



Review

Critical review on the passive film formation and breakdown on iron electrode and the models for the mechanisms underlying passivity

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ABSTRACT

Iron and its alloys acquire stability because of the phenomenon of passivity. Though several theories, models and experimental works on passivity have been published in the literature, the mechanisms underlying the stability of the passive oxide over the metals remain still a mystery. This review presents recent developments on theoretical and experimental results besides the literature available in other reviews and critically review selected experimental results on iron/electrolyte system and theoretical developments in general and specific to iron by invoking high field model, modified high field model, point defect model (PDM), variants of PDM (VPDM), diffusion Poisson coupled model (DPCM), density functional theory based atomistic model. The experimental and model-predicted dependencies on applied voltage, pH, chloride and temperature are also presented and discussed.

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Nomenclature

i_{ss}	steady state current density
L_{ss}	steady state thickness
C	capacitance
C_{sc}	space charge capacitance
ϵ_r	relative permittivity
ϵ_0	permittivity of vacuum
E	electron charge
D_0	diffusivity
R	gas constant
ϵ	electric field strength
F	Faraday constant
N_D	donor concentration in the passive film
N_A	acceptor concentration in the passive film
E, V_{ap}, V_m	applied potential
E_{fb}	flatband potential
$\phi_{f/s}$	potential drop at f/s interface
$\phi_{m/f}$	potential drop at m/f interface
$\phi_{f/s}^0$	value of $\phi_{f/s}$ under standard conditions
$\phi_{m/f}^{oc}$	open circuit potential at m/f interface
ϕ_R	reference potential drop at m/f interface
V_{oc}	open circuit potential
E_{SHE}	potential of the standard hydrogen electrode
E_{bif}	bifurcation potential
K_B	Boltzmann constant
T	temperature
χ, δ	oxidization state of the metal cation in the barrier layer, Oxidization state of the metal cation in the solution
V_o^{**}	oxygen vacancy
V_m^*	cation vacancy
O_o	oxygen in the oxygen sublattice
M_M	cation in cation site on the cation sublattice
V_m	metal vacancy at the metal
Fe_{Fe}	iron in the iron sublattice
M^{6+}	cation in the solution
M_i^{*+}	interstitial cation
$MO_{\chi/2}$	stoichiometric oxide
L	thickness of the passive film
α	polarizability of m/f interface
β	dependence of the potential drop at f/s interface on pH

α_i	Transfer coefficient of i^{th} defect reaction
K	$K = F\epsilon/RT$
k_i^0	standard rate constant for i^{th} defect reaction
γ	F/RT
k_i	rate constant of the i^{th} of the defect reaction
a_i, b_i, c_i	parameters appearing in the rate constant k_i
C_{H^+}	concentration of hydrogen
$C_{H^+}^0$	standard hydrogen ion concentration
R_{PB}	Pilling-Bedworth ratio
R_{const}	electronic contact resistance at m/f interface
P_f	electronic resistivity of the oxide film
Ω_{ox}, Ω	molar volume of the metal oxide
Ω_m	molar volume of the metal
t_{ind}	induction time
J_{CA}	flux of cation vacancy
I_{pass}	passivation current
I_{act}	reactivation current
K_4^0	base rate constant for the 4th defect reaction
$K_{eq}(T)$	equilibrium constant
R_L	rate of change of boundary layer thickness
J_o	flux of oxygen vacancy
L_{ss}^0	thickness of barrier layer before chloride addition
K_1, K_2	potential and pH dependent functions defined in [38]
C_m^{ss}	steady state metal vacancy concentration before chloride addition
$C_m(\chi = \chi_b(t), t)$	metal vacancy concentration at the moving boundary at $C_m(\chi = \chi_b(t))$
V_{pit}	pitting potential

1. Introduction

The exploitation of metals and alloys, especially the iron based materials for domestic and industrial purposes started even before 150 years [1–6] by virtue of their stability at room temperature and at neutral pH. However passivity and its breakdown continue to pose several challenges and are of current interest [7]. These metals acquire stability by reacting immediately with oxygen/oxide at room temperature in the environments forming a compact oxide layer over the metal surfaces which prevents corrosion of the metals. The stability [8–10] provided by these oxides known as passivity remained a mystery for several years with no unifying theoretical treatments [3,5,11–33]. Though in-

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