The importance of understanding metal passivity

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In 1979, Digby D. Macdonald developed the Point Defect Model (PDM). This theory describes Oxide Film growth by considering the creation and annihilation of point defects (vacancies and interstitials) within the film. Before Macdonald, passivity was treated merely as a conceptual means of explaining metal passivity. The PDM represents an ideal 2-dimensional Oxide Film (which could also be a Hydride film) of uniform composition, describing the reactions (occurring only at the interfaces of the film). Macdonald introduced an accurate and robust model based on point defects that offers a comprehensive understanding of passivity and its breakdown. Several other authors had adopted the PDM and, along with Macfonald, had suggested additional improvements to the model by relaxing the hypothesis and making the model more realistic and general. The EIS (Electrochemical Impedance Spectroscopy) + Mott–Schottky + PDM = the most complete picture available to learn about oxide film characteristics, film oxide design, understand and predict film breakdown, and film behavior.

GENERATIONS OF MACDONALD'S POINT DEFECT MODEL (PDM)

Macdonald's Point Defect Model has evolved through three PDM generations—PDM-I, PDM-II, and PDM-III—with a fourth generation under development to address alloy passivity.

- PDM-I: Single defective-oxide layer with cation and oxygen vacancies, no film dissolution
- PDM-II: Bi-layer structure (barrier layer + outer precipitation layer), added metal interstitials, recognized barrier-layer dissolution and reaction conservativity
- PDM-III: Extended to valve metals where a highly resistive outer layer governs impedance and corrosion rate
- Generation IV (in development): Targets multi-component alloy films and the interplay of alloying elements in passive behavior. Several PDM "assumptions" are relaxed.

If a potential is applied between a metal and a reference electrode, the additional potential drop across the electrolyte can be considered or not. For simplicity, Macdonald frequently defines V_{app} (or U_{ext} or V) as the difference between the metal potential (ϕ_m) and the solution potential (ϕ_s) (ignoring the existence of any outer reprecipitated film and the potential drop across the electrolyte and not considering the resistance of an outer reprecipitated film (PDM I).

If an outer film is present (PDM II) and is considered, we will assume the film has constant resistance R and negligible thickness, or that it is a combination of passive elements. That is a reasonable assumption given that the precipitate film is frequently highly porous and the electrolyte is highly conductive. If the outer precipitate film grows too thick, the resistance of that outer film will increase. Eventually, it may shut down the reactions at the oxide film/electrolyte interface, and the Faradic impedance calculated from the PDM for the passive Oxide film will become too small relative to the outer film resistance. The PDM will no longer be applicable.

In the PDM III, additional assumptions are relaxed, and a more sophisticated oxide film can be modeled.

INTRODUCTION

In this paper, we list the PDM "Hypothesis," we summarize the most important "Assumptions" of the PDM (I and II), and discuss their implications, areas, and limitations. We also analyze the types of mathematical equations that the PDM yields and the techniques available to optimize (minimize) the difference between the theoretical and measured Impedance. Finally, we mention pitfalls to avoid when using optimization techniques.

We use the PDM II bilayer formulation to discuss how to simplify the mathematical expression and reduce the number of variables we are seeking to obtain from the optimization procedures, thereby avoiding pitfalls.

As mentioned in the Abstract of this paper, a combination of Electrochemical Impedance Spectroscopy (EIS), combined with Mott–Schottky analysis and interpreted through the Point Defect Model (PDM [1-4]), as developed by Macdonald and co-workers (see passivity at DigbyDMacdonald.com) provides the clearest picture of film idealized thickness, defect density, semiconducting behavior, stability, and growth mechanisms, all of which determine how protective the passive film will behave.

EIS is explicitly described as a powerful, non-destructive technique that provides quantitative, time-dependent information about oxide films, including their resistance, capacitance, and growth behavior. It is widely used to characterize oxide films formed during anodization and corrosion processes. EIS indicates film quality: whether the film is too porous, whether defect density is high, or whether growth conditions (potential, pH, alloying) produce a stable barrier.

Mott–Schottky Analysis extracts the carrier (defect) concentration, doping profile, and flat-band potential of the passive film [4, 5]. It is widely used to characterize the semiconducting properties of passive films on many metals. Mott–Schottky tells you about Donor/Acceptor density → Defect concentrations, Semiconducting type (n-type or p-type), Flat-band potential → energetics of oxide/electrolyte interface. Mott–Schottky analysis is performed by measuring the capacitance of the passive film as a function of applied potential.

The PDM treats a passive oxide (or hydride) as a lattice that hosts point defects—cation vacancies, anion vacancies, and interstitials. The PDM [1-4] explains how point defects (oxygen vacancies, cation vacancies, interstitials) control film growth, dissolution, and breakdown (pitting). The PDM combines EIS and Mott–Schottky analysis; each technique reveals a different part of the oxide film "story," and PDM provides the mechanistic framework that connects them [6-9]. When those two techniques and the PDM are combined, they allow you to extract (via optimization) defect densities, film thickness, dominant defect types, transport properties, and growth kinetics—all of which define how protective the passive film is. In summary, the PDM is a model of the passive state, not of the trans-passive state. The PDM does not require explicit electronic transport to explain passivity. In the passive regime, ionic defect fluxes dominate. Electronic leakage currents are negligible compared to ionic currents. Therefore, including electrons and holes in the model formulation is unnecessary. The PDM treats the films as uniform (in its 3D representation) and amorphous rather than crystalline semiconductors. Their electronic structure is dominated by localized defect states rather than band conduction. Therefore, semiconductor-style modeling is not physically appropriate for the passive regime. The PDM describes passive films in which ionic

defect transport dominates, and the electric field is governed by high-field conduction in thin, uniform amorphous oxides (or hydrides). Notice that even if the film thickness is constant, the problem is dynamic, because the film's steady state is the result of continuous film formation at the metal-film interface and film dissolution at the film-solution interface. The PDM is the only model that can account for all types of passive film compositions [10-12].
The potential drop across the *oxide* film can adopt different profiles, depending on the oxide characteristics. Figure 1 shows two of the most common profiles found in *oxide* films.

