thickness (Eq. (9)), the change in oxide film thickness during polarization is calculated by integrating the rate of film growth (Eq. (11)), and film dissolution (Eq. (12)).

\[
d = d_0 + \epsilon_p \frac{M}{n F \rho} \int_{0}^{t} j_{fi}(t)dt - \frac{M}{\rho} \int_{0}^{t} R_{diss}(t)dt
\]

Where $d_0$ is the thickness of the air-formed oxide film already present at the surface before immersion in the electrolyte. Finally, the anodic current contribution, $j_{hf}$, can be calculated by solving Eqs. (8) and (13) together.

### Table 1. Parameters used in the simulation of $j_{hf}$ in 0.62 M NaH$_2$PO$_4$ and 3.5%wt NaCl.

| Parameters | NaH$_2$PO$_4$ | NaCl |
|------------|---------------|------|
| C(t) (µF·cm$^{-2}$) | 16 | 21 |
| $E_e$ (V vs. SCE) | $-0.82$ | $-0.773$ |
| $E_{Al_2O_3}$ (V vs. SCE)$^{70}$ | $-1.9$ | $-2.0$ |
| $A$ (A·cm$^{-2}$)$^{28}$ | $6.5 \times 10^{-12}$ | $6.5 \times 10^{-12}$ |
| $\beta_a$ (V·cm$^{-1}$)$^{-1}$ | $3.6 \times 10^{-6}$ | $3.6 \times 10^{-6}$ |
| $M$ (g·mol$^{-1}$) | 101.96 | 101.96 |
| $\rho$ (g·cm$^{-3}$)$^{28}$ | 3 | 3 |
| $n$ | 6 | 6 |

### Table 2. Variables obtained by fitting simulation of $j_{hf}$ to experimental PDP in 0.62 M NaH$_2$PO$_4$ and 3.5 wt% NaCl.

| Fitted variables | NaH$_2$PO$_4$ Fitted | NaH$_2$PO$_4$ Experimental | NaCl Fitted$^*$ | NaCl Experimental |
|------------------|----------------------|---------------------------|----------------|------------------|
| $d_0$ (nm)       | 2.44                 | 2.38 ± 0.51               | 2.7            | 2.38 ± 0.51 |
| $R_{diss}$ (mol·cm$^{-2}$·s$^{-1}$) per year | $2.1 \times 10^{-11}$ 225 | $5.51 \times 10^{-12}$ 59.1 | $2.0 \times 10^{-12}$ 21.5 | $3.44 \times 10^{-12}$ 36.9 |
| $\epsilon_p$     | 0.85                 | -                         | 36             | -               |
| $j_{fi}$ (V·cm$^{-2}$) | 30                  | -                         | 3.7            | -               |
| $\beta_a$ (V·cm$^{-1}$) | $-250$              | -                         | $-600$         | -               |

$^*$To simulate pitting in NaCl, the fitted $R_{diss}$ and $\epsilon_p$ take values of $1 \times 10^{-9}$ mol·cm$^{-2}$·s$^{-1}$ and 0, respectively when $E_{app} > -0.773$ V vs. SCE. $^b$ $R_{diss}$ is given in mol·cm$^{-2}$·s$^{-1}$ and µm per year.

The cathodic current density ($j_c$) for an AA in an aerated aqueous solution originates from both the hydrogen evolution reaction (HER) and the oxygen reduction reaction (ORR)$^{62,68}$.

\[
2H^+ + 2e^- \rightarrow H_2
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^-
\]

To make things simpler as we are focusing on the anodic current described by the high field model, we assume that both cathodic reactions can be described by a single Tafel-like expression and that it is not strongly affected by the change in oxide thickness.

\[
j_c = -j^0_\text{fit} \beta_c (E_{app} - E_c)/\beta_c
\]

Where $j_c$ is the cathodic current density, $j^0_c$ is the cathodic exchange current density, $E_c$ is the mixed equilibrium potential for the cathodic reactions, $\beta_c$ is the cathodic Tafel slope.

