Passivity Breakdown and the Evolution of Localized Corrosion Damage on Type 316L Stainless Steel

Shoufeng Yang and Digby D. Macdonald
Center for Electrochemical Science and Technology
Dept. of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802, USA

Presented at

210th Meeting of the Electrochemical Society/XXI Congreso Nacional de la Sociedad Mexicana de Electroquímica (SMEQ)
Cancún, Mexico

October 29 – November 3, 2006

The Department of Materials Science and Engineering

Acknowledgement and Disclaimer

- Support of the Science and Technology Program of the Office of the Chief Scientist (OCS), Office of Civilian Radioactive Waste Management (OCRWM), U.S. Department of Energy (DOE) is gratefully acknowledged. The work was performed under the Corrosion and Materials Performance Cooperative, DOE Cooperative Agreement Number: DE-FC28-04RW12252

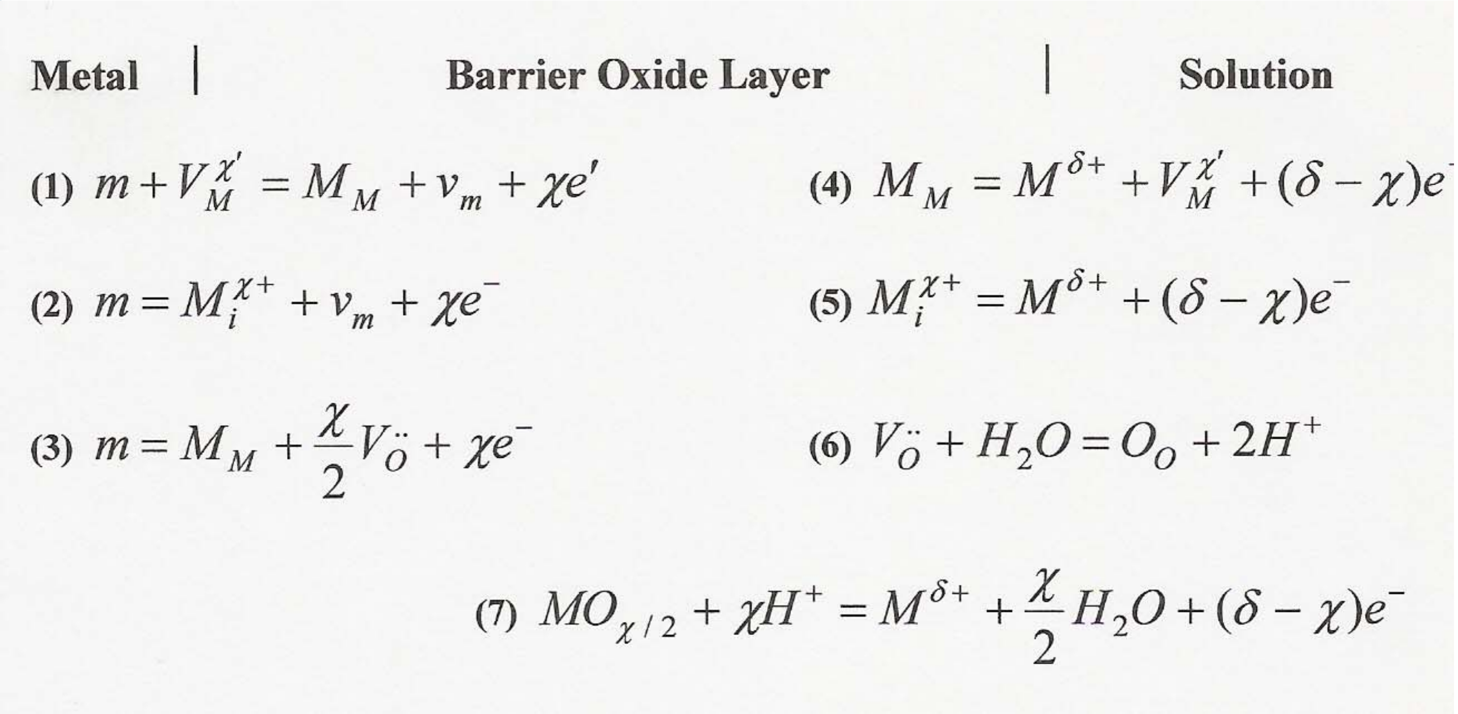
- The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM/OCS

Objectives

- Evaluate the applicability of the point defect model (PDM) for describing passivity breakdown on Type 316SS in chloride-containing solutions
- Extract values for parameters in the PDM that can then be used to predict the accumulation of localized corrosion damage using damage function analysis (DFA)
- Account for inhibition of passivity breakdown by oxyanions

Passivity Breakdown

- Passivity breakdown is described analytically by the PDM, which postulates that "aggressive" anions adsorb into surface oxygen vacancies that leads to cation vacancy generation
- Certain anions (e.g., nitrate) are known to inhibit passivity breakdown
- Competitive adsorption has been previously proposed as the mechanism (Strehblow and Titze, McCafferty, and others), but details on how this occurred were missing (e.g., adsorption site?)
- Current treatment postulates that the adsorption sites are surface oxygen vacancies



Metal | **Barrier Oxide Layer** | **Solution**

(1) $m + V_M^{\chi'} = M_M + v_m + \chi e'$

(2) $m = M_i^{\chi+} + v_m + \chi e^-$

(3) $m = M_M + \frac{\chi}{2} V_O^{\cdot\cdot} + \chi e^-$

(4) $M_M = M^{\delta+} + V_M^{\chi'} + (\delta - \chi)e$

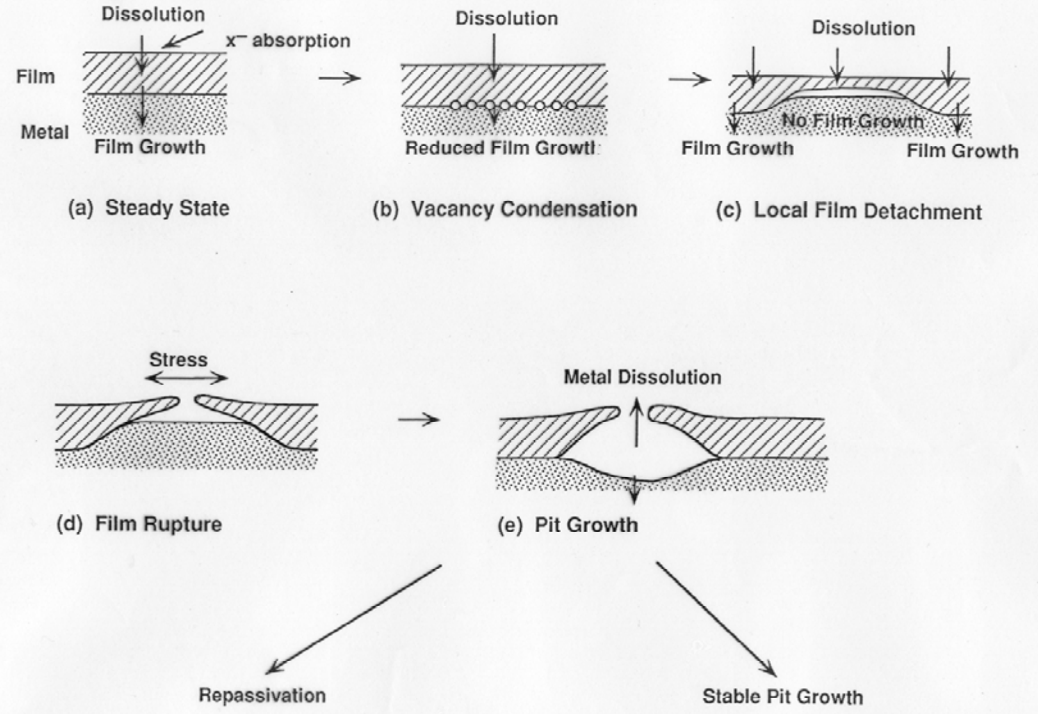
(5) $M_i^{\chi+} = M^{\delta+} + (\delta - \chi)e^-$