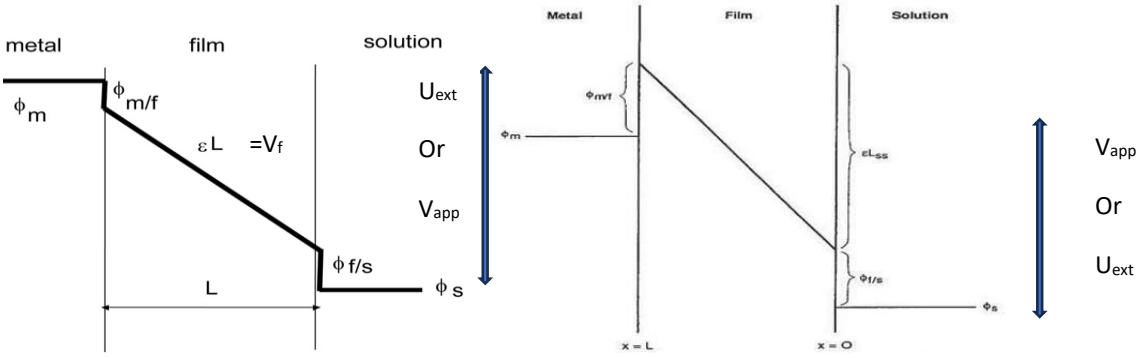

Figure 1. Schematic potential distribution across the metal/barrier-layer/solution $\varphi_{m/f} > 0$ or $\varphi_{m/f} < 0$; $\varphi_{f/s} > 0$.

The Metal–Film Interface Potential ($\varphi_{m/f}$) can be Positive or Negative (or even zero). In the Point Defect Model, $\varphi_{m/f}$ is the potential drop between the metal and the passive-film inner boundary. Its sign indicates the direction in which electrons and point defects are driven at that interface.

- $\varphi_{m/f} > 0$ (*positive*) when the metal is more anodic than the film, driving net oxidation of metal atoms into cation defects. This occurs in cation-conducting films (e.g., Ni in phosphate buffer), where metal cations migrate outward through the oxide lattice. In the semiconductor view of passive films, cation-conducting films—with metal cation vacancies as the dominant mobile defects—behave as *p-type* semiconductors because those vacancies act like acceptor states that support hole-like conduction. Dominant defect: cation vacancies (e.g., metal vacancies). Vacancies act as acceptor states, generating hole-like carriers. A Mott–Schottky plot ($1/C^2$ vs. E) with a *negative slope* indicates *p-type behavior*.
- $\varphi_{m/f} < 0$ (*negative*) when the metal is more cathodic than the film, favoring reduction or inward migration of anion defects. This is typical for anion-conducting films (e.g., WO_3 or tungsten trioxide), where oxide-forming anions move toward the metal/film interface while electrons accumulate on the metal side. Anion-conducting passive films behave as *n-type* semiconductors since their dominant mobile defect—oxygen vacancies—acts as an electron donor, populating the conduction band. Dominant defect: oxygen vacancies or metal interstitials. Vacancies/interstitials act as donor states, releasing electrons to the conduction band. Mott–Schottky plots show a *positive slope* in $1/C^2$ vs. E, indicating an n-type semiconductor.

The PDM defines the potential drop at the film/solution interface as

$$\phi_{f/s} = \alpha V + \beta \mathrm{pH} + \phi^0_{f/s} \quad (1)$$

Also, in the PDM formulation, the anodic and cathodic rate constants for reactions occurring at the film interface are calculated using the Butler-Volmer equation. The rate constants are expressed for the cathodic and anodic reactions as

$$k_{ci} = k_{oi} \exp\left[-(\alpha_{ci}\, n\, F\, (E - E_i^o))\right) / (R\, T)] \qquad k_{ai} = k_{oi} \exp\left[(1-\alpha_{ai})\, n\, F\, (E - E_i^o)\right) / (R\, T)] \quad (2)$$

Where

k_{oi}: Heterogeneous electron transfer rate constant (cm/s) of reaction i.

$E - E_i^0$: Overpotential (η). The difference between the applied potential E at the interface where the reactions occur ($\varphi_{m/f}$ or $\varphi_{m/f}$ -in the PDM, the reaction occurs at those interfaces) for each reaction i, and E_i^o is the equilibrium (thermodynamic) potential where no net current flows (i = 0).

α_{ci} and α_{ai} : Cathodic and anodic transfer coefficient (dimensionless, typically near 0.5) for reaction i.

n: Number of electrons transferred in the rate-determining step.

F: Faraday's constant (96,485 C/mol).

R: Gas constant (8.314 J/(K-mol))

T: Temperature (K)

The PDM defines the rate constants as functions of the externally applied potential, film thickness, and pH, using the definition of the potential across the film interfaces (Equation 1) and assuming the potential drop at the time is constant. The definition used by Macdonald is shown in Table 1,

Table 1. PDM II. Coefficients for the rate constants for the reactions that generate and annihilate point defects at the metal/film (m/f) interface (reactions (1)–(3)) and at the f/s interface (reactions (4)–(6)), and for dissolution of the film.

