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The Influence of Halide Ions on the Passivity Breakdown of Carbon Steel Based on the Point Defect Model

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ABSTRACT

An important factor in determining the breakdown of the barrier layer of the passive film on carbon steel in halide-containing solutions is the anion size. In this study, the influence of the size of aggressive anions on the passivity breakdown of UNS K02700 grade carbon steel exposed to saturated $Ca(OH)_2$ solutions with the addition of different halides was investigated by using the potentiodynamic polarization (PDP) experiments. The PDP results were interpreted by using a mechanistic description based on the Point Defect Model (PDM). The experimental results revealed a linear dependence of the critical breakdown potential (E_c) on the logarithm of the activity of the breakdown-inducing halide (F^-, Cl^-, Br^-, and I^-), as predicted by the PDM. Furthermore, the PDM successfully accounted for the order with which the halides induce passivity breakdown, $F^- < Cl^- > Br^- > I^-$, in terms of competitive Gibbs free energy of anion dehydration and expansion of surface oxygen vacancies, into which the halide must absorb as the initial event in the breakdown process.

Keyword: Passivity breakdown, Point Defect Model, Halide ion size

INTRODUCTION

UNS K02700[1] grade carbon steel is currently the reference material for the fabrication of the overpack in the supercontainer design that is developed for the geological disposal of the High-Level Nuclear Waste (HLNW) in Belgium.[1] Damage to the supercontainer is envisioned to possibly occur by localized corrosion resulting from the presence of aggressive species in the annulus between the carbon steel overpack and the stainless steel envelope, which is filled with a cementitious material similar to Portland cement. The aggressive species may lead to passivity breakdown of carbon steel and to the development of pits. Therefore, the reliability and the corrosion performance of these metallic containers are of great importance in assuring the public safety. However, only using the empirical approach for studying the corrosion damage and passivity breakdown of the metallic parts of the barrier layer, cannot satisfy the need for predicting the corrosion performance over many millennia.

The Point Defect Model proposes a mechanistic, atomic scale description of the evolution of passivity breakdown of metals and alloys.[2,3] With the theoretical approach that was developed in the PDM, the dependence of the critical breakdown potential on the size of the aggressive anions, which is generally observed for metallic structures such as those fabricated from stainless steels, iron, aluminum, and nickel, can be readily explained.[4,5]

Based on the PDM, passivation and passivity breakdown of metals and alloys can be described in terms of seven elementary reactions involving point defect at the interfaces of the barrier layer (bl) of the passive film.[3] Due to the absorption of agressive anions, such as Cl⁻, into the oxygen vacancies via cation emission (an autocatalytic phenomena with the aggressive anion acting as a catalyst),, movement of the cation vacancies toward the metal/ barrier layer (m/bl) is enhanced and leads to the condensation of the cation vacancies at the metal/barrier layer (m/bl) interface if the cation vacancies cannot be annihilated at a sufficiently high rate via cation injection from the metal. The formation of a cation vacancy condensate leads to cessation of the growth of the barrier layer into the metal substrate at the breakdown site. However, the barrier layer continues to dissolve at the bl/ol interface resulting in the local thinning of the barrier layer and, ultimately, in passivity breakdown (Figure 1). Passivity breakdown occurs if the rate of cation vacancy condensation at the m/bl interface is higher than the rate of cation vacancy annihilation via cation injection from the metal at the same location, as depicted in Figure 1.[2,3] The breakdown potential (E_c) for that specific site, can be expressed as: [2,3]

$$E_c = A + \frac{\Delta G_A^0}{\alpha F} - \frac{2.303RT}{\alpha F} log(a_{x^-}) \qquad (1)$$

where A is:

$$A = \frac{2.303RT}{\chi \alpha F} ln \left[\frac{J_m}{\chi K D [N_v/\Omega]^{1+\frac{\chi}{2}} exp[-\Delta G_3^0/RT]} \left(\frac{N_v}{\Omega}\right)^{\frac{\chi}{2}} \right] - \frac{\beta pH + \phi_{f/s}^0}{\alpha} \qquad (2)$$