(6) $V_O^{\cdot\cdot} + H_2O = O_O + 2H^+$

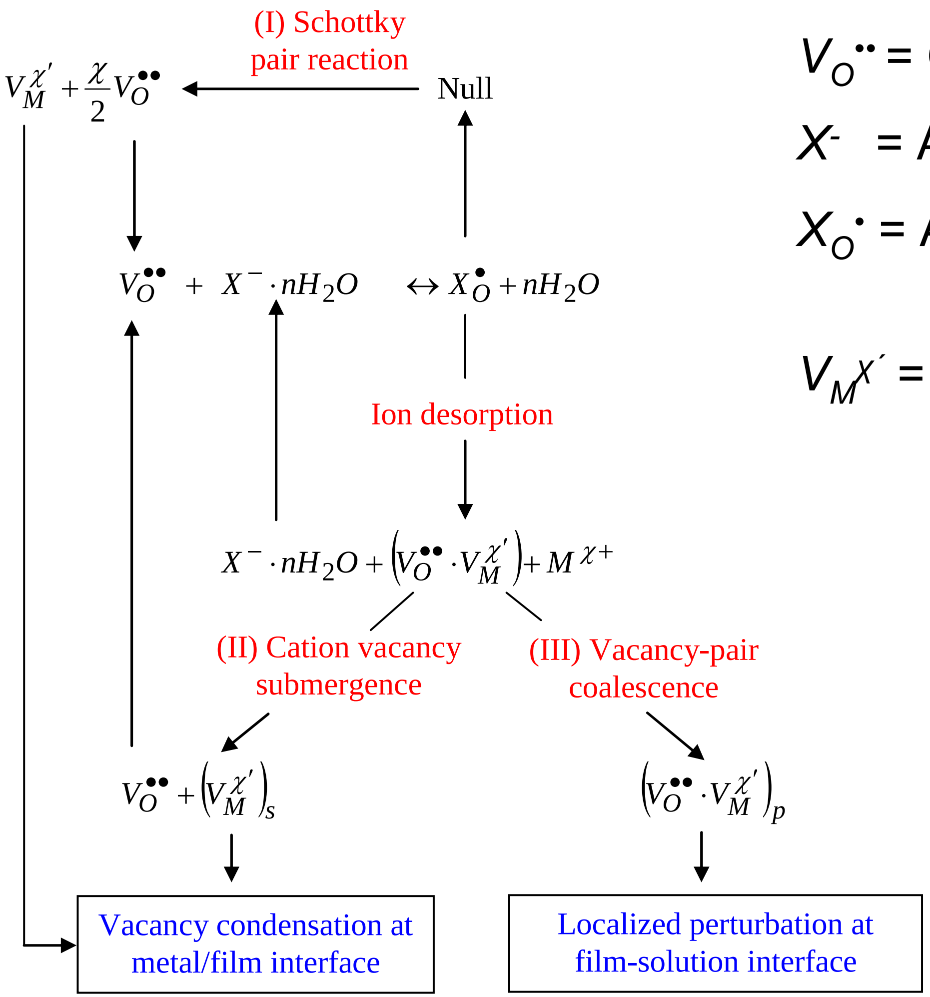
(7) $MO_{\chi/2} + \chi H^+ = M^{\delta+} + \frac{\chi}{2} H_2O + (\delta - \chi)e^-$

Schematic of physico-chemical processes that occur within a passive film according to the PDM

- Barrier layer is defective $Cr_{2+x}O_{3-y}$
- N-type – principal defects are cation interstitials and/or oxygen vacancies



Cartoon of the passivity breakdown process as envisioned by the Point Defect Model. The key concept is that a necessary condition for passivity breakdown is that the growth of the barrier layer into the substrate must be prevented; this is achieved in the PDM by cation vacancy condensation, which effectively separates the film from the metal, while allowing for the continual dissolution of the barrier layer at the barrier layer/solution interface. Note also, that cation vacancy condensation can only occur where the barrier layer is still connected to the metal, and hence the preferred site of cation vacancy condensation is at the periphery of the blister, resulting in the growth of the blister until breakdown occurs. The size of the blister is determined by competition between the rate of expansion of the blister by cation vacancy condensation and the dissolution of the barrier layer above the breakdown site.



(I) Schottky pair reaction

$V_M^{\chi'} + \frac{\chi}{2} V_O^{\bullet\bullet} \leftarrow \text{Null}$

$V_O^{\bullet\bullet} + X^- \cdot nH_2O \leftrightarrow X_O^{\bullet} + nH_2O$

Ion desorption

$X^- \cdot nH_2O + \left(V_O^{\bullet\bullet} \cdot V_M^{\chi'}\right) + M^{\chi+}$

(II) Cation vacancy submergence

(III) Vacancy-pair coalescence

$V_O^{\bullet\bullet} + \left(V_M^{\chi'}\right)_s$

$\left(V_O^{\bullet\bullet} \cdot V_M^{\chi'}\right)_p$

Vacancy condensation at metal/film interface

Localized perturbation at film-solution interface

$V_O^{\bullet\bullet}$ = Oxygen vacancy

X^- = Aggressive anion

$X_O^{\bullet}$ = Aggressive anion absorbed into an oxygen vacancy

$V_M^{\chi'}$ = Cation vacancy

Summary of reactions postulated to be involved in passivity breakdown, according to the Point Defect Model.