$k_i = k^0_i \exp(a_i V_{app}) * \exp(-b_i L) * \exp(c_i\, \mathrm{pH})$

Reaction	$a_i\,(V^{-1})$	$b_i\,(cm^{-1})$	c_i	Units of k_i^0
$(1) m + V_M^{\chi'} \xrightarrow{k_1} M_M + v_m + \chi e'$	$\alpha_1(1-\alpha)\chi\gamma$	$\alpha_1\chi K$	$-\alpha_1\beta\chi\gamma$	$\frac{1}{s}$
$(2) m \xrightarrow{k_2} M_i^{\chi+} + v_m + \chi e'$	$\alpha_2(1-\alpha)\chi\gamma$	$\alpha_2\chi K$	$-\alpha_2\beta\chi\gamma$	$\frac{mol}{cm^2 s}$
$(3) m \xrightarrow{k_3} M_M + \frac{\chi}{2} V_O^{\cdot\cdot} + \chi e'$	$\alpha_3(1-\alpha)\chi\gamma$	$\alpha_3\chi K$	$-\alpha_3\beta\chi\gamma$	$\frac{mol}{cm^2 s}$
$(4) M_M \xrightarrow{k_4} M^{\Gamma+} + (\delta-\chi)e'$	$\alpha_4\alpha\delta\gamma$		$\alpha_4\beta\delta\gamma$	$\frac{mol}{cm^2 s}$
$(5) M_i^{\chi+} \xrightarrow{k_5} M^{\Gamma+} + (\Gamma-\chi)e'$	$\alpha_5\alpha\delta\gamma$		$\alpha_5\beta\delta\gamma$	$\frac{cm}{s}$
$(6) V_O^{\cdot\cdot} + H_2O \xrightarrow{k_6} O_O + 2H^+$	$2\alpha_6\alpha\gamma$		$\alpha_6\beta\delta\gamma$	$\frac{cm}{s}$
$(7) MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\Gamma+} + (\chi/2)H_2O + (\Gamma-\chi)e'$	$\alpha_7\alpha(\delta-\chi)\gamma$		$\alpha_7(\delta-\chi)\beta\gamma$	$\frac{mol}{cm^2 s}$

The "over potential" in the exponential term on the Butler Valmer (BV) expression (equation 2) is the local overpotential at the metal/film (or film/solution) interface— The overpotential, $\eta = E - E_i^o$ (E is the potential across the interface (PDM use notation $\phi_{m/f}$ or $\phi_{f/s}$ instead E). E_i^o is the

equilibrium potential of the reaction considered). E_i^o of an electrochemical half-reaction is the electrode potential at which the rates of oxidation and reduction are precisely balanced, and the reaction is at proper thermodynamic equilibrium. It can be measured or calculated using the Nerst equation. In the B-V equations, the actual driving force for the interfacial electron-transfer is the interfacial overpotential (η), not the $V_{app,}$ Butler-Volmer, and related expressions always plug in the overpotential η, which is the difference between the real potential drop felt by the redox couple at that interface and the equilibrium (Nernst) potential for the half-reaction. On the other hand, Macdonald PDM works by expressing the BV in terms of the potential drop across the metal/film and, for simplicity, deduces a direct dependence of the BV rate constants on the externally applied potential rather than on the internal potential drop across the film. The Volmer equation describes how the electrical current through an electrode depends on the voltage difference between the electrode and the bulk electrolyte for a simple, unimolecular redox reaction, assuming that both cathodic and anodic reactions occur on the same electrode. The PDM adopts the BV equation to define the rate constant but expresses it more naturally, i.e., in terms of the applied potential rather than the overpotential. A relation between the V_{app}, the definition of the potential drop across the film, and Equation 1 is used to calculate the potential drop at the metal/oxide interface (ignoring the potential drop at the outer reprecipitate film) as

$$V_{\text{app}} = \phi_{\frac{m}{f}} + \Delta\phi_{\text{f}} + \phi_{\frac{f}{s}} \tag{3}$$

This partitioning and the linear forms for $\phi_{m/f}$and $\phi_{f/s}$These are the standard PDM starting points. The fraction of the applied potential that acts at this boundary, often written as:

$$\phi_{m/f}(L, \alpha, \beta, \text{pH}) = (1-\alpha)\, V_{\text{appl}} - \varepsilon L - \beta\ \text{pH} - \phi^0 \tag{4}$$

where α, β, γ are empirical partition coefficients (often determined by fitting) and $\phi^0$are reference offsets. These linear forms are used to obtain closed-form steady-state solutions for defect fluxes and $L(V_{\text{ap}}$,pH)

The Generation II PDM (Figure 2) was developed to address shortcomings in Generation I of the PDM model (which considered only 4 reactions: two at the f/s and two at the m/f interfaces). Specific features and assumptions of PDM-II, in addition to those invoked in the development of PDM-I, include:

Recognizes the role of barrier layer dissolution – allowing the film to reach steady states in thickness and current.

- The barrier layer dissolves at the barrier layer/solution (outer layer) interface by either chemical or electrochemical processes.
- Recognizes and classifies interfacial reactions as to whether they are lattice-conservative or non-conservative processes.
- Introduces interstitials in addition to cation vacancies and oxygen vacancies as the defects in the barrier layer. It has been shown that, in many cases, the interstitials are the dominant defects (Fe, Zn, Pt, stainless steel, Alloy 22, etc.).