As can be seen, Equation (1), predicts that the breakdown voltage is a function of the activity of the aggressive species, (a_{x^-}) and the changes in the standard Gibbs energy due to the absorption of anion species in the solution ($X^-.nH_2O$) into the oxygen vacancies (ΔG_A^0), R is the gas constant, T is the temperature, χ is the stoichiometry of the oxide, α is the polarizability of the bl/ol interface that correlates the potential drop across the interface with the applied potential, D is the diffusivity of the cation vacancy in the barrier layer, J_m is annihilation rate of cation vacancies at m/f interface, F is the Faraday constant, ε is the electric field strength within the barrier layer, Ω is the volume per mole of
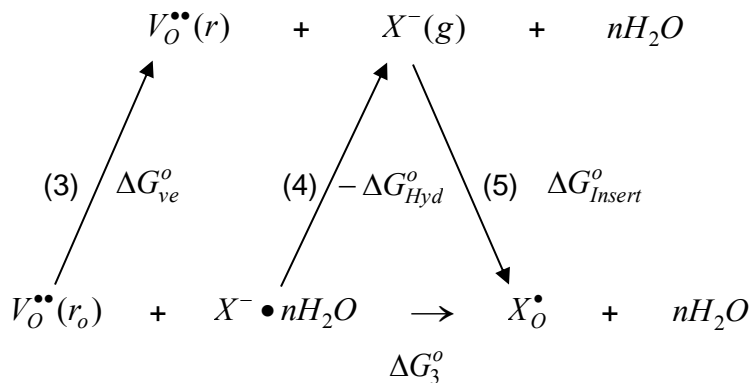
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[1] UNS K02700; ASTM A516 gr. 70; EN 10028-6 P355 QL2 (1.8869).

cations in the film, N_v is Avogadro's number, β is a constant that relates the potential drop across the f/s interface to the pH, ΔG_s^0 is the standard Gibbs energy change for the Schottky pair or cation extraction reaction, and $\varphi_{f/s}^0$ is the potential drop at the film/solution interface (f/s) at pH = 0 and $E_{app} = 0$.

(a) Steady State   (b) Vacancy Condensation
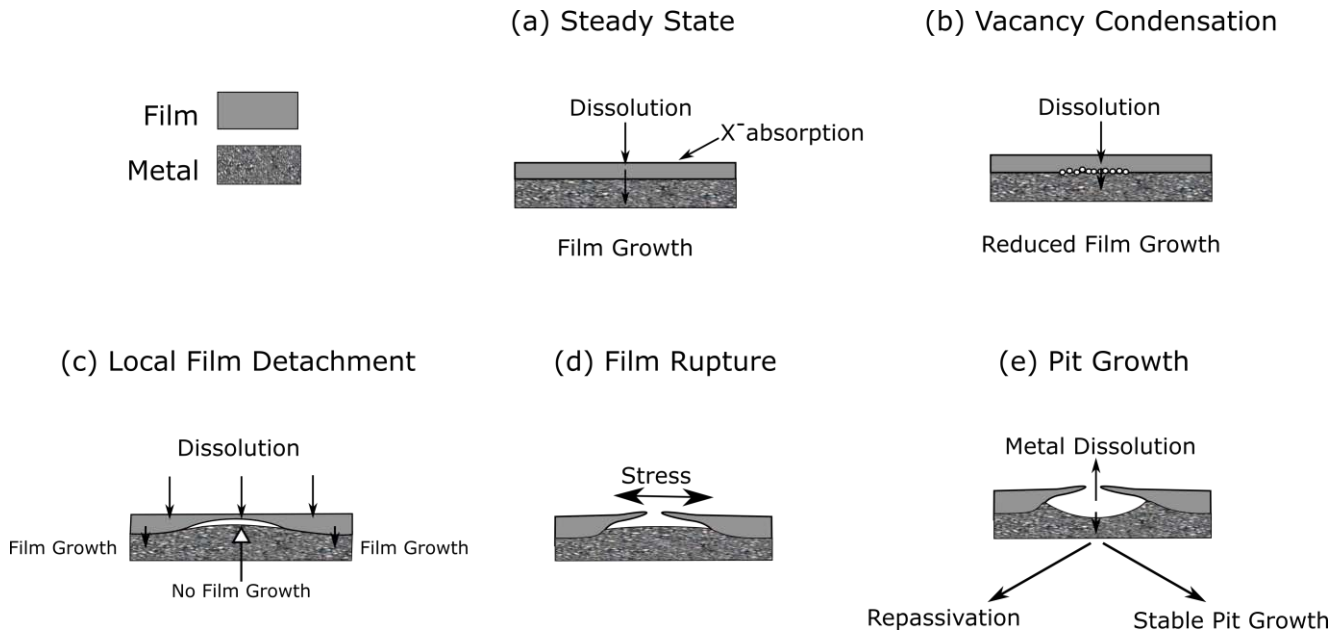
Figure 1. Cartoon showing the events that are envisioned to occur in passivity breakdown of a metal that is induced by aggressive anion absorption into a surface oxygen vacancy at the bl/ol interface. [2,3]