Competitive Adsorption of H_2O, X^- (Aggressive Anion), and Y^{z-} (Inhibitor) into Oxygen Vacancies

Adsorption Equilibria

$$H_2O + (V_O^{\bullet\bullet})_s \xleftrightarrow{K_I} (O_O)_s + 2H^+$$

$$X^- \bullet nH_2O + (V_O^{\bullet\bullet})_s \xleftrightarrow{K_{II}} (X_O^{\bullet})_s + nH_2O$$

$$Y^{z-} \bullet mH_2O + (V_O^{\bullet\bullet})_s \xleftrightarrow{K_{III}} (Y_O^{(2-z)\bullet})_s + mH_2O$$

Vacancy Conservation

$$\Gamma^0 = \Gamma_{V_O} + \Gamma_{O_O} + \Gamma_{X_O} + \Gamma_{Y_O}$$

Mass Action

$$K_I = K_I^0 e^{\frac{2\alpha FV}{RT}} e^{\frac{2\beta FpH}{RT}} \qquad K_{II} = K_{II}^0 e^{\frac{\alpha FV}{RT}} e^{\frac{\beta FpH}{RT}} \qquad K_{III} = K_{IIII}^0 e^{\frac{z\alpha FV}{RT}} e^{\frac{z\beta FpH}{RT}}$$

where

$$K_I^0 = e^{-(\Delta\mu_I^0 - 2F\phi_{f/s}^0)/RT} \qquad K_{II}^0 = e^{-(\Delta\mu_{II}^0 - F\phi_{f/s}^0)/RT} \qquad K_{III}^0 = e^{-(\Delta\mu_{III}^0 - zF\phi_{f/s}^0)/RT}$$

Specie Surface Concentrations

$$\Gamma_{V_O} = \Gamma^0 / \left\{ 1 + \frac{K_I^0 G_I}{a_{H^+}^2} + K_{II}^0 G_{II} a_X + K_{III}^0 G_{III} a_Y \right\}$$

$$\Gamma_{O_O} = K_I^0 G_I \Gamma_{V_O} / a_{H^+}^2 \qquad \Gamma_{X_O} = K_{II}^0 G_{II} \Gamma_{V_O} a_X \qquad \Gamma_{Y_O} = K_{III}^0 G_{III} \Gamma_{V_O} a_Y$$

$$G_I = e^{2F(\alpha V + \beta pH)/RT} \qquad G_{II} = e^{F(\alpha V + \beta pH)/RT} \qquad G_{III} = e^{zF(\alpha V + \beta pH)/RT}$$

$$\Gamma_{X_O} = \frac{K_{II}^0 \Gamma^0 e^{(\alpha V + \beta pH)F/RT} a_X}{1 + K_I^0 e^{2(\alpha V + \beta pH)F/RT} a_{H^+}^2 + K_{II}^0 e^{(\alpha V + \beta pH)F/RT} a_X + K_{III}^0 e^{z(\alpha V + \beta pH)F/RT} a_Y}$$

Inhibitor Absent

$$\Gamma_{X_O} = \frac{K_{II}^0 \Gamma^0 e^{(\alpha V + \beta pH)F/RT}}{1 + K_I^0 e^{2(\alpha V + \beta pH)F/RT} a_{H^+}^2} a_X$$

Inhibitor Present

$$\Gamma_{X_O} = \Gamma^0 \frac{K_{II}^0 e^{(\alpha V + \beta pH)F/RT}}{K_{III}^0 e^{z(\alpha V + \beta pH)F/RT}} \left(\frac{a_X}{a_Y} \right)$$

Anion Inhibition

$$V_c = \frac{2.303RT}{\alpha\left[1 - z + \alpha_0(\delta - 1)\right]F} ln\left(\frac{J_m K_{III}^0 k_{-2}^0 e^{\alpha_{-2}\chi\varepsilon\gamma d}}{\chi\varepsilon\gamma D k_0^0 K_{II}^0 \Gamma^0}\right) - \frac{\beta}{\alpha} pH - \frac{2.303RT}{\alpha\left[1 - z + \alpha_0(\delta - 1)\right]F} log\left(\frac{\left[X^-\right]}{\left[Y^{z-}\right]}\right)$$

z = 1, δ = 2:

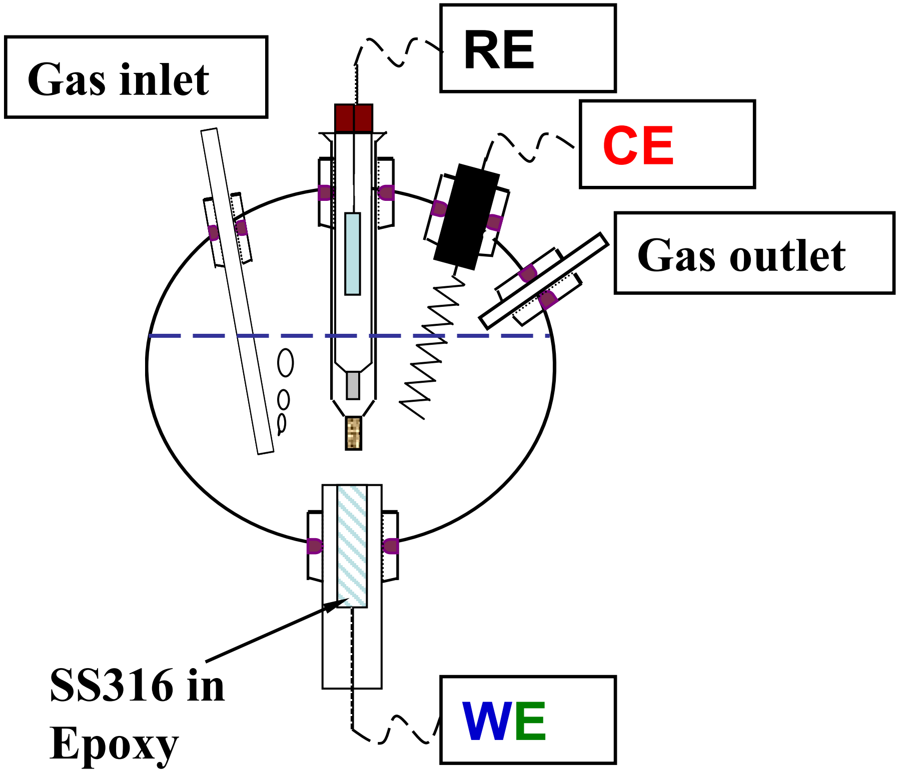
$$V_c = \frac{2.303RT}{\alpha\alpha_0 F} ln\left(\frac{J_m K_{III}^0 k_{-2}^0 e^{\alpha_{-2}\chi\varepsilon\gamma d}}{\chi\varepsilon\gamma D k_0^0 K_{II}^0 \Gamma^0}\right) - \frac{\beta}{\alpha} pH - \frac{2.303RT}{\alpha\alpha_0 F} log\left(\frac{\left[X^-\right]}{\left[Y^{z-}\right]}\right)$$

Theory is now being extended to account for the impact of inhibitor anions on the induction time for the nucleation of a pit and on the damage function. The theory will provide a quantitative basis for assessing the credit that can be claimed for the presence of nitrate in the ground water as far as pitting corrosion is concerned

SS316L Selected for Experimental Study

- Extensive localized corrosion studies have been reported
- Relatively susceptible to localized corrosion, so that metastable pitting experiment can be performed to evaluate various theoretical concepts
- Yields reasonably reproducible data