The main reactions, considered in the PDM II, that cause the formation and dissolution of the film are shown in Figure 2

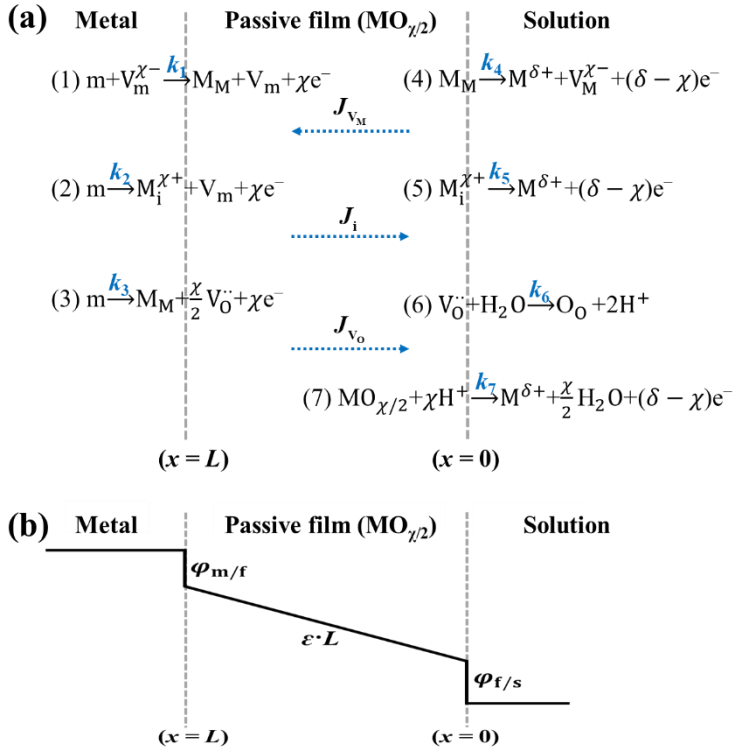

Figure 2. (a) Schematic diagram illustrating the physicochemical basis of the PDM, where defect generation and annihilation reactions occur at the m/f and f/s interfaces of the passive film on a metal. m = metal atom, V_m = metal atom vacancy, $V_M^{\chi-}$ = metal cation vacancy, $M_i^{\chi+}$ = metal cation interstitial, M_M = cation in the cation site of the sublattice of $MO_{\chi/2}$, $V_O^{\cdot\cdot}$ = oxygen vacancy, O_O = oxygen in the oxygen anion site of the sublattice of $MO_{\chi/2}$, $M^{\delta+}$ = metal cation in electrolyte. (b) Schematic representation of the potential distribution at the metal/passive film/solution interface.

The fact that the potential V_f in the PDM represents the total potential drop across the passive film—rather than just at the metal/film interface—has profound implications for how we understand and predict corrosion rates, especially in passive systems. Defect transport requires a field across the film: The migration of defects through the oxide layer is governed by electromigration, which depends on the electric field $\varepsilon = V_f/L$, where L is the film thickness and V_f is the potential difference across the film. Notice that if you consider only the potential drop at the metal/film interface, you'd miss the driving force that moves defects through the bulk of the film.

In the PDM, film growth is a bulk process: the steady-state thickness results from a balance between defect generation at the metal/film interface and annihilation at the film/solution interface. Defect fluxes sustain this balance across the entire film, which are field-driven. So, the relevant potential is the one across the film, not just at one boundary. Corrosion rate is field-driven, not just interface-controlled. Since the electric field drives defect migration across the film $\varepsilon = V_f / L$, the corrosion rate becomes a function of both the applied potential and the film thickness (note that the applied potential differs from the potential across the film or across the film's interfaces). A higher potential increases the field, accelerating defect flux and potentially increasing the rate of metal ion dissolution at the film/solution interface.

Steady-state thickness modulates corrosion: The steady-state thickness, L_{ss}, implies that thicker films form at higher potentials, assuming defect annihilation rates remain constant. Thicker films reduce the electrical field ε, which can slow down defect migration, thereby reducing corrosion rates over time. Thicker passive oxide films often exhibit a lower measured dielectric constant because the dominant polarization mechanisms and structural quality shift as the film grows. In ultrathin films (<5–10 nm), strong interfacial polarization at the metal/oxide and oxide/solution boundaries and a highly compact, defect-poor inner layer boost the effective permittivity. As the film thickens, bulk-oxide properties—with lower density, higher defect/porosity content—and the series combination with low-permittivity "dead" interfacial layers prevail, pulling the apparent dielectric constant down. However, if the film becomes too resistant or unstable, it may lead to localized breakdown (e.g., pitting).

PDM HYPOTHESIS

We call "Hypothesis" the fundamental physical postulates of the PDM. In the PDM II, the seven defect reactions that form its backbone are treated as physically real processes occurring in the passive film. The core hypotheses of Macdonald's PDM II are that passive film growth, dissolution, and breakdown are governed by point-defect generation, annihilation, and transport within a *bilayer* oxide, with the barrier layer controlling the passive current. Here are the seven main *Hypotheses* of the PDM:

1. *Structura* . Passive films are unlayered (PDM-I) and bilayer (PDM-II). The bilayer is composed of an inner barrier layer, a compact (highly defective semiconductor oxide type), and an outer resistive porous layer (formed by compounds resulting from the reaction of cations in the barrier layer with solution species).
   Defects dominate transport, not electrons or holes. The defect species include cation vacancies. $V_M^{\chi-}$, anion vacancies $V_O^{\cdot\cdot}$ and cation interstitials $M_i^{\chi+}$. The barrier layer is treated as a defected -mediated ionic conductor.

2. *Kinetic.* PDM-II assumes seven (five reactions in the PDM I) fundamental reactions at the metal/film and film/solution interfaces (anodic reaction occurs at the metal/film (M/F) interface [1-4], and the cathodic reaction occurs at the film/solution (F/S) interface). These include: (1) Generation and annihilation of cation vacancies, (2) Generation and annihilation of anion vacancies, and (3) Generation and consumption of cation interstitials. To each reaction is assigned a rate constant with Arrhenius and field-dependent terms, a stoichiometric contribution to film growth or dissolution, and a classification as lattice-conservative or non-conservative.

3. *Transport.* Point defects migrate under the electric field across the barrier layer; diffusion is not dominant. The PDM's constant-field assumption comes from high-field ion transport theory (Cabrera–Mott [13], Fromhold–Cook [14]). The barrier layer alone controls the passive current (a key PD hypothesis). The outer layer does not control the measured current (this hypothesis was modified in PDM-III).