So now, the PDP current density, $j_{PDP}$, can be expressed as the sum of the anodic high field current density, the cathodic current density, and the capacitive current density.

\[
j_{PDP} = j_{hf} + j_c + j_{cap}
\]

PDP curves were simulated in COMSOL Multiphysics v6.2 using the DAE and ODE physics in 0D to calculate $j_{PDP}$ from Eq. (17), $j_{hf}$ from Eqs. (8) and (13), $j_c$ from Eq. (16) and $j_{cap}$ from Eq. (2) (details are in section 8 of the SI and the COMSOL report is also available). To limit the number of fitting variables, the passivation kinetic parameters $A$, $\beta_a$, discussed in more details in the following sections, were taken from reference28, by approximating that they do not change significantly between different Al alloys and from an electrolyte to another. The density of $Al_2O_3$ ($\rho$) was taken from the literature, however, it can change according to the electrolyte composition and anodization conditions since it will affect the morphology and composition of the oxide film$^{59,60,69}$. The number of electrons, $n$, involved in the growth of $Al_2O_3$ is assumed to be 6, based on Eqs. (5) and (7). $E_e$ was approximated by the respective value of OCP in 0.62 M NaH$_2$PO$_4$ and 3.5 wt% NaCl, while values of $E_{Al_2O_3}$ were taken from the Pourbaix diagram factoring in the electrolyte pH$^{70}$. Based on our EIS measurements, C(t) of 16 µF·cm$^{-2}$ was used for 0.62 M NaH$_2$PO$_4$ and 21 µF·cm$^{-2}$ for 3.5 wt% NaCl. Although, there is an increase in C(t) as the scan rate decreases, the effect on $j_{cap}$ is negligible within the range of scan rates used in this work (Fig. 4), and C(t) was assumed constant. The parameters taken from the literature are estimates that might not strictly apply in the context of an alloy, but nevertheless, the objective is to demonstrate that the high field model used in this work can explain the experimental PDP trends. All parameters used for the simulations are presented in Table 1. The remaining parameters, most of them hard to characterize accurately, were left to be fitted ($R_{diss}$, $d_0$, $\epsilon_p$, $j_{fi}$, $\beta_a$), and a single set of parameters was used to fit measurements from all the scan rates simultaneously (Table 2).
The Anodic High Field Current as the Dominant Factor in High Scan Rates PDP

The simulated $j_{hf}$ inherently changes with increasing scan rates (Fig. 6a, c). At the beginning of the potential scan, $j_{hf}$ increases exponentially but the progressive thickening of the oxide film (Supplementary Fig. 2) will affect the magnitude of the electric field, which is controlled by $j_{hf}$ and $R_{diss}$, will settle into a dynamic equilibrium, and $j_{hf}$ will converge to a steady-state ($j_{ss}$). At higher scan rates, a higher potential is reached for the same oxide thickness relative to a slower scan rate (Supplementary Fig. 2a, b), resulting in a larger $E$ and $j_{hf}$. The perception of $j_{hf}$ is further skewed because it is plotted as a function of the potential; for a skewed due to the oxide growth and negative potential scan (Supplementary Fig. 3). The simulated PDP curves (Supplementary Fig. 3) show that the high field model can describe the trend for the decay of the anodic current for different scan rates.

In the 0.62 M NaH$_2$PO$_4$ electrolyte, the $E_{corr}$, visually corresponds to the potential at which $j_{hf}$ and $j_c$ intersect (Fig. 6a) since the contribution from $j_{cap}$ is negligible. At scan rates of 5, 25, and 100 mV·s$^{-1}$, $j_{hf}$ still increase beyond the steady-state at 0.167 mV·s$^{-1}$, but they start to diverge as the $j_{hf}$ of higher scan rates continue to increase, while for lower scan rates they settle into a steady-state. However, $j_c$ intersect with $j_{hf}$ from scan rates of 5, 25, and 100 mV·s$^{-1}$ before the $j_{hf}$ are diverging significantly, thus explaining the $E_{corr}$ overlap and the shift from −0.770 V to −0.848 V vs. SCE (purple dotted line and red, green, blue line in Fig. 6a). Moreover, as can be seen in Fig. 6b, the overall shape and trend of the experimental anodic branches with increasing scan rates match with the simulated $j_{hf}$. However, the high field model predicts that a steady-state current, $j_{ss}$ will eventually be reached during the potential scan, but in the experimental anodic branch, the current density keeps increasing, a trend that becomes more apparent as the scan rate is lowered. Lee et al. attributed the continuous increase in $j_{ss}$ to a decrease in passivation efficiency, $\varepsilon_{sp}$, from a change in the surface pH. In an unbuffered solution, the surface pH would drop, thus hindering the formation of O$_2$ produced by water dissociation (Eq. (4)) at the oxide/electrolyte interface, and reducing the probability for Al$^{3+}$ to bond with O$_2$. In our case, the use of an equimolar buffer solution of 0.564 M NaH$_2$PO$_4$/0.056 M Na$_2$HPO$_4$ (Fig. 7) stabilized $j_{ss}$ by preventing a change in surface pH during the potential scan. Moreover, the difference in pH from 3.6 to 5.5, between both electrolytes, contributed to shifting the onset of oxide growth to a more positive potential and decreasing $j_{pdp}$. This result highlights the impact of surface pH change on the measured PDP, which can be linked to change in properties such as $\varepsilon_{sp}$, $R_{diss}$, $\varepsilon_{Al(OH)}$, $A$.