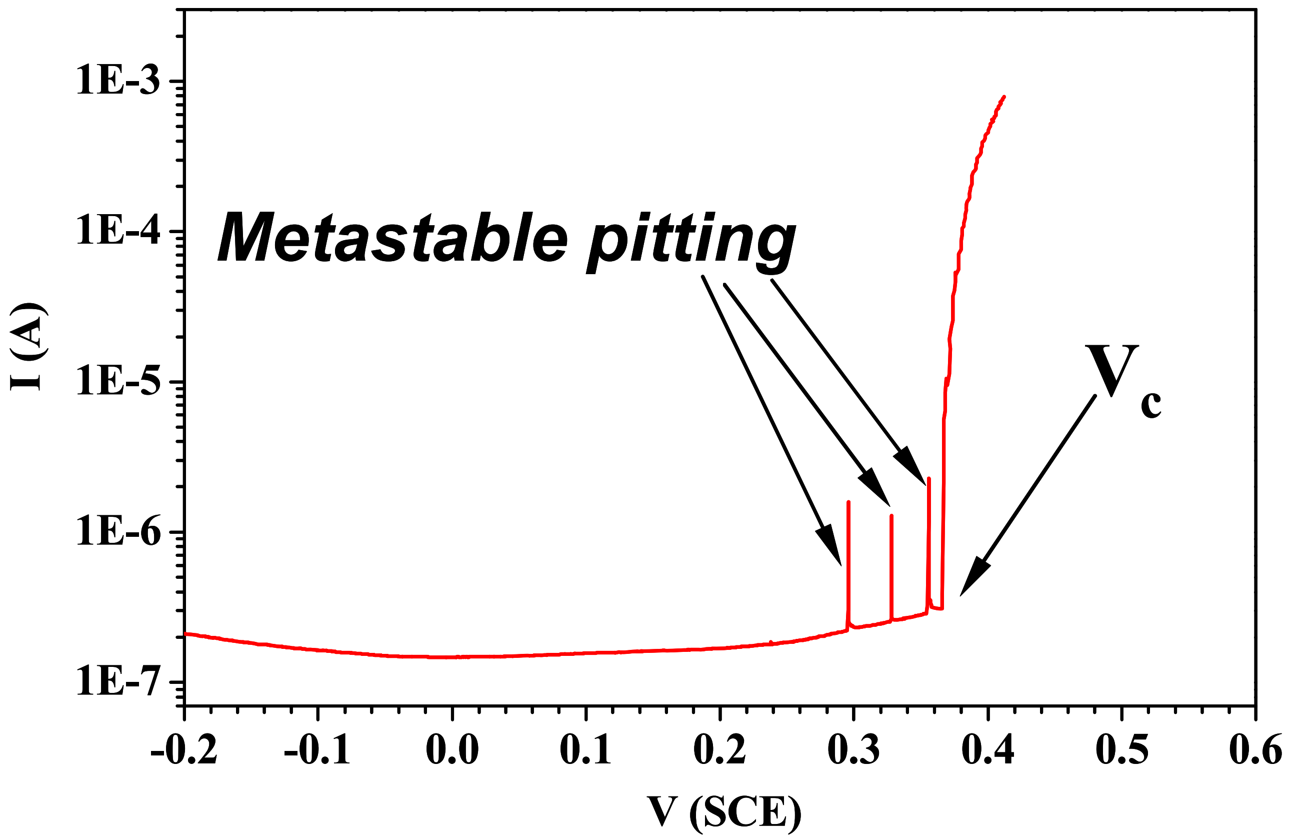
Experimental Setup



Schematic diagram of experimental setup

- All inlets/outlets sealed by o-rings
- SS316 mounted in epoxy, polished until no scratches are apparent under optical microscopy
- Solution: NaCl solution and borate buffer, pH adjusted, may have NO_3^- if necessary
- Solution N_2 (99.995%) sparged for 2 hours, working electrode cathodically stripped at -1.0 V (SCE) for 5 min

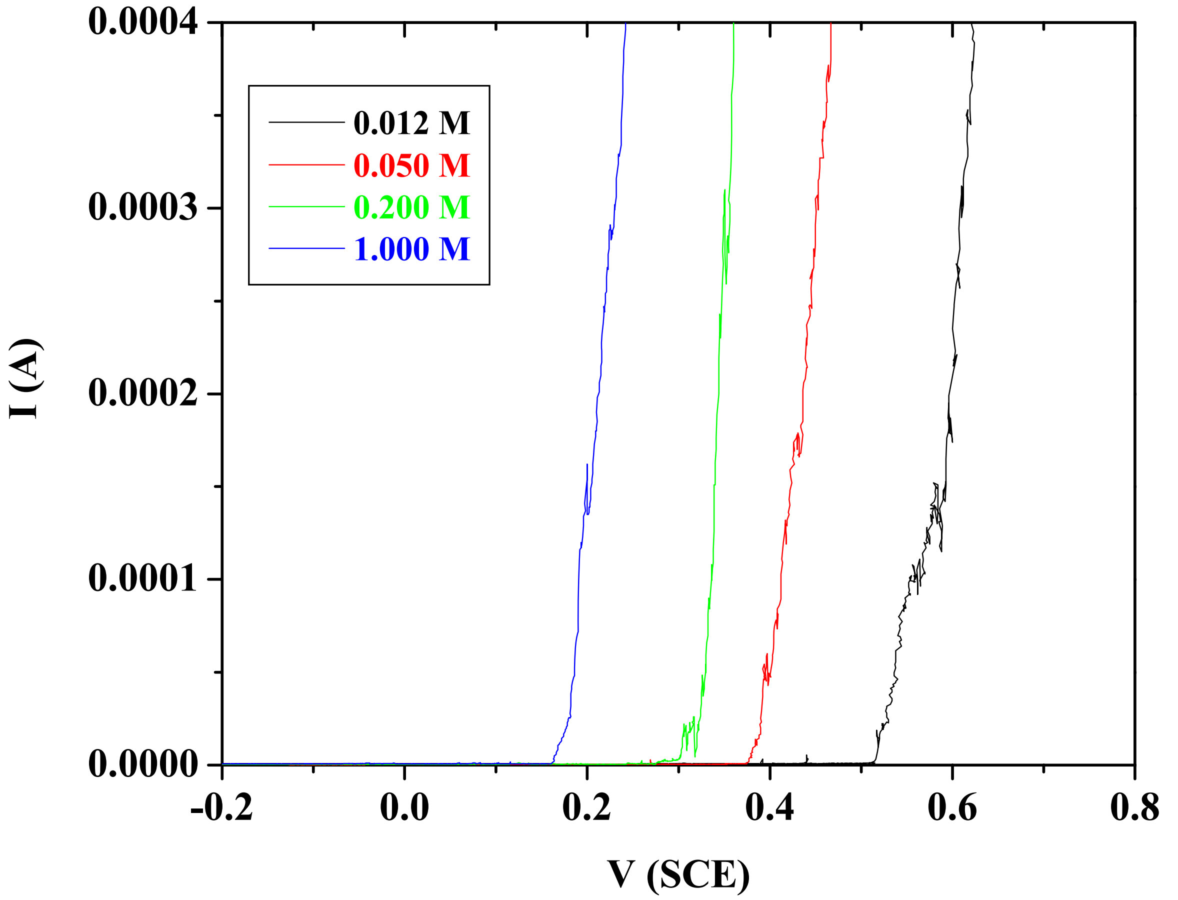
Typical Potentiodynamic Scanning



SS316 in NaCl/borate buffer solution, critical breakdown potential determined unequivocally; accurate V_c is critical for future experiment: metastable pitting and pitting survivability measurement

