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Article

Proposition of a New Power Dissipation Model and Its Analytic Formulation for Electric-Field-Driven Water Dissociation in the Cationic/Anionic Bipolar Polymer Membranes Junctions

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Abstract

Bipolar Polymer Membranes (BPMs) enable the creation of large, stable pH gradients by driving water dissociation (WD) at the cation/anion junction under reverse bias, a process central to electrodialysis, CO₂ capture, and emerging acid–alkaline water electrolysis. Yet, despite decades of study, the mechanism by which intense interfacial electric fields accelerate WD remains debated and is often modeled with ad hoc assumptions. Here, we outline key limitations of existing models of field-enhanced WD in BPMs and we present a power-dissipation model and its formalism that address them. In this new framework, we emphasize that minority ions from water autoprotolysis act as carriers that continuously dissipate field-supplied power in the hydrated nanometric junction. This dissipative input raises the local probability of heterolytic O–H bond cleavage and leads analytically to the dissociation rate's quadratic dependence on the field. Without adjustable parameters, the model reproduces the required orders of magnitude for the enhancement ratio $k_d(E)/k_d(0)$, where $k_d(E)$ is the field-enhanced water-dissociation rate constant and $k_d(0)$ its zero-field value, across typical BPM fields and yields a quadratic current–voltage junction law. A proof-of-principle measurement on a commercial Fumasep® FBM confirms the quadratic current–voltage trend, supporting a power dissipation field-driven WD and providing a concise, falsifiable baseline for future studies.

Keywords: bipolar membranes; new formalism; water dissociation; electric field; autoprotolysis dissipated power; nano metric junction; water dissociation rate constant; current-voltage curves

1. Introduction

Bipolar membranes (BPMs) are a unique class of polymer ion-exchange membranes (IEMs) [1], characterized by a laminated structure consisting of a cation-exchange membrane (CEM) on an anion-exchange membrane (AEM) [2]. This configuration enables BPMs to promote water dissociation (WD) at the junction of the two layers under reverse polarization [3], thereby sustaining large pH gradients across the membrane by generating hydronium (H₃O⁺) and hydroxide ions (OH[−]) [4]. Originally developed for electrodialysis (ED) to produce acids and bases [5,6], BPMs Have Recently garnered substantial interest in advanced electrochemical applications [7], including brine valorization [8], CO₂ capture [9], fuel cells [10], and particularly in water electrolysis for hydrogen production [11,12].

Until now, the detailed mechanism of WD in BPMs—especially under intense interfacial electric fields—remained poorly understood. Under reverse bias, counterions migrate away from the

CEM/AEM interface, creating a narrow space-charge region where an electric field exceeding $10^8 \text{ V}\cdot\text{m}^{-1}$ is established [13]. This field accelerates the dissociation of water molecules at the interface into H_3O^+ and OH^- ions [8], which then migrate through the CEM and AEM, respectively. Using mass conservation, the flux of H_3O^+ and OH^- out from the junction, cannot exceed the rate of their generation. Thus, the maximum WD current density in a BPM junction, was given by [5,14] :

$$J = F \times c_{\text{H}_2\text{O},j} \times k_d \times \delta, \quad (1)$$

where the parameters J , F , k_d , $c_{\text{H}_2\text{O},j}$, and δ are, respectively, the maximum WD current density in ($\text{A}\cdot\text{m}^{-2}$), the Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$), the water dissociation rate constant in (s^{-1}), the water concentration at the interface in ($\text{mol}\cdot\text{m}^{-3}$) and the thickness of the BPM junction in (m). Eq. (1) explicitly assumes a reaction-limited WD with negligible recombination inside the junction, which is plausible for abrupt BPM junctions, where the transition region is a few nanometers [1], thus the nascent H_3O^+ and OH^- are rapidly extracted into the CEM and AEM. In homogeneous BPMs with a uniform functional group distribution [15], the junction thickness does not exceed 1 nm [1,16]. In the absence of external field ($E=0$), the calculated water dissociation rate constant at 25°C is $k_d(0)=2.5\times 10^{-5} \text{ s}^{-1}$ [17]. Assuming this nanometric junction is fully hydrated with pure water ($c_{\text{H}_2\text{O},j}=55.5 \text{ mol}\cdot\text{L}^{-1}$) [5], the predicted current density is only $\sim 1.4 \times 10^{-4} \text{ A}\cdot\text{m}^{-2}$ [5]. However, experimentally observed BPM current densities can exceed $1000 \text{ A}\cdot\text{m}^{-2}$ [5], implying an enhancement of k_d by at least 7×10^6 times the thermal value $k_d(0)$ at 25°C . This striking discrepancy is at the heart of a longstanding theoretical challenge.