4. *Film-Growth.* Film thickness evolves from the balance of defect fluxes: cation vacancy annihilation → film growth. Anion vacancy annihilation → film growth. Cation interstitial flux → dissolution at the film/solution interface. Steady state occurs when defect generation and annihilation rates balance, giving a constant barrier-layer thickness. Note that the process remains dynamic.

5. *Breakdown (Pitting [15]).* Metal vacancies accumulate at the metal/film interface when their generation exceeds their annihilation (by absorption into the metal). Accumulated vacancies coalesce into voids, causing local film collapse, exposure of bare metal, and pit nucleation. This mechanism is central to PDM's explanation of chloride-induced pitting.
6. *Thermodynamic & Electrostatic.* The electric field in the barrier layer is high. Reaction rate constants depend exponentially on the field (high-field approximation). The oxide is treated as a defective semiconductor, enabling Mott–Schottky analysis.
7. *Assumptions about metal substrate*. Metal vacancies diffuse rapidly into the bulk (the metal) and do not accumulate unless breakdown is imminent. The metal/film interface is atomically sharp and supports well-defined defect reactions.

PDM ASSUMPTIONS AND THEIR CONSEQUENCES

On the other hand, "Assumptions" are practical choices that make the equations tractable. The hypotheses are not optional; the Assumptions are. They are the axioms of the model. Hypotheses define Physics and Chemistry. If you change them, you no longer have the PDM.
Assumptions define the model's solvability. If you change them, you still have the PDM, just a more complex and realistic version. This is why Macdonald's later "third and fourth-generation PDM" keeps the same seven hypotheses, but relaxes several assumptions (e.g., allowing for space-charge effects and non-constant fields).

Assumption 1

In the PDM, the field strength in the passive oxide layer is considered independent of applied voltage and of distance through the film. It only depends on the film composition.
The electric field strength (ε) across the film is defined as the force exerted on a unit positive charge placed in an electric field, typically measured in newtons per coulomb (N/C) or volts per meter (V/m). It is a property of the oxide film. The applied electrostatic potential is distributed across the interphase, with drops at the m/f interface ($\phi_{m/f}$), the film/solution interface ($\phi_{f/s}$), and the film (εL), where L is the film thickness**.**
We need to ask ourselves when Assumption 1 of the PDM renders the model inapplicable. Assumption I adopt that the film has a high field that can be approximated as a constant for very thin films. Research has indicated that the assumption of a constant field is not always valid, particularly in complex or non-ideal systems:

- *High Film Thickness:* If the passive film becomes thick (nm), the electric field may vary with position throughout the film rather than remaining constant.
- *Narrow Band Gap Materials:* For materials with narrow band gaps, or under specific interfacial reaction conditions, the field is not constant and requires the incorporation of electron and hole transport models.
- *Transient States:* During rapid potential changes, the field is not uniform or constant as the film adjusts its thickness to reach a new steady state.
- *Electronic Charge Carriers:* The assumption of a purely ionic vacancy-controlled field fails if high densities of electrons and holes are present, which can partially compensate for the potential drop.
- *"Buffering" Effects:* While band-to-band tunneling is often cited, detailed modeling shows that electron/hole transport can buffer the field but not necessarily make it completely constant across all conditions. Macdonald PDM does not rely on band-to-band tunneling

(BTBT) to justify a constant electric field (Assumption 1). The PDM does **not** assume BTBT, does **not** require BTBT, and that the electric field is constant because of the physics of high-field ion transport in amorphous barrier layers—not because of electronic tunneling (Contrary to suggested elsewhere [16]).

In most cases, when an oxide film is formed, Assumption 1 holds.

Assumption 2

The film–solution potential drop $\phi_{f/s}$ is treated as a linear function of the applied potential and pH. This Assumption is satisfied over a limited potential window, a stable surface and capacitance, and no strong specific adsorption or mass-transport coupling.

The voltage drop across the film/solution interface is considered to be linearly dependent on the applied voltage, V (or sometimes denoted as V_{app}), and the pH [17, 18] (Equation 1). The $\phi_{f/s}$ assumes that the interface capacitance does not vary with potential or ionic strength; large changes in capacitance produce nonlinear voltage partitioning and break the linear law. Furthermore, specific adsorption (chloride, sulfate, organic inhibitors) changes the surface charge and can introduce nonlinear, hysteretic behavior. $\phi_{f/s}$responses; absence or weak adsorption supports linearity. A linear $\phi_{f/s}$ is most consistent when the film behaves as a barrier with well-defined defect chemistry (for thin-to-intermediate films, where surface charge controls the drop). For thick, highly resistive passive films, or when internal redox dominates, the simple linear partition is less. Because the V_{app} is known, the potential drop at the m/f can be calculated easily using Equation (1) and the adopted potential drop at the interfaces (Figure 1). Assuming a linear dependence of the film/solution potential drop on applied potential and pH makes the PDM predict a nearly constant internal field and simple, linear scaling of defect fluxes and film thickness; this simplifies analysis but can produce large errors when charge distribution, non-ideal interfaces, thick films, or strong non-linear kinetics dominate — in those cases, the PDM I and II become unreliable. In summary, for Assumption 2, the user must be aware of which cases this mathematical simplification is not applicable.

When the linear-$\varphi_{f/s}$ dependency of the applied potential assumption makes the PDM I and II useless

- *Thick films or multilayer oxides:* when the film is thick enough that internal charge separation, space-charge layers, or band bending occur, the uniform-field assumption fails, and predictions of fluxes, impedance, and breakdown are wrong.
- *Strongly non-ideal interfaces or adsorbed species:* if $\varphi_{f/s}$ is controlled by surface chemistry (specific adsorption, complexation) that is non-linear with V or pH, the linear model misrepresents driving forces.
- *Temperature or composition regimes where α and β vary (Equation 1):* if α and β are not constant (e.g., temperature-dependent or composition-dependent), fitted constants lose predictive power.
- *When localized phenomena dominate:* pitting initiation, local acidification, or mechanical rupture involve spatially
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Assumption 3

BV hypothesizes that the reactions are unimolecular redox reactions. Macdonald's PDM makes the same assumption.