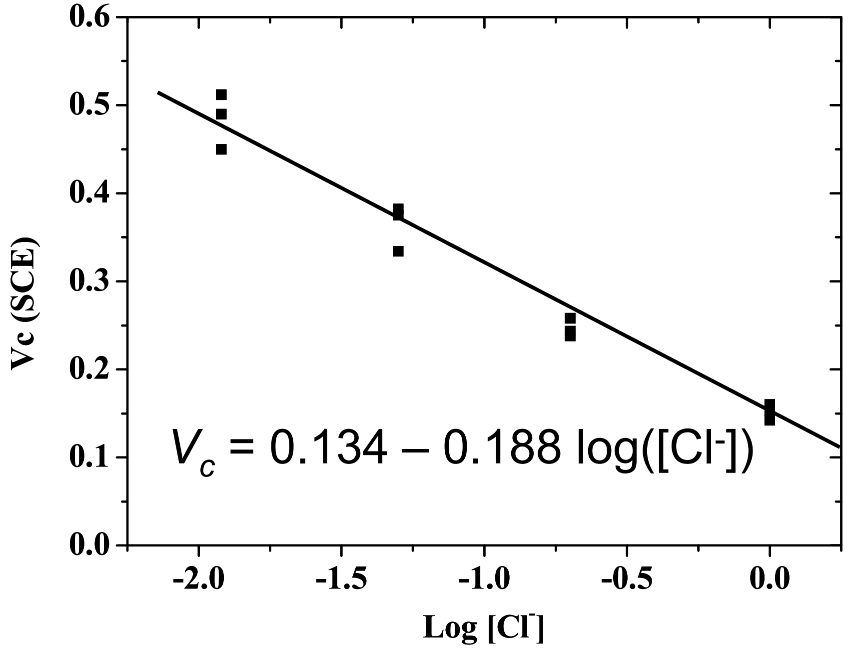
.

Potentiodynamic Scanning at Various [Cl$^-$]



Solution: 0.200 M H_3BO_3/NaOH, pH = 8.55 ± 0.05, NaCl range from 0.012 M to 1.00 M, voltage scan rate = 0.5 mV/s

V_c vs. $[Cl^-]$



$V_c = 0.134 – 0.188 \log([Cl^-])$

PDM model:

$$\boxed{V_c = \frac{4.606RT}{\chi\alpha F}\log\left(\frac{J_m}{J^o u^{-\chi/2}}\right) - \frac{2.303RT}{\alpha F}\log([X])}$$

Here α is the polarizability of the film/solution interface

$$\boxed{\phi_{f/s} = \alpha V_{ext} + \beta pH + \phi_{f/s^o}}$$

α is estimated to be 0.32

Solution: 0.200 M H_3BO_3/NaCl/NaOH.

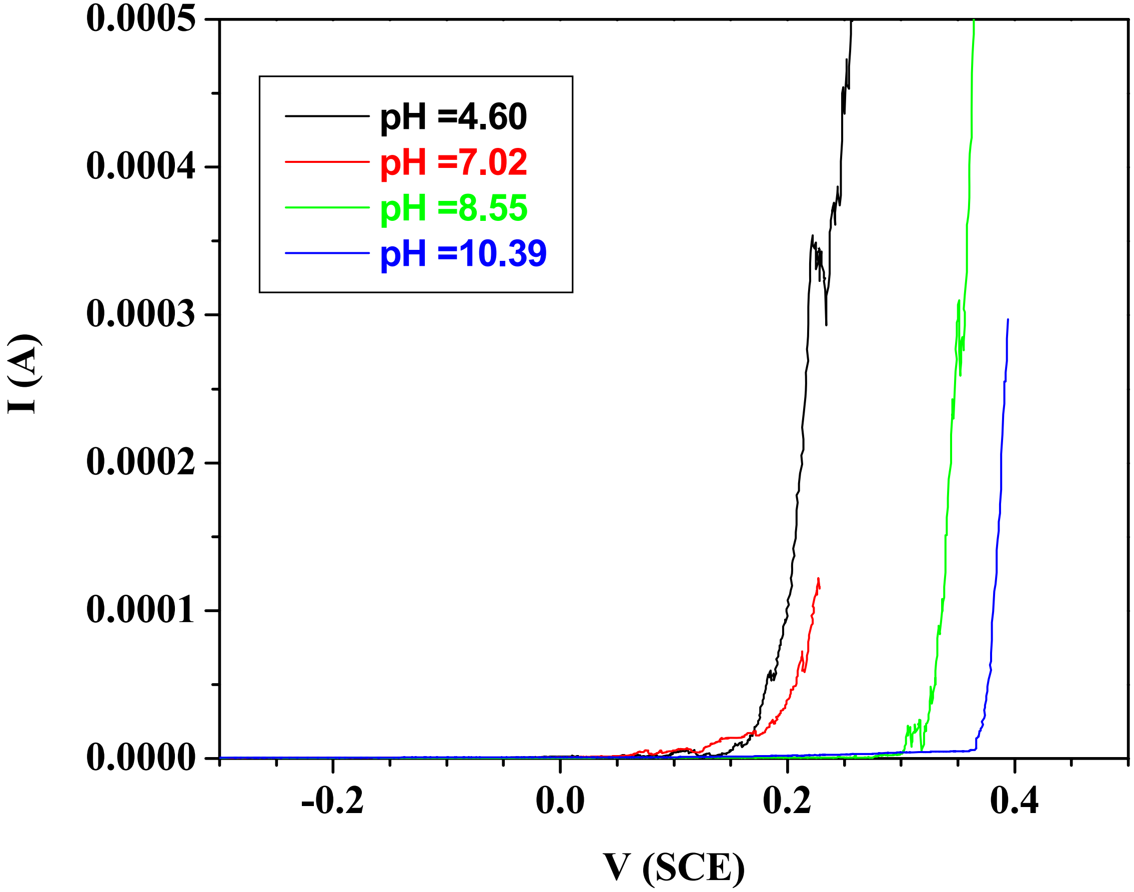
pH: 8.50 ± 0.05

T: 25.5 ± 0.5°C, potential scan rate: 0.5 mV/s

J_m = rate of annihilation of cation vacancies at metal/film interface

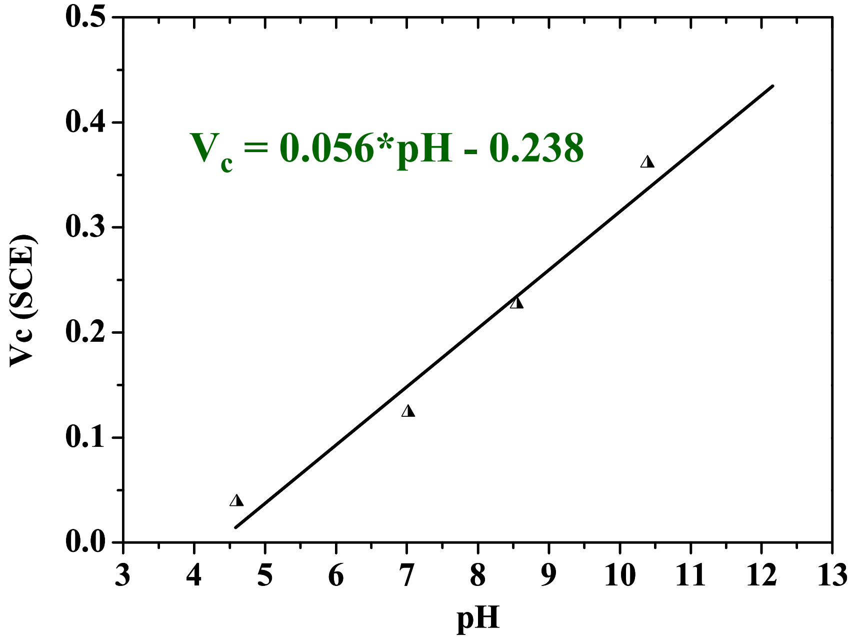
J^0, u, χ, β = constants

Potentiodynamic Scanning at Various pH Values



Solution: 0.200 M H_3BO_3/0.200M NaCl with NaOH if necessary, T = 25.5 ± 0.5°C, potential scan rate = 0.5 mV/s