Existing models—such as the Second Wien Effect (SWE) and catalytic protonation–deprotonation mechanisms—do not consistently explain this increase. Consequently, new theoretical frameworks are needed to predict and optimize BPM performance. In this context, we propose a power dissipation-based model in which WD is driven by field-supplied power to autoprotolysis ions in water. The model establishes a quadratic dependence of k_d on the field E , which yields to a quadratic current–voltage junction law.

This manuscript is organized as follows. Section 2 reviews the state-of-the-art theoretical models of water dissociation in bipolar membranes. Section 3 details the theoretical development of our power dissipation model, its mathematical relations and associated theoretical results, while Section 4 presents the experimental methods. Section 5 provides results and discussion, and Section 6 the conclusion.

2. State-of-the-Art Models for Water Dissociation (WD) Enhancement in BPMs Junctions

Understanding the sharp increase in the WD rate in BPMs has been a long-standing challenge. Several theoretical models have been proposed, two of which dominate current discussions: the SWE and the catalytic protonation–deprotonation mechanism involving membrane functional groups. Despite their respective limitations, these models are widely used in BPM modeling [3,18–20]. We briefly summarize their scope and limitations, together with alternative approaches.

2.1. Second Wien Effect (SWE)

The Second Wien Effect (SWE) was the first mechanism proposed to account for the increase in WD under an electric field [21,22]. Based on Onsager's theory [23], it describes how a strong electric field enhances the dissociation of ion pairs in weak electrolytes. For high electric fields ($E > 10^8 \text{ V}\cdot\text{m}^{-1}$), the ratio $k_d(E)/k_d(0)$ can be determined by [23].

$$\frac{k_d(E)}{k_d(0)} = \sqrt{\frac{2}{\pi}} \times (8b)^{-\frac{3}{4}} \times e^{\sqrt{8b}} \quad (2)$$

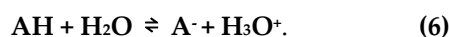
where $b \approx 0.096 \times \frac{E}{\epsilon_r T^2}$, E is the field strength ($\text{V}\cdot\text{m}^{-1}$), ϵ_r is the relative permittivity, and T is the temperature in (K). While pure water is often treated as a weak electrolyte due to its low ionic concentration ($\sim 10^{-7} \text{ mol}\cdot\text{L}^{-1}$), applying SWE to water has serious limitations [24–26]. First, Onsager's

theory assumes pre-existing ion pairs, not neutral water molecules [27,28]. Second, water's high dielectric constant (~ 80 at 25°C) makes the formation of stable ion pairs unlikely [22,23]. Moreover, the SWE-predicted dissociation rates remain far too low to explain the experimental results obtained using BPM. According to Strathmann [5], it can only match observed values if ϵ_r is reduced below 10. Krol [14] discussed the role of relative permittivity in SWE, highlighting the difficulty of determining ϵ_r and its complexity when considering it as field-dependent, especially under high fields where ϵ_r can drop from 78 to 16 for $E = 2 \times 10^9 \text{ V}\cdot\text{m}^{-1}$ [14]. Empirical formulas support this trend [29,30].

However, this points out a conceptual issue: ϵ_r may decrease because of an increase in ion concentration, as supported by the Hückel's theory [31], which could mean the field-induced dissociation itself causes the drop in ϵ_r , reversing the assumed causality. Furthermore, the SWE's exponential sensitivity to E results in numerical instability when varying ϵ_r with E : applying Eq. (1) and (2) gives $1210 \text{ A}\cdot\text{m}^{-2}$ at $10^9 \text{ V}\cdot\text{m}^{-1}$, but an unrealistic $10^8 \text{ A}\cdot\text{m}^{-2}$ at $2 \times 10^9 \text{ V}\cdot\text{m}^{-1}$. Also, water's ϵ_r may drastically decrease in confined environments [32] even without an electric field—yet inserting such values into SWE remains problematic.