The caveat here, when adopting this hypothesis, is that for thick films, high defect densities, or mechanisms involving recombination/aggregation, unimolecular assumptions can yield

qualitatively incorrect predictions for pitting initiation and trans-passive behavior. In PDM terms, a film is thick when it no longer allows significant electronic coupling/tunneling across the barrier and when transport inside the film (defect diffusion, ionic migration) controls the kinetics rather than interfacial charge transfer.

Assumption 4

In Macdonald PDM, the reverse reactions are not ignored but considered negligible.

Notice that the PDM of Macdonald adopts the Butler-Volmer equations to describe the anodic and cathodic reactions occurring at the two oxide film interfaces, not on a single surface. This Assumption is not strictly physically correct in a steady-state model, but it *is* mathematically convenient and important for analyzing the conditions under which this approximation is valid [19]. The Butler–Volmer (BV) is a steady-state interfacial kinetic law. The irreversible (single-exponential) Butler–Volmer approximation used in Macdonald's PDM is valid when the electrochemical steps are *far* from equilibrium, so one exponential term dominates, or if the interfacial electron transfer is fast relative to defect transport, or if the passive film is thin enough for tunneling or charge transfer, or finally, if mass-transport or other parallel resistances are negligible.

Under these conditions, the PDM's "dynamic equilibrium" treatment is self-consistent. It is important to remember:

- *PDM defines a dynamic steady state, not thermodynamic equilibrium.* The PDM balances defect generation, migration, and annihilation to produce a steady film thickness and composition while allowing net Faradaic current. Treating interfacial electron transfer as dominated by a single exponential does not eliminate the dynamic balance within the film.
- *Irreversible BV is an asymptotic approximation, not a replacement of fundamental laws.* When one exponential term in BV overwhelmingly dominates, the two-term expression reduces to a single exponential without violating detailed balance — the backward flux is simply negligible under those conditions.
- *Macdonald's modeling goal is to capture the rate-limiting physics.* If defect transport or film growth is rate-limiting, simplifying the fast interfacial kinetics reduces model complexity while preserving the controlling mechanisms. That is standard asymptotic modeling practice.
- The irreversible (single-exponential) Butler–Volmer approximation in Macdonald's PDM is valid when the interfacial electron-transfer is driven far from equilibrium, so one exponential term dominates, the Faradaic step is fast relative to defect transport, mass-transport is negligible, and the passive film allows strong electronic coupling (thin/tunneling).

When the irreversible BV approximation is self-consistent

- *Large activation overpotentials, so one BV branch dominates***.** The BV equation reduces to a single exponential (Tafel form) when
- $|\ \alpha z F\eta/RT\ | \gg 1$; practically, for $z = 1$and $\alpha \approx 0.5$ This means overpotentials of order. $\gtrsim 75$–150 mV produce clear single-exponential behavior.
- *Fast interfacial kinetics are related to film defect transport.* If the exchange current density (j_0) is large and the rate-limiting step in the system is defect migration or film growth/annihilation (the PDM internal processes). Treating the interfacial reaction as effectively irreversible is justified because the film dynamics set the "dynamic equilibrium."

- *Thin or electronically coupled passive films (tunneling or strong coupling).* When the barrier is thin enough to tunnel or has sufficient electronic conductivity, the backward-reaction probability is suppressed, and the net current is dominated by a single direction, supporting the irreversible form.
- *Negligible concentration or mass-transport limitations.* The single-exponential limit assumes surface concentrations are not strongly depleted; if diffusion or convection limits supply, mixed control invalidates the irreversible BV simplification.
- *Single dominant electron-transfer pathway and roughly constant transfer coefficient.* Multiple parallel pathways or strongly potential-dependent αreduce the accuracy of a single-exponential approximation.

A final caveat: Near equilibrium ($|\ \alpha zF\eta/RT\ | \lesssim 1$Mixed control, or thick insulating films, require the full Butler–Volmer form and coupling to transport equations; the irreversible simplification will produce errors.

Assumption 5

In Macdonald's Point Defect Model, each elementary step at the metal–film or film–solution interface is written as a single-site redox event—basically a "one-defect" (unimolecular) reaction.
Assumption 5 and Assumption 3 appear similar, but there is an important difference; however, in some instances, those assumptions can be considered the same. The reaction proceeds via a single elementary step (no intermediate states or separate chemical substeps).
*Implication***:** the stoichiometry of the elementary step equals the molecularity of that step; the rate law follows directly from that elementary step.

$$\mathrm{M} \rightarrow \mathrm{M_f^{n+}} + \mathrm{v_m} + \mathrm{ne^-}$$

or (R1)

$$\mathrm{M_f^{n+}} + \mathrm{ne^-} \rightarrow \mathrm{M^{aq}}$$

and so on. Kinetically, you treat each of those as first order in the active defect concentration and describe its potential dependence with a Butler–Volmer–type expression.
Why do PDM Vacancies and holes look "unimolecular"? In the PDM, vacancies or interstitials of holes are always creating or annihilating one vacancy/interstitial or dissolving one lattice ion. The counter-species (metal atom activity in the bulk metal, or solvent species activity in solution) is effectively constant—so the rate law reduces to first order in the single defect species. Each step carries a well-defined n-electron transfer, making it straightforward to plug into the BV or Tafel form.
When does that assumption hold?