**Fig. 6** Simulated PDP with the addition of the high field anodic current, $j_{hf}$. a) Simulated $j_{hf}$, $j_{cap}$ and $j_c$ for PDP in 0.62 M NaH$_2$PO$_4$. b) Fitted curves for PDP in 0.62 M NaH$_2$PO$_4$. c) Simulated $j_{hf}$, $j_{cap}$ and $j_c$ for PDP in 3.5 wt% NaCl. d) Fitted curves for PDP in 3.5 wt% NaCl.
There is a large discrepancy of $A$ and $\beta_s$ reported in the literature relative to the characterization method used. When it is calculated from the slope and intercept of the linear fit of the $\ln(j_{ss})$ vs. $\nu/j_{ss}$ plot using Eq. (18), $A$ is on the order of $10^{-6}$ A cm$^{-2}$ \cite{34,35}; comparatively, it is on the order of $10^{-12}$ A cm$^{-2}$ when it is obtained through fitting \cite{42}. In our case it follows the same pattern, the $A$ ($4.35 \times 10^{-5}$ A cm$^{-2}$) and $\beta_s$ ($5.17 \times 10^{-7}$ cm$V^{-1}$s$^{-1}$) calculated from Fig. 8a, are vastly different from the ones used in our simulation ($A = 6.5 \times 10^{-12}$ A cm$^{-2}$ and $\beta_s = 3.6 \times 10^{-6}$ cm$V^{-1}$s$^{-1}$). When they are used to simulate PDP, it predicts accurately the steady-current, $j_{ss}$, but vastly overestimates the initial $j_{dpd}$ and gives a poor fit of the PDP. Moreover, the simulated oxide growth (Fig. 8c) is unrealistic in comparison to our initial simulation (Supplementary Fig. 2a), especially at $0.167 \text{ mV} \text{s}^{-1}$. In 0.62 M NaH$_2$PO$_4$ and most electrolytes, the passivation efficiency is less than 100%, the oxide dissolves chemically and the high field properties are not constant during a measurement, especially in unbuffered electrolytes (Fig. 7). Thus, the assumption from which Eq. (18) were derived are broken and leads to the erroneous evaluation of $A$ and $\beta_s$.

Although Eq. (18) is inaccurate regarding $A$ and $\beta_s$, it can still be used to confirm that the oxide growth follows a high field kinetic. Moreover, $j_{ss}$ is accurately calculated by Eq. (18) and can be used to extract $j_{ss}$ at lower scan rates from PDP measurements obtained at high scan rates. This is of particular interest for microscale PDP, where they are typically performed at scan rates upward of 50 mVs$^{-1}$. Especially, if the objective is to evaluate the corrosion rate occurring at OCP, it is not necessary to obtain a perfect fit but rather to extrapolate $j_{ss}$ for low scan rate ($<0.167 \text{ mV} \text{s}^{-1}$), where the system is close to steady-state.

Before the occurrence of pitting, $R_{diss}$ and more importantly $j_{o}$, are higher in NaH$_2$PO$_4$ compared to NaCl (Table 2). This is consistent with results from the literature, where corrosion is found to be more active under acidic or alkaline conditions in a process known as cathodic dissolution \cite{74,75}. The greater dissolution rate of Al$_2$O$_3$ in acidic conditions leads to higher cathodic activity and higher repassivation rate, which increases $j_{o}$ and $j_{dpd}$ respectively \cite{28}. Similarly, in 0.62 M NaH$_2$PO$_4$, $\varepsilon_p$ is smaller than 1 because in acidic conditions, the production of $O^2-$ from the water dissociation reaction, essential to produce Al$_2$O$_3$ (see the mechanism in Fig. 5), is unfavorable. But the value of $\varepsilon_p$ in 3.5 wt% NaCl is exceptionally high, knowing that it should be bound between 0 and 1. Physically, this high passivation efficiency rendered by the model means that the electric field, $E$, drops faster than what would normally be predicted by the high field model from an increase in oxide layer thickness (Eqs. (9) and (13)). It is not clear if it is a sign that the high field model does not apply in this case, especially since a $\ln(j_{ss})$ vs. $\nu/j_{ss}$ plot could not be obtained to confirm the high field growth of the oxide due to the occurrence of pitting before the field properties are not constant during a measurement. Alternatively, this could be the result of unaccounted processes that are not presently considered in the high field model, especially considering the good prediction obtained using the high field model (Fig. 6d). For example, all properties were assumed to be constant, but this assumption might be incorrect for certain electrolytes or AA. The oxide layer properties are known to change as it grows from the incorporation of ions present in the electrolyte \cite{59}, especially for chloride ions \cite{69}. For unbuffered electrolytes, there can be a significant change in pH at the surface of the metal which in turn can affect the dissolution rate and potential for oxide growth, $E_{Al2O3}$ (Fig. 7). However, from these results, it is still clear that oxide growth plays a large part in the anodic current density observed.