The thermodynamic parameter ΔG_A^0 can be estimated by considering the changes of the standard Gibbs free energy of simultaneous occurrence of various reactions at the (bl/ol) interface as expressed by the thermodynamic cycle:[3]

$$V_O^{\bullet\bullet}(r) \quad + \quad X^-(g) \quad + \quad nH_2O$$

$$(3) \; \Delta G_{ve}^o \qquad (4) \; -\Delta G_{Hyd}^o \qquad (5) \; \Delta G_{Insert}^o$$

$$V_O^{\bullet\bullet}(r_o) \quad + \quad X^- \bullet nH_2O \quad \longrightarrow \quad X_O^{\bullet} \quad + \quad nH_2O$$

$$\Delta G_3^o$$

Figure 2. Thermodynamic cycle used for estimating the change in standard Gibbs energy for the absorption of an anion ($X^- \bullet nH_2O$) into a surface oxygen vacancy.[3]

to yield the overall reaction as

$$\ddot{V}_O(r_o) + X^-.nH_2O \xrightarrow{\Delta G_A^0} \dot{X}_O(r_{X^-}) + nH_2O \qquad (6)$$
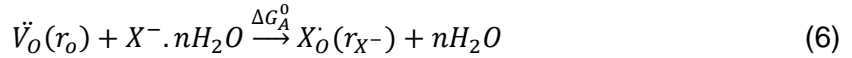
Reaction (3), Figure 2, corresponds to enlarging the surface oxygen vacancy, $\ddot{V}_O(r_o)$, to the size necessary to accommodate the aggressive anion (X^-), with the enlarged vacancy (radius r_{X^-}) containing dehydrated X^- being designated $\dot{X}_O(r_{X^-}$ and ΔG_{ve}^0 is the change in the standard Gibbs energy for that process. Reaction (4) corresponds to dehydration of $X^-.nH_2O$ to form the dehydrated anion, $X^-(g)$ in the gas phase (standard state of 1 mol/l) and $-\Delta G_{Hyd}^0$ is the change in standard Gibbs energy for the dehydration process. Reaction (5) describes the absorption of the aggressive anion into the expanded oxygen vacancy with the associated change in standard Gibbs free energy of insertion being ΔG_{Insert}^0.

From Figure 2 it is evident that the change of the standard free energy ΔG_A^0 can be written as:[3]

$$\Delta G_A^0 = \Delta G_{ve}^0 - \Delta G_{Hyd}^0 + \Delta G_{Insert}^0 \qquad (7)$$

Among the different theories that are available for calculating the standard Gibbs energy of hydration of halide ions, in this work we employed Equation (8), which is based on Born model:[5–7]

$$\Delta G_{Hyd}^0 = -50.676 - 5.0137 \times \frac{10^{-6}}{r} \qquad (8)$$

Now, the required energy to expand a surface oxygen vacancy to accommodate anion of increasing size is expected to become increasingly positive with the caveat that if the anion is smaller than the oxygen vacancy no expansion is necessary and hence no energy is expended. Such is the case for F⁻. However, fluoride is the most strongly hydrated anion and hence has the largest negative value for ΔG_{Hyd}^0 while iodide, being the largest of the anion considered in this work is the most weakly hydrated (with the smallest, negative ΔG_{Hyd}^0) but requires the largest energy to expand the vacancy. These relationships are such that the change in the standard Gibbs energy of adsorption, ΔG_A^0 is predicted to pass through a minimum at an anion the size of chloride.[5]

It is important to note that in this paper, the value of ΔG_{Insert}^0 is not considered, due to the lack of information on some parameters such as dielectric proprieties of the barrier layer, although it might be important in a more comprehensive analysis. Thus, the effect of anion size on E_c is attributed to a competition between the Gibbs energy necessary to expand the vacancy (if necessary) and the Gibbs energy required to dehydrate the aggressive anion.

Therefore, depending on the barrier layer properties and also on the size of the aggressive anion, the change of the standard Gibbs free energy of absorption of a halide anion into the surface oxygen vacancy is different for the different halides, resulting in different E_c values.