- Defect concentrations are low enough that interactions (pairing, clustering) can be ignored.
- The non-defect reagent (metal atom, oxide lattice site, solvent ligand) is "in excess" or at constant activity.
- No surface coverage effects—i.e., you're not blocking sites with adsorbates or intermediates.
- You're in the activation-controlled regime (charge-transfer limited), with negligible mass-transport or ohmic limitations at that interface.
- The film is uniform—so there's a single, well-defined interfacial population of defects.

Macdonald's Point Defect Model treats the passive electrode as hosting both anodic and cathodic defect–reaction pairs—one set at the metal–film (m/f) interface and another at the film–solution (f/s) interface—even though they occur on the same physical electrode surface.

Summary of Assumptions and their Limitations

PDM applies when the passive film can be treated as a single, compact, defect-mediated barrier layer. Use PDM-I when the passive film behaves as a *single defective oxide layer* whose growth and breakdown are governed solely by cation and anion vacancies. This corresponds to the original Macdonald formulation (1981–1992). Typical systems: simple passive films on Ni, Fe, and Cr in mild environments, where the outer layer is negligible. In contrast, PDM-II applies when the film is bilayered and requires explicit treatment of cation interstitials, barrier-layer dissolution, and lattice-conservative vs. non-conservative reactions. The oxide consists of a barrier layer + outer precipitated layer. Cation interstitials must be included as mobile defects. Barrier-layer dissolution must be modeled. Reactions must be classified as lattice-conservative vs. non-conservative. The barrier layer alone controls the passive current (the outer layer is not rate-controlling). Typical systems: stainless steels, Ni-based alloys, and metals in which an outer hydrated/precipitated layer forms but does not dominate the electrical resistance.

PDM Canonical Equations

Optimizing the admittance of a bilayer PDM (Poisson–Nernst–Planck/Macdonald model) is typically treated as a black-box, discrete, constrained, and non-convex optimization problem. The optimization problem does NOT become discontinuous just because the *measured* impedance data are discrete. The objective function you minimize is still continuous with respect to the model parameters, even though the data points are sampled at discrete frequencies. This is a subtle but important point in inverse modeling and impedance spectroscopy. That combination makes it a moderately to highly difficult problem to solve. In summary, the bilayer PDM Macdonald impedance optimization problem is a continuous, constrained, nonlinear, nonconvex, derivative-free (black-box), and potentially stiff inverse optimization problem.
The difficulties in the optimization process come from.

A. The objective is to compute through a numerical model

The Macdonald PDM admittance is usually obtained by: Solving coupled differential equations, using numerical integration, or possibly fitting to impedance spectroscopy data
This means the objective function is not an explicit analytic formula you can differentiate.

B. Derivatives are not available

You cannot compute gradients analytically. So, the optimizer must treat the model as a **black-box**:
→ You give it parameters, it gives you admittance error, but no derivative information.

C. The function may be noisy or multi-modal

Small changes in parameters can produce sharp changes in admittance, multiple local minima, non-smooth behavior, and discrete, constrained variables. Then, gradient-based methods are not usable. Because the typical constraints in PDM models are Physical bounds (e.g., diffusion coefficients > 0), layer-thickness limits, and conditions such as charge neutrality holding, among

others, the search space is non-convex and irregular. The difficulty level of the PDM optimization ranges from Moderate to High, not only because the number of variables and parameters to be found is large, but also because the problem, by nature, is a Black Box type with constraints, discrete variables, and a convex space. The main problem is not dimensionality but structure. Reducing the dimensionality of the variables greatly helps find a global minimum rather than a local one during the optimization process.

You are minimizing something like:

$$F(\theta) = \sum_k | Z_{\text{model}}(\omega_k; \theta) - Z_{\text{measured}}(\omega_k) |^2 \quad (5)$$

Where:
$Z_{\text{model}}(\omega; \theta)$is continuous in the parameters θ
$Z_{\text{measured}}(\omega_i)$is discrete (sampled at finite frequencies)
The sum is over discrete frequencies ω_i
If you are optimizing impedance, or something like the below, you are optimizing Admittance.

$$J(\theta) = \sum_k | Y_{\text{model}}(\omega_k; \theta) - Y_{\text{data}}(\omega_k) |^2 \quad (6)$$

where θ is your n-dimensional parameter vector (where n is a number corresponding to the number of variables you want to find from the Optimization exercise as rate constants, BV factors, etc.), and $Y_{\text{model}}$is the double-layer PDM admittance. Y_{data} is the measured Admittance. Depending on the measured impedance signature, you may be able to optimize in the Admittance plane rather than the impedance plane when impedance varies greatly with a small signal variation.

OPTIMIZATION

The bilayer PDM Macdonald impedance optimization problem is a continuous, constrained, nonlinear, nonconvex, derivative-free (black-box) inverse optimization problem.
Now, let's ask which models will suit a large number of variables/parameters for this specific type of optimization. Let's think we need to find 20 parameters/variables from the optimization. Then, which models can handle 20 variables/parameters?

- *Python (CMA-ES → LM)*: scales well; you can run large populations in parallel, then refine with gradient methods; compute Jacobian analytically or with AD (JAX) to resolve correlations.
- *IGOR GA*: explores space but lacks robust AD and advanced UQ; handoff to local solver is manual and less reproducible.
- *MATLAB*: similar to Python for local refinement; global search OK but less flexible for modern surrogate/Bayesian workflows.

IGOR offers the best for curve fitting and visualization [20].