**Correlation Between the Increasing Variance from PDP at Higher Scan Rates and the Oxide Layer Thickness**  
Another characteristic of PDP obtained at high scan rates is the larger variance between replicates. For example, $j_{dpd}$ in 3.5 wt% at

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**Fig. 7 Effect of pH and buffer on PDP.** Current density of PDP measured in 0.62 M NaH$_2$PO$_4$ and 0.564 M Na$_3$HPO$_4$/0.056 M NaH$_2$PO$_4$.

and $\beta_s$. Nevertheless, even with the use of constant properties, the inclusion of the $j_{hf}$ parameter in this work can still effectively predict the main changes occurring in a PDP curve at a higher scan rate in the acidic NaH$_2$PO$_4$ solution; namely, the shift and the overlap of the cathodic branches and $E_{corr}$, but also the increase of the anodic branch current density at different scan rates.

In the case of PDP in 3.5 wt% NaCl (Fig. 6c), a step function was used to increase $R_{diss}$ and decrease $\varepsilon_p$. In order to simulate the sudden increase in $j_{uf}$ associated with the occurrence of pitting corrosion. At 0.167 mVs$^{-1}$, the measured $E_{corr}$ corresponds to the intersection of $j_{uf}$ with the pitting region of the $j_{uf}$ (purple dotted line and black line in Fig. 6c). While, at higher scan rates 5, 25, and 100 mVs$^{-1}$, $E_{corr}^{app}$ is the result of $j_{uf}$ being canceled out by the combined contribution of $j_{cap}$ and $j_{hf}$ transient (purple dotted line and red, green, and blue line in Fig. 6c). Before the occurrence of pitting, the inclusion of $j_{hf}$ captures well the movement of $E_{corr}^{app}$ and the PDP shape across all scan rates (Fig. 6d) from a single set of fitting variables. However, the region near the pitting area is not as well described, indicating that the high field model cannot be used to explain pitting corrosion.

**Validation of the high field model parameters**

Although the simulated PDP was in good agreement with the experimental data, it relied on a large number of fitting variables and validation is necessary to ensure that the fitted parameters in Table 2 have realistic values. The air-formed oxide thickness was measured by X-ray photoelectron spectroscopy (Supplementary Fig. 4 and Table 4) and an average $d_0$ value of 2.38 nm with a 95% confidence interval of 0.51 nm was obtained from three measurements in different sites within a 1 cm$^2$ AA7075 sample. Our values of $d_0$ used in the simulation for both electrolytes are consistent with our oxide thickness measurement and the ones reported in literature \cite{69,72,73}.

The oxide dissolution rate was estimated by quantification of Al ions in their respective electrolyte by ICP-OES after a 24 h exposure. For 3.5 wt% NaCl, the measured dissolution rate agrees with the fitted $R_{diss}$. For 0.62 M NaH$_2$PO$_4$ there is a larger difference between both values, but the difference is still within 1 order of magnitude. Moreover, the measured dissolution is most likely underestimated since it was performed without any polarization of the sample. Under polarization, the sample oxide dissolution rate would be expected to increase as the surface pH change (Fig. 7).

The kinetic parameters $A$ and $\beta_s$ play a large role in determining the oxide growth rate but it is difficult to characterize them properly.
However, at 100 mV·s⁻¹, the difference between each replicate (Fig. 9b) becomes much more apparent and it translates into a much larger distribution of $E_{\text{corr}}$ and $E_{\text{pit}}$, which was determined by the onset of the pitting current from the PDP (Fig. 9c). Consequently, PDP curves obtained at higher scan rates are less reproducible compared to those obtained at slower scan rates. Furthermore, for this work, the increased variance from high scan rates PDP contributes to a larger error in the fitting procedure.