V_c vs. pH



PDM model:

$$V_c = V_c^0 - \frac{\beta}{\alpha} pH - \frac{2.303RT}{\alpha F}\log(a_x)$$

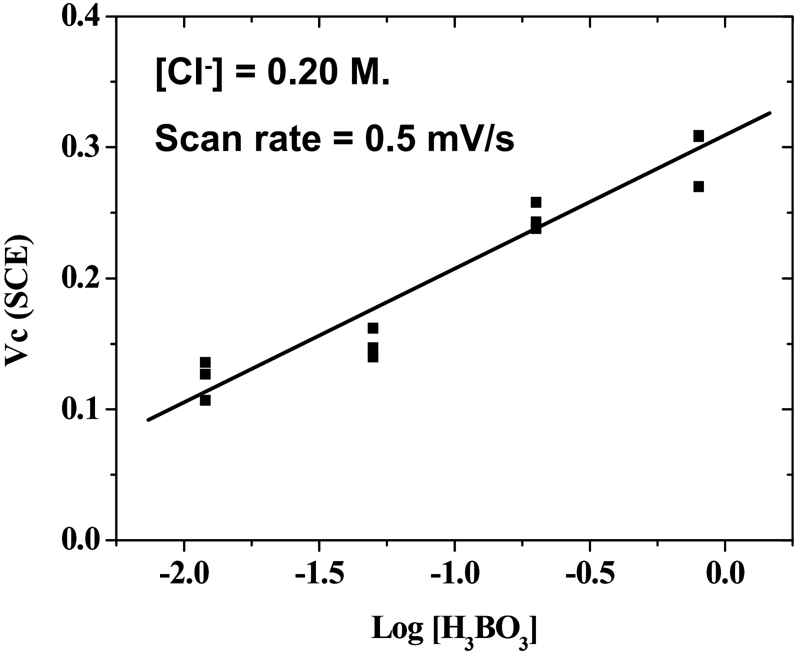
Here β is film/solution potential dependence on pH

$$\phi_{f/s} = \alpha V_{ext} + \beta pH + \phi_{f/s^o}$$

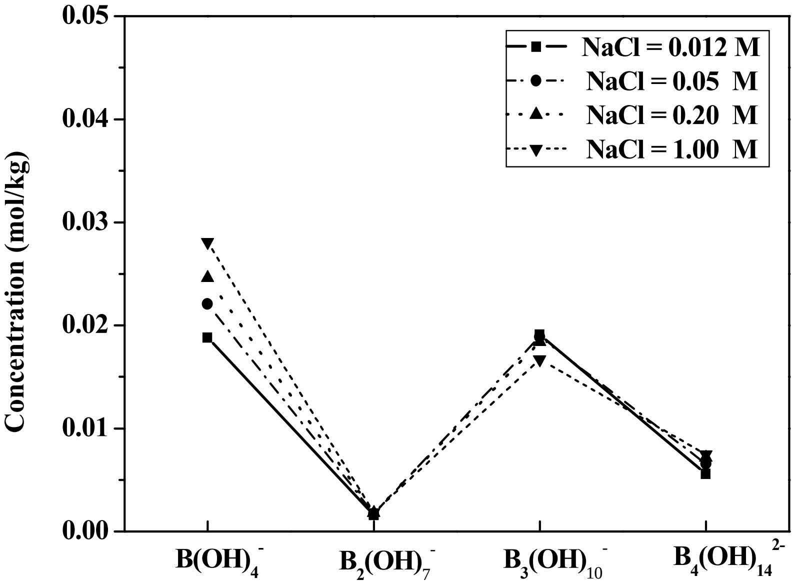
β is estimated to be -0.018, in good agreement with other systems

Influence of Boric Acid Concentration and Speciation

$$V_c = \frac{2.303RT}{\alpha\alpha_0 F}\ln\left(\frac{J_m K_{III}^0 k_{-2}^0 e^{\alpha_{-2}\chi\varepsilon\gamma d}}{\chi\varepsilon\gamma D k_0^0 K_{II}^0 \Gamma^0}\right) - \frac{\beta}{\alpha}pH - \frac{2.303RT}{\alpha\alpha_0 F}\log\left(\frac{[Cl^-]}{[NO_3^-]}\right)$$

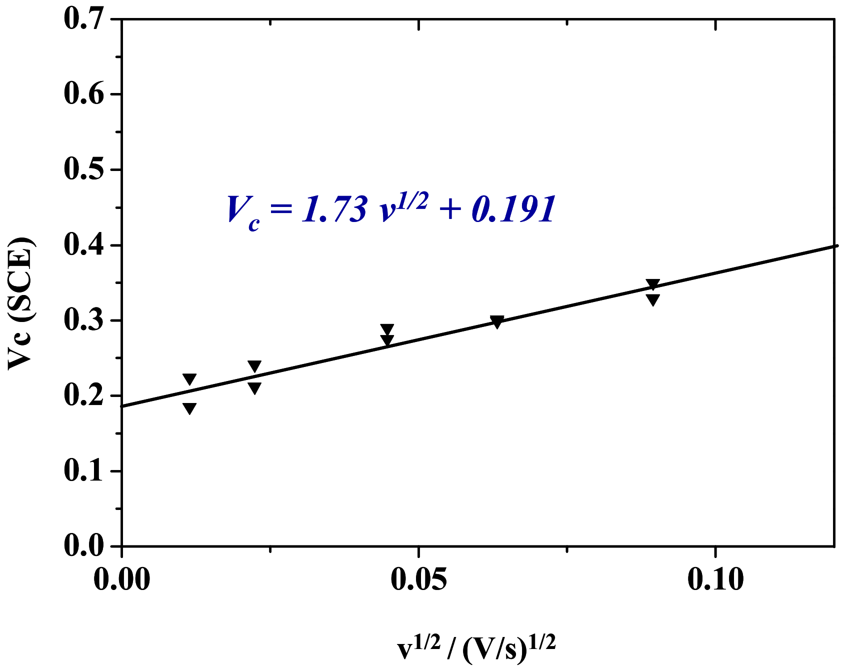

$[Cl^-]$ = 0.20 M.