Giving the mathematical difficulty to optimize the PDM, we need to ask ourselves, what is there that can help to simplify the optimization exercise, not because having several variable (as 20 or

30) are not considered too many, but because the characteristics of the problem to solve represent a difficult optimization problem, It is good to remember that in those cases, to reduce dimensionality (number of variables) is a good option—fewer parameters → fewer failure modes, fewer local minima, easier global search.
Then, if your goal is to reduce the *effective* dimensionality of the problem while keeping the physics intact, you would like to group your parameters into three categories:

- Fix (or almost fix)
- Bound tightly
- Free optimize (core set)

1. Good candidates to FIX (or keep extremely tight)

These are usually weakly identifiable from impedance alone or strongly correlated with others. These parameters usually have weak sensitivity in impedance or are highly correlated with others**,**

- α_1–α_7*:* voltage/pH/temperature dependencies of rate constants (often exponential). Unless you have multi-pH / multi-T / multi-potential datasets, these are poorly identifiable. → Fix from literature or prior work or keep 1–2 representative ones and fix the rest.
- β_1–β_7*:* Same logic as α's—often exponents/slopes in T, pH, or potential dependencies. → Fix or tie to α's (e.g., same value for groups of reactions).
- *ε (epsilon, permittivity of inner layer):* Impedance is usually not very sensitive to ε in the frequency range of interest. → Fix to a reasonable oxide value (e.g., 10–30).
- *Outer film porosity:* Often weakly identifiable and strongly correlated with outer resistance and thickness. → Fix or bind very tightly around a plausible value.
- *pH, voltage, and temperature dependencies of the rate constant*
- *Permittivity of the inner layer:* Fix to a literature value (e.g., 10–30 for oxides).
- *Outer film porosity*

2. Parameters to KEEP but TIGHTLY BOUND

These matter, but they can easily blow up the solver or create crazy landscapes.

- K_1^0, K_2^0, K_3^0, K_4^0, K_5^0, K_6^0, K_7^0 *(rate constants):* Typical safe bounds (order-of-magnitude):
$$10^{-12} \leq K_i \leq 10^{2}\ \mathrm{s}^{-1}$$
- *Diffusivity of oxygen vacancy, diffusivities of metal vacancy, and diffusivities of interstitials.* Typical bounds:
$$10^{-18} \leq D \leq 10^{-10}\ \mathrm{m}^2/\mathrm{s}$$
- *Outer film resistance:* Bound to avoid near-zero or absurdly large values:
$$1\ \Omega \leq R_{\mathrm{outer}} \leq 10^{6}\ \Omega$$
- *Potential film–solution, potential metal–film:* These control exponentials are too large → overflow. Reasonable bounds:
$$-0.5\ \mathrm{V} \leq \Delta\phi \leq 0.5\ \mathrm{V}$$
- *α (alpha, a transfer coefficient/symmetry factor):* You can either fix it (e.g., 0.5) or optimize within that range.
$$0.2 \leq \alpha \leq 0.8$$
- *Bounded/estimated:* αvalues, activation energies (from literature or temp series), and diffusivity orders of magnitude.

3. Core set to OPTIMIZE FREELY

Please do not optimize all 20+ at once. A good target is 6–10 free parameters. Given your list, a strong, physically meaningful core set would be:

- *Film thickness (inner and outer):* Inner and outer film thicknesses strongly shape the impedance spectrum. These should almost always be free (with physical bounds).
- *2–4 key rate constants from K_1^0–K_7^0:* Choose those corresponding to the dominant reactions (e.g., main defect generation/annihilation steps). Fix the less important ones or tie them to the main ones (e.g., same order of magnitude).
- *1–2 key diffusivities:* Often, oxygen-vacancy diffusivity and the diffusivity of a representative metal vacancy/interstitial are sufficient to capture transport behavior. Fix the others to literature or to ratios.
- *Outer film resistance:* Strongly affects the high-frequency semicircle and overall impedance level. Good to keep free (with bounds).
- *Possibly α or one interface potential:* If your data are very sensitive to charge transfer, you can keep **α** or one of the interface potentials free, but not both.
- *Potential drop at interfaces.* This affects the shape of the semicircle and the high-frequency response.

These parameters strongly influence the impedance spectrum and are usually identifiable.

RESULTS' ANALYSIS

Now, the question that follows is: once you have reduced the number of variables and feel that your optimization results make physical sense, is there one additional check we would like to mention?

If you are still handling many variables, or you have "noise" impedance data (especially at low frequencies), please check your optimization results further. If you have measured data at different pH values and/or at different applied voltages, it is useful to perform an optimization for each pH and/or voltage. Zoom in on the parameters that are independent of pH and/or applied voltage and check whether the optimization results for those independent variables yield values that are indeed independent of pH or applied voltage; i.e., the same value across all variations in pH and applied Voltage. Please check the trends in parameter optimizations that depend on pH and Voltage, and analyze whether they vary smoothly with pH and applied voltage, as expected. You may suspect that something in your optimization went wrong (for example, you got stuck in a local minimum) if a parameter, such as K_i, calculated from the optimization, does not increase smoothly with applied voltage (Equation 2, Table 1). Or variables as in Equation 1, the $\phi_{m/f}$ increases and decreases when you increase the applied potential (as an author unknown phrase says: Natura non facit saltum ("Nature does not make a jump")). You must feel comfortable with your results, know you haven't gotten stuck in a local minimum, and feel that your optimization is a success.

SUMMARY

PDM II is powerful but rests on several restrictive assumptions — thin, uniform, defective barrier layers. If any of these assumptions fail, the model must be modified by relaxing those assumptions,

or the results will be non-physical. The PDM requires the Optimization of a “Black Box”-type model, which entails taking precautions during optimization, and we advise reducing the number of variables to achieve successful optimization.

AUTHOR CONTRIBUTION

My contribution to this paper is to be part of the team working with Professor Macdonald on the PDM, and to summarize and organize the hypotheses and assumptions so that users can understand the area of application and avoid incorrect applications. I hope new users will continue to develop the model by relaxing assumptions and expanding the PDM's applications to include complex scenarios.

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