Under the high field model, for the same difference in the value of an AA property, such as the air-formed oxide layer thickness ($d_0$), the disparity in $j_{\text{hf}}$ will be larger for higher scan rates, making it more sensitive to a slight difference in properties. This could explain the increase in variance observed between each replicate PDP performed at higher scan rates since a different region of the sample is probed per replicate. To verify this, PDP curves were simulated with $d_0$, ranging from 2.60 to 2.75 nm and they were able to emulate the $E_{\text{corr}}$ trend seen in PDP replicates (Fig. 9d). However, it is unclear what the variance in $j_{\text{hf}}$ at the macroscale entails since the properties are averaged over a large area.

Fig. 8  Validation of $\alpha$ and $\beta_a$ values reported in literature.  

(a) Plot of $\ln(j_{\alpha})$ vs. $\nu/j_{\alpha}$ based on the values of $j_{\text{PDP}}$ at $-0.4$ V for scan rates of 0.167, 5, 25, 50 and 100 mV·s⁻¹ in 0.62 M NaH₂PO₄.  
(b) Simulated PDP in 0.62 M NaH₂PO₄ with $A = 4.35 \times 10^{-5}$ A·cm⁻² and $\beta_a = 5.17 \times 10^{-7}$ cm·V⁻¹ obtained from (a).  
(c) Simulated $d$ with the same $A$ and $\beta_a$ in (b).

Fig. 9  Effect of scan rates on the variance between PDP replicates in 3.5 wt% NaCl.  

(a) 5 PDP replicates at 0.167 mV·s⁻¹.  
(b) 5 PDP replicates at 100 mV·s⁻¹, the inset shows an enlargement of the $E_{\text{corr}}$ region.  
(c) Distribution of the $E_{\text{corr}}$ and $E_{\text{pit}}$ at scan rates of 0.167, 5, 25, and 100 mV·s⁻¹. Error bars represent the standard deviation of data of 5 replicates at each scan rate.  
(d) Simulated effect of air-formed oxide thickness, $d_0$, and comparison with PDP replicates measured at 100 mV·s⁻¹.

0.167 mV·s⁻¹ varies slightly, but overall, the shape of each replicate is virtually the same and they mostly overlap (Fig. 9a). However, at 100 mV·s⁻¹, the disparity in $j_{\text{hf}}$ will be larger for higher scan rates, making it more sensitive to a slight difference in properties. This could explain the increase in variance observed between each replicate PDP performed at higher scan rates since a different region of the sample is probed per replicate. To verify this, PDP curves were simulated with $d_0$, ranging from 2.60 to 2.75 nm and they were able to emulate the $E_{\text{corr}}$ trend seen in PDP replicates (Fig. 9d). However, it is unclear what the variance in $j_{\text{hf}}$ at the macroscale entails since the properties are averaged over a large area.
Investigation at the microscale will be required for a better understanding of the observed variance at high scan rates.

In conclusion, the $h_{q}$ was the dominant factor over capacitive current in explaining the characteristics of PDP emerging at higher scan rates for AA7075. Compared to the Tafel equations, the high field model can describe, using a single set of parameters, the PDP trends in 2 different electrolytes and for multiple scan rates. Moreover, the kinetics is defined in terms of the oxide layer where some of the parameters ($\gamma_{p}$, $R_{\text{pass}}$, $\alpha_{p}$) have a physical meaning that is complementary to the information conventionally obtained from PDP measurements (e.g. $j_{\text{corr}}$, $E_{\text{corr}}$, $R_{\text{p}}$).

This work is also crucial in bringing microscale PDP measurements, which require these high scan rates, to the rank of quantitative techniques, but important issues need to be addressed beforehand:

- Improve the quality of characterization of the high field model key parameters.
- A better understanding of the effect of localized corrosion events such as micro-galvanic coupling and local oxide breakdown by chloride ions in relation to the high field model.

METHODS

Materials and Sample Preparation

AA7075 samples were provided by the NRC (National Research Council Canada, Saguenay), which were then cut into 8 x 5 cm pieces of 2 mm thickness. Samples were lightly abraded using a general-purpose hand pad (Scotch Brite™). All samples were successively rinsed with anhydrous ethanol (Greenfield Global, Canada) and Milli-Q water (Millipore, 18.2 MO-cm resistivity at 25°C), and then dried under a stream of air. The electrolyte solutions were prepared with NaCl (99.0% purity, Sigma-Aldrich) and NaH$_2$PO$_4$ (>99.0%, Sigma-Aldrich) in Milli-Q water. The solution’s pH was measured using a pH meter (XL200, Fisherbrand™) which was calibrated in buffer solutions of pH 4, 7, and 10.