In this paper, our goal is to shed light on the influence of different halides (F⁻, Cl⁻, Br⁻, and I⁻) on passivity breakdown of UNS K02700 grade carbon steel in pH 8.9 solutions using the theory that was proposed in the PDM.[5]

EXPERIMENTAL PROCEDURE

The UNS K02700 grade carbon steel with an exposed surface area of 0.2 cm² was electrically connected to a copper wire from the backside and mounted in an epoxy resin. This sample was used as the working electrode (WE) in a three-electrode, conventional electrochemical cell. The chemical composition of the UNS K02700 grade carbon steel is: C 0.15 wt.%, Mn 0.98 wt.%, P 0.005 wt.%, S 0.0005 wt.%, Si 0.324 wt.%, Cu 0.043 wt.%, Ni 0.05 wt.%, Cr 0.082 wt.%, Mo 0.009 wt.%, Al 0.034

wt.%, Nb 0.006 wt.%, Zr 0.001 wt.%, V 0.001 wt.%, Ti, 0.001 wt.%, Co 0.005 wt.%, B 0.0001 wt.%, N 0.0034 wt.% with the balance being Fe. A saturated calomel electrode (SCE) and a platinum mesh were used as the reference electrode (RE) and the counter electrode (CE), respectively. The WE was wet ground to the final finish of 1200 grit and then rinsed and cleaned with deionized water and ethanol.

Potentiodynamic polarization experiments (PDP) with 0.167mV.s^{-1} scan rate using a commercailly available potentiostat, were conducted in a clear, saturated Ca(OH)$_2$ solution with 0.2 M borate buffer in the presence of different halide concentrations of 0.01, 0.05, 0.1, 0.5 and 1 M. All experiments were performed in deaerated conditions (deoxygenized with N$_2$) and ambient temperature (20 $^{\circ}$C) with a pH of 8.9. All tests were repeated at least five times. Prior to the PDP experiments, samples were cathodically cleaned at -1 V$_{SCE}$ for 5 minutes to remove any air-formed oxide film and were then left at OCP for another 15 minutes.

RESULTS AND DISCUSSION

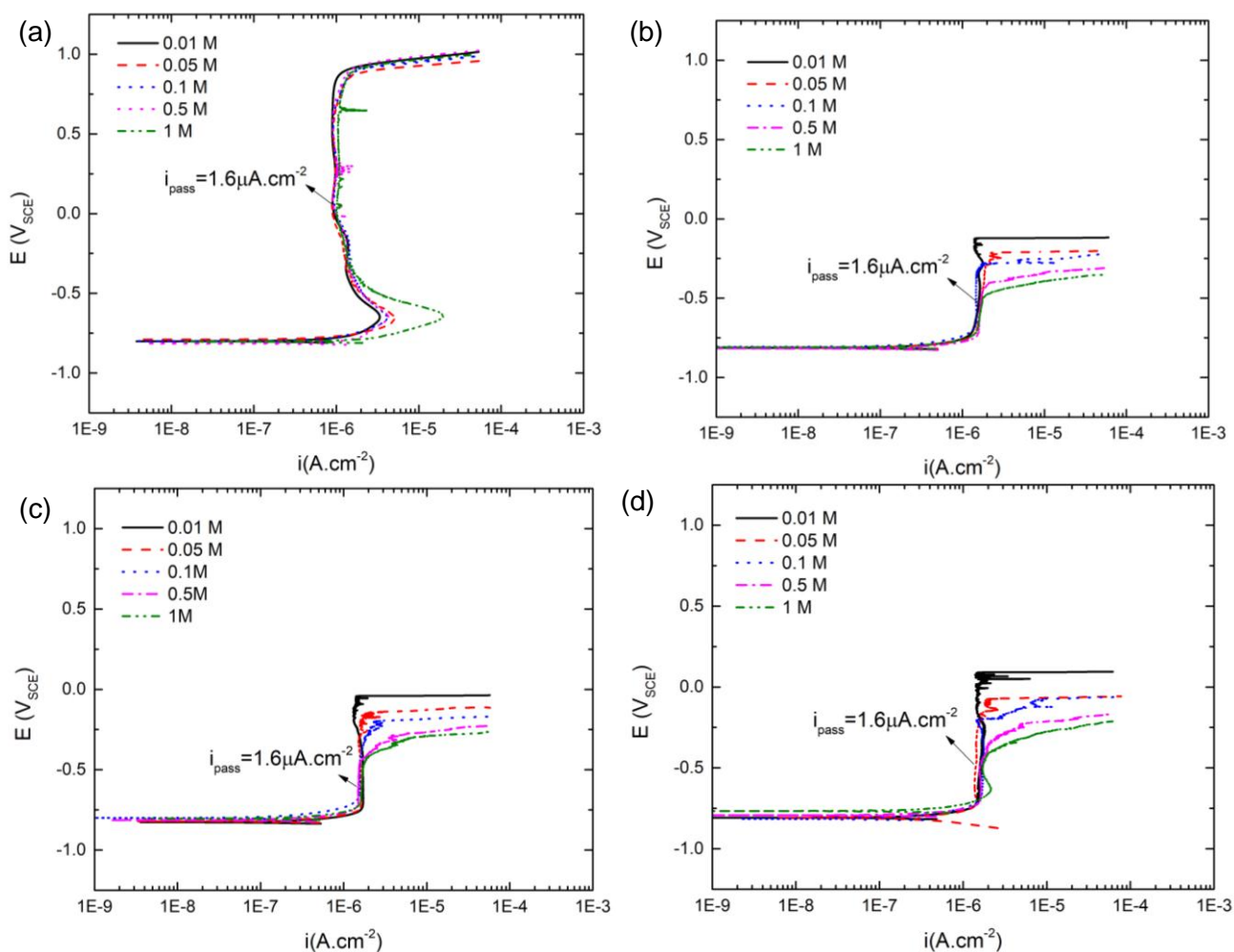Figure 3, shows the typical PDP curves for UNS K02700 grade carbon steel in saturated Ca(OH)$_2$ solution with 0.2 M borate buffer solution at pH 8.9 and for different halide concentrations. As shown in this figure, the value of the passive current density (i_{pass}) is almost constant (1.6 µA.cm^{-2}), irrespective of the halide concentration. Similar behavior was also reported for stainless steel in contact with halide-containing solutions.[5] This observation is consitent with the barrier oxide layer on carbon steel being primarily a cation interstitial conductor and is in agreement with a principal hypothesis of the PDM, that the aggressive anions only participate in the breakdown of the barrier layer of the passive film by absorption into surface oxygen vacancies and hence in affecting only the transmission of oxygen vacancies and cation vacancies; the former being affected by reducing the annihilation rate by water at the bl/ol interface and the latter by halide catalyzing cation extraction at the same location.[5] Because the transmission of cation vacancies and oxygen vacancies make a small contribution to the passive current density (each < 0.01 %) any impact that the aggressive anion may make on the fluxes of cation and oxygen vacancies is so small as to be not noticeable.[8]