Scan rate = 0.5 mV/s



- Constant pH
- Boric acid clearly inhibits passivity breakdown
- Dominant species are $B(OH)_4^-$ and $B_3(OH)_{10}^-$

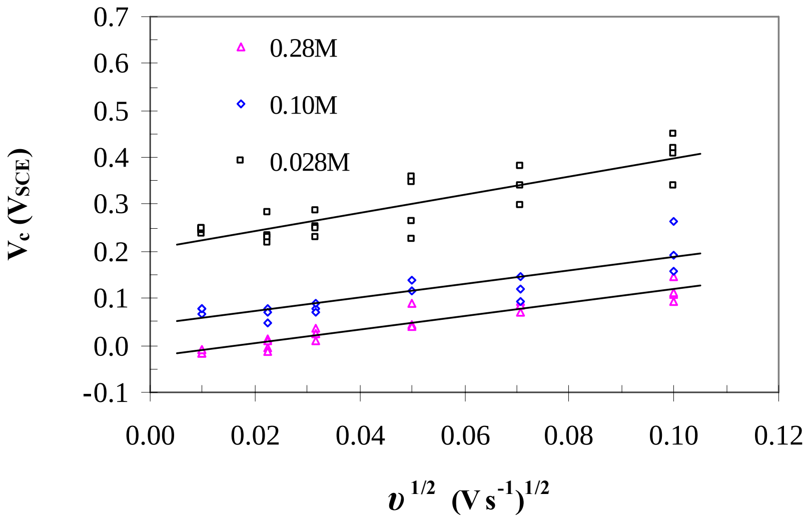
V_c vs. $\nu^{1/2}$



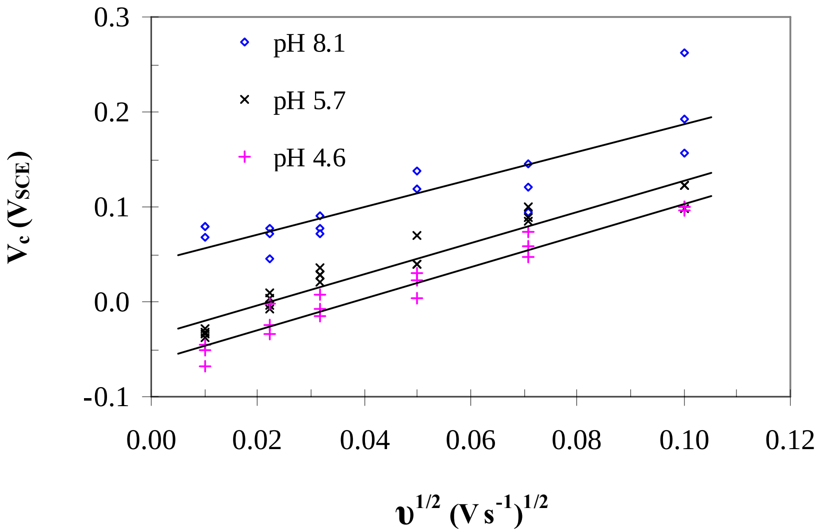
$$V_c(\nu) = -\left(\frac{2\xi RT}{J_m \chi \alpha F}\right)^{1/2} \nu^{\frac{1}{2}} + V_c(\nu = 0)$$

- Passive film is modeled as Cr_2O_3, based on crystal structures, Cr concentrations on Cr and Cr_2O_3 metal surface are $1.2*10^{15}$ cm^{-2} and $4.0*10^{14}$ cm^{-2} respectively
- Slope is 1.73 $(V/s)^{1/2}$, ξ/J_m = 56 second;
- I_{ss} is less than 12 $\mu A/cm^2$ before breakdown; $J_{ca} = I_{ss}N_0/(\chi F) = 2.4*10^{13}\ cm^{-2}s^{-1}$
- $J_m \le 2.4*10^{13}\ cm^{-2}s^{-1}$, ξ should be less than $J_{ca}*56 = 1.3*10^{15}\ cm^{-2}$, demonstrating excellent validity of the PDM model, which has been the case for other metals

Similar results for SS403 low pressure steam turbine blade alloy
Y. Zhang, Ph.D. Dissert., Pennsylvania State University



(a): Function of [NaCl], pH = 8.1 ± 0.1

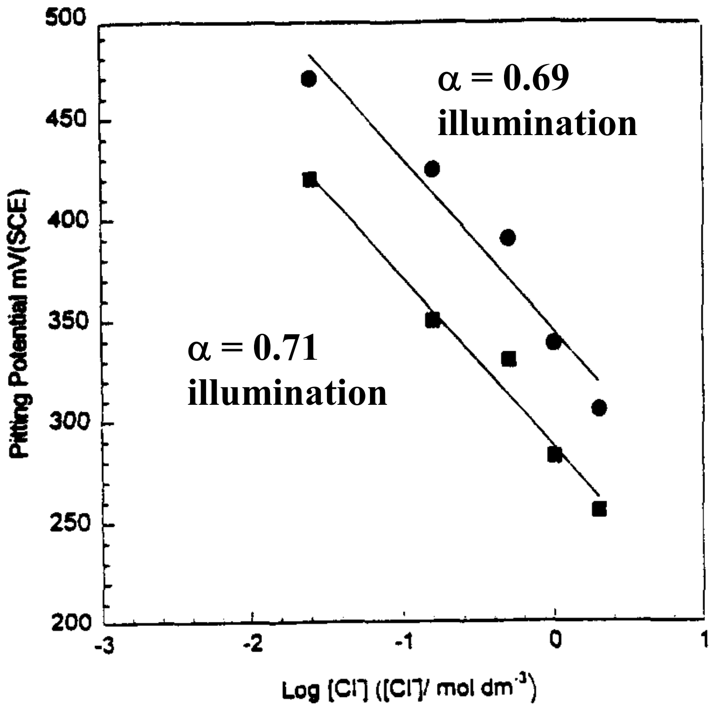


(b): Function of pH, [Cl^-] = 0.10 M

Solution: 0.20 M H_3BO_3 + NaOH to achieve the desired pH

Temperature = 22 ± 2 °C

Previous Study of Passivation Behavior of SS316



Similar results has been obtained for SS316 previously: α = 0.70, which is different from our current research (0.32), the difference maybe be attributed to the lack of borate buffer in the previous study. The influence of borate will be studied in this work, as it may not be as "inert" as is commonly assumed.