Instrumentation

Electrochemical measurements were performed with a multi-channel VSP-300 potentiostat (Biologic Science Instruments, France) in a Faraday cage. A three-electrode corrosion cell (K0235 Flat Cell, Princeton Applied Research, AMETEK Scientific Instrument) with an exposed working area of 1 cm$^2$ was used for all electrochemical measurements, with a saturated calomel electrode (SCE) (CHI 150, CH Instruments) as the reference electrode and a platinum mesh (2.54 cm x 2.54 cm, Goodfellow) as the counter electrode.

Potentiodynamic Polarization Measurements

The experimental procedure was based on standards ASTM G-94$^{19}$ and ASTM G61-86$^{26}$. Naturally aerated 3.5 wt% NaCl and 0.62 M NaH$_2$PO$_4$ solutions were used as the electrolyte solutions for all the electrochemical tests to simulate severe corrosion conditions. In both electrolytes, prior to PDP measurements, the sample was left under open circuit potential (OCP) until the variation in OCP fell below 10 mV per minute. Then the sample potential was held at $-0.25$ V vs. OCP for 20 s before acquiring complete PDP curves at scan rates of 0.167, 5, 25, and 100 mV·s$^{-1}$, from $-0.25$ V vs. OCP to 1 V vs. SCE (with a current density cutoff of 1 mA·cm$^{-2}$). PDP curves were acquired in 5 replicates per scan rate and the average value is considered for analysis. For each measurement, a new uncorroded 1 cm$^2$ area of the sample was exposed. All the presented current densities (i) are normalized to the geometric area of the working electrode.

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed in potentiostatic mode with a voltage perturbation amplitude of 10 mV ($V_{\text{rms}} = 7.07$ mV) in the frequency range from 10$^3$ to 1 Hz, in both 0.62 M NaH$_2$PO$_4$ and 3.5 wt% NaCl. The measurements were also performed at multiple potentials between $-1$ V vs. SCE to OCP, as well as before and after PDP measurements. Equivalent circuit fitting was performed using EC-lab (Biologic Science Instruments, France) version 11.33.

X-ray Photoelectron Spectroscopy

XPS analyses were carried out using an Al Kα X-ray photoelectron spectrometer (Thermo Scientific, K-Alpha). The beam size was 400 μm in diameter, the take-off angle of the beam was 90° and ten scans were performed per spectrum. The peak fitting was performed using the Avantage software (Thermo Scientific) using a ‘smart’ background which is based on the ‘Shirley’ background with the additional constraint that it should not be of a greater intensity than the actual data at any point in the region. For asymmetric Al 2p (metal) peaks, tail mix and tail exponents were allowed. A spin-orbit splitting ratio of 1:2 was assigned to aluminum metal peaks 2p$_{3/2}$ and 2p$_{1/2}$.

Inductively Coupled Plasma Optical Emission Spectroscopy

To measure the dissolution rate of Al$_2$O$_3$ in 3.5 wt% and 0.62 M NaH$_2$PO$_4$, the AA7075 samples were immersed in both electrolytes for 24 h. Then the sample solutions were collected, by rinsing the AA7075 surface with 5% v/v with nitric acid to dissolve any precipitated Al ions for measurements by ICP-OES (Agilent 7100, USA). The wavelengths of Al at 308.215 nm, 394.401 nm, 306.152 nm with minimal elemental interference were chosen as the analytical line. The Al$^{3+}$ standard solutions were prepared in concentrations of 1 ppm, 10 ppm, 20 ppm, and 50 ppm by addition of AlCl$_3$ powder to the electrolyte of interest (NaCl or NaH$_2$PO$_4$) which were acidified to a concentration of 5% v/v with nitric acid.

DATA AVAILABILITY

The data sets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

CODE AVAILABILITY

The COMSOL file is available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

H.Z. and D.C. are co-first authors. H.Z. performed all experiments. D.C. performed the COMSOL simulation. H.Z and D.C. analyzed the data, discussed the results, and co-wrote the paper. J.M. supervised the project. A.M. and D.G. discussed the results and advised the work. All authors contributed to revision of the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

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