Based on the PDM, the annihilation rate of cation vacancies at the m/bl interface (J_m) via injection of cations from the metal, which may lead to the passivity breakdown, depending on the flux of cation vacancies across the barrier layer, can be calculated by Equation (10):[2,9]

$$J_m \leq \frac{i_{pass} N_v}{\chi F} \tag{10}$$

with the oxidation state of +3 being assumed for the cation in the barrier layer (assuming that γ-Fe$_2$O$_3$ is the barrier layer), the value of J_m is calculated to be $J_m \leq 3.43 \times 10^{12} cm^{-2}.s^{-1}$ for all four halides considered in this work. This finding is inconsistent with halide penetration models that postulate that passivity breakdown is due to penetration of X$^-$ through the barrier layer to initiate passivity breakdown at the m/f interface, because if halide penetration occurred the vacancy annihilation rate should have been affected. Although occasional references are made in the literature to the PDM being an "ion penetration" model, those claims are incorrect as the anion is postulated to absorb into a surface oxygen vacancy only. We have found no convincing evidence for ion penetration in the literature or in our own work.[10] Parenthetically, we note that such claims are commonly based upon surface analytical studies (e.g., AES, SIMS) involving ion milling with heavy ions (e.g., Ar$^+$) that mixes the underlying matrix before the analysis is actually accomplished. In the case of passive films on the transition metals, the barrier layer is typically 1 – 3 nm thick but may be covered by an outer layer that is is hundreds or thousands of times thicker. The sputtering rate is set to mill through the film in a reasonable time, such the barrier layer is transited in the "blink-of-an-eye" and definitive composition data on the composition of the barrier layer is lost. Theoretically, the problem might be resolved using angle-resolved XPS[11] or preferably SALI (Surface Analysis by Laser Ionization).[12] Neither technique involves heavy ion sputtering.