D. D. Macdonald, et. al., Electrochim. Acta, Vol. 42, p127, 1997

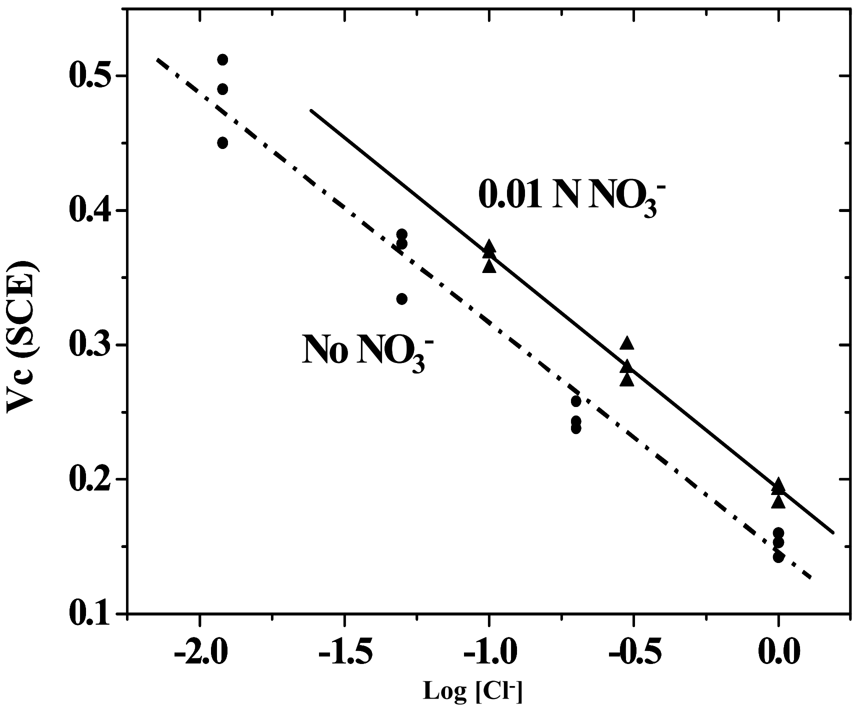
Calculation of ξ at m/f Interface Using PDM

Previous Reports

Material studied	**ξ calculated from crystal structure**	**ξ calculated from PDM**	**References**
Al 2024-T3	$2.4*10^{15}$ cm^{-2} (Al) $3.4*10^{15}$ cm^{-2} (Al_2O_3)	≤ $3*10^{15}$ cm^{-2}	Ref. 1
Nickel/polycrystalline	$8.1*10^{14}$ cm^{-2}	≤ $1.4*10^{15}$ cm^{-2}	Ref. 2
Nickel/single crystal	$5.7*10^{14}$ cm^{-2}	≤ $3.8*10^{14}$ cm^{-2}	Ref. 2
Alloy 403	$4*10^{14}$ cm^{-2}	≤ $7*10^{14}$ cm^{-2}	Ref. 3
SS316	$4*10^{14}$ cm^{-2}	≤ $1.3*10^{15}$ cm^{-2}	Current work

1. I. Fonseca, etc, Electrochem Commu, **4**, p353, 2002
2. T. Haruna, D. D. Macdonald, JES, **144**, p1574, 1997
3. Y. Zhang, PhD thesis, Penn State University, 2005

V_c vs. a_{Cl} / a_{NO3}



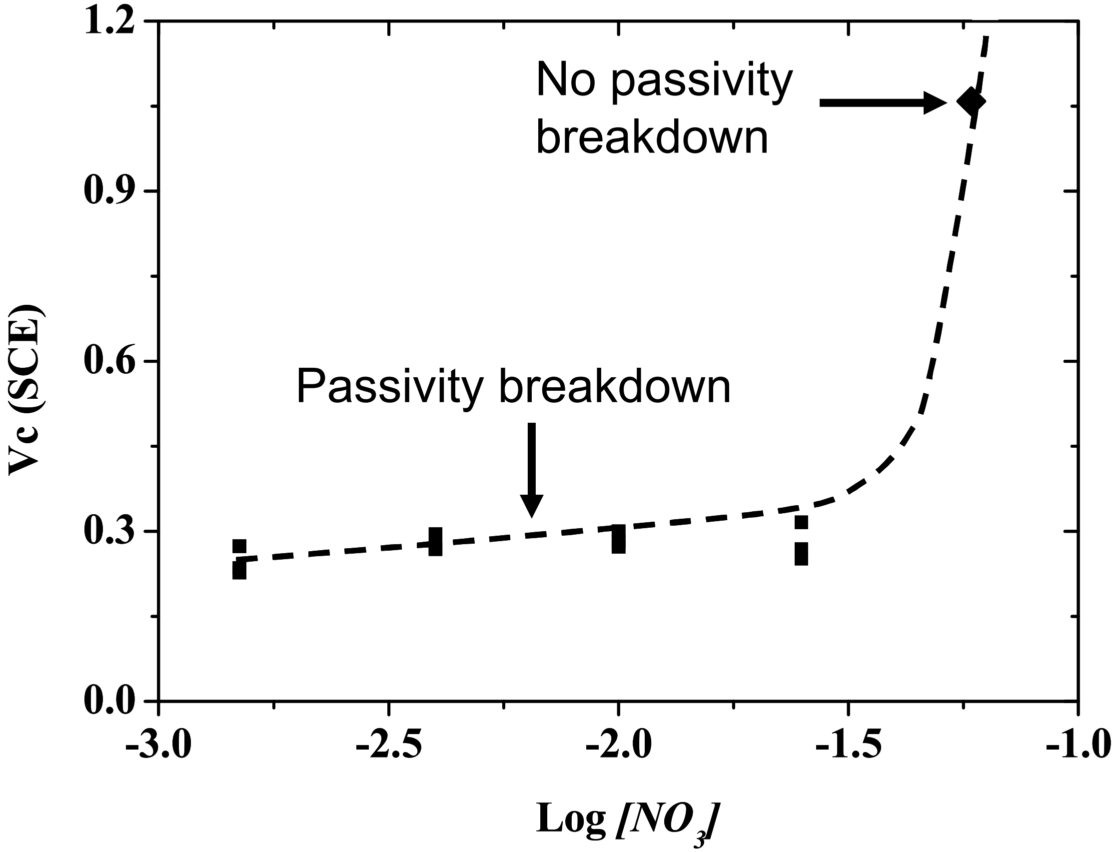
PDM model:

$$V_c = V_c^0 - \frac{\beta}{\alpha} pH - \frac{2.303RT}{\alpha\alpha_0 F} \log(a_{Cl} / a_{NO3})$$

$\alpha\alpha_0$ is estimated to be 0.33, α was previously found to be 0.32, so that α_0 is estimated to be 1.0

The chloride-catalyzed ejection of a cation from the barrier layer is a highly potential-dependent process, possibly corresponding to: Cr(III) → Cr(VI) in the form of CrO_4^{2-}

V_c versus $[NO_3^-]$



Critical breakdown potential for Type 316 SS as a function of nitrate concentration at ambient temperature (22 ± 2 ^oC) and at pH = 8.50 ± 0.05. The voltage scan rate was 0.5 mV/s

Summary and Conclusions

- The PDM, combined with the theory of competitive adsorption of water, aggressive anions, and inhibitor anions into surface oxygen vacancies successfully accounts for the inhibition of passivity breakdown by oxyanions.
- Measurement of V_c as a function of [Cl^-], pH, and $v^{1/2}$ confirms the applicability of the PDM for describing passivity breakdown on Type 316SS in chloride-containing environments.
- Borate anion does not appear to be “inert” as far as passivity breakdown in Type 316SS is concerned, in that it induces a significant change in the polarizability of the barrier layer/solution interface and shifts the breakdown potential in the positive direction.
- Nitrate ion is found to be an effective inhibitor of chloride-induced passivity breakdown on Type 316SS, with the mechanism of inhibition being described in terms of competitive adsorption of the anions into surface oxygen vacancies and inhibition of cation vacancy generation at the film/solution interface.