As expected, for the entire concentration range of F⁻ ion as shown in Figure 3(a), this halide did not induce passivity breakdown on UNS K02700 grade carbon steel due to the excessively high dehydration Gibbs energy. All of the other halides (Cl⁻, Br⁻, I⁻) induced passivity breakdown as indicated by the sharp increase in the current at the breakdown potential (E_c).
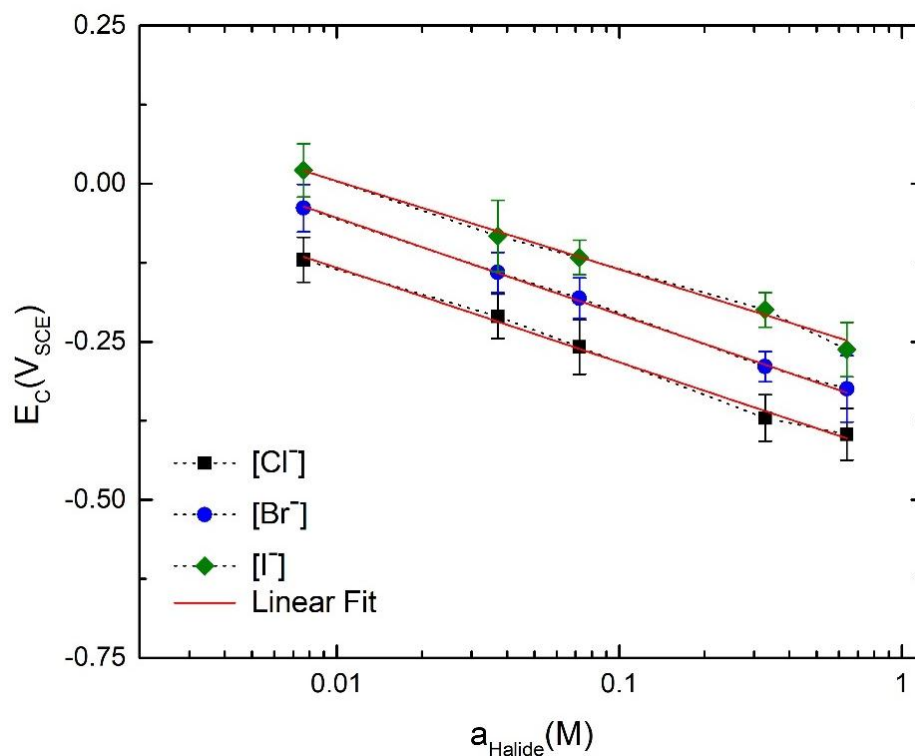

Figure 3. Potentiodynamic polarization curves of UNS K02700 grade carbon steel in clear saturated Ca(OH)$_2$ solution with 0.2 M borate buffer solution at pH 8.9 and different halide concentrations, a) NaF, b) NaCl, c) NaBr, d) NaI.

Figure 4 shows the mean value of the E_c with the standard deviation obtained from five repeated experiments at different halide activities in a saturated Ca(OH)$_2$ solution with 0.2 M borate buffer. It can be seen that regardless of the halide type, there is a linear decrease of the E_c with increase of logarithm of a_{X^-} which is in agreement with the PDM prediction as given by Equation (1).[13] By applying the slope of the linear fits in Figure 4 into Equation (1), the value of α was calculated to be 0.40, 0.39, and 0.42 for Cl⁻, Br⁻ and I⁻, respectively. Essentially, the value of α, which is a property of the bl/ol interface is independent of the halide size as expected from the PDM.

Considering the anion size, Figure 4 shows that at the constant concentration of the halides, with increasing the anion size from Cl⁻ to I⁻, the value of E_c is minimal at Cl⁻. That is, E_c lies in the order: F⁻ >> Cl⁻ < Br⁻ < I⁻. This tendency can be explained by the competitive effects of oxygen vacancy expansion and halide dehydration as discussed above.

Figure 4. The passivity breakdown potential of UNS K02700 grade carbon steel in the clear saturated Ca(OH)$_2$ solution with 0.2 M borate buffer solution at pH 8.9 vs. the activity of different halides.

CONCLUSIONS

Using the theory that was previously proposed in the Point Defect Model, the effect of halide size on inducing passivity breakdown on UNS K02700 grade carbon steel at pH 8.9 was investigated. Experimental results show satisfactory agreement with the prediction of the PDM, in which, Cl$^-$ is the most aggressive anion in inducing the breakdown potential, while F$^-$ was unable to induce breakdown of the barrier layer. The critical breakdown potential is found to lay in the order F$^-$ << Cl$^-$> Br$^-$ > I$^-$. This is due to the competing action of the required energy for oxygen vacancy expansion, entropy change and required energy of dehydration.

ACKNOWLEDGMENTS

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