2.2. Catalytic Protonation–Deprotonation Mechanism

The second mechanism, introduced by Simons [33,34], proposes that WD is catalyzed by membrane functional groups—namely, BH^+ in the AEM and A^- in the CEM—through the following reactions:



However, this mechanism yields dissociation kinetics that are too slow [28]. This low kinetics prediction led to the development of the Chemical Reaction Model (CRM) [35–37], where the electric field is assumed to accelerate protonation reactions between water and fixed charges. Relying on statistical arguments about the field-induced alignment of water molecules and catalytic sites [28,38], the water dissociation enhancement based on the Chemical Reaction Model through its rate constant given as:

$$k_d^{cr}(E) = k_d^{cr}(0) \times e^{\frac{\alpha FE}{RT}} \quad (7)$$

where $k_d^{cr}(E)$ is the field-enhanced WD rate constant due to protonation-deprotonation reactions of water molecules with fixed charges, α is a fitting parameter homogenous to a length, F is the Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$), E is the applied field ($\text{V}\cdot\text{m}^{-1}$), R the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and $k_d^{cr}(0)$ is the rate constant when no field is applied given by an Arrhenius expression [28,38]:

$$k_d^{cr}(0) = A \times e^{-\frac{E_A}{RT}} \quad (8)$$

where A is the pre-exponential factor and E_A is the activation energy, R is the gas constant and T is the temperature.

According to CRM model, the maximum WD current density J in the BPM junction, depends on the concentration of catalytic fixed groups c_{cag} , and is given by:

$$J = F \times c_{cag} \times k_d^{cr}(E) \times \delta = F \times c_{cag} \times A \times e^{-\frac{E_A}{RT}} \times e^{\frac{\alpha FE}{RT}} \times \delta \quad (9)$$

where all the parameters are defined in the above corresponding relations. This CRM model formulation relies on multiple poorly defined parameters that are difficult to determine independently: The concentration of the catalytic groups, the pre-exponential factor A , and the constant α . Thus, making difficult an accurately modeling ion transport in BPMs.

Recent literature [18,38] often identifies the parameter α with the Bjerrum length l_b , over which a dipole is dissociated into its respective ions in a medium, using an SWE approximation at

low fields. However, the SWE exponential formula with l_b overestimate the increase in k_d leading to unphysical divergences [18].

2.3. Alternative Models

Martinez and Farrell [13] used quantum chemical simulations to evaluate k_d under strong electric fields. Their results resemble SWE predictions and rely also on a reduction in ϵ_r . Saitta et al. [39] reported water dissociation thresholds of $3.5 \times 10^9 \text{ V}\cdot\text{m}^{-1}$ and up to 15–20% dissociation at $10^{10} \text{ V}\cdot\text{m}^{-1}$ using molecular dynamics, but such field strengths far exceed those in BPMs. Hurwitz and Dibiani [25,40] attempted to propose an electrochemical model, where the WD is seen as a redox-like process involving H^+ and OH^- ions by exploiting its heterolytic nature [25,40], thereby justifying Tafel or Butler–Volmer treatments [28]. However, such an analogy lacks a solid basis in BPMs, where no electron Transfer occurs, and WD is better described as a chemical reaction, not governed by an electrochemical reaction involving electron transfer at electronic/electrolyte interface, in the strict sense. Additional proposals invoke semiconductor p– n junction analogies [41,42] or ion solvation kinetics [43], but still fail to recover the orders of magnitude required for $k_d(E)/k_d(0)$ quantitatively. Recent transport models even omit a specific WD mechanism and assume “sufficiently fast” dissociation [44].

Overall, despite clear evidence that strong fields enhance WD, existing models do not consistently explain this increase. Motivated by the quantitative mismatch summarized above, we propose a power dissipation-based framework in which WD is driven by dissipated field-supplied power to autoprotolysis ions. The resulting picture establishes a quadratic dependence of k_d on the field E and provides a compact route to device-level predictions.

3. Theoretical

3.1. Power Dissipation Model for Electric-Field-Driven WD

3.1.1. Framework and Working Hypothesis

In aqueous electrolytes, field-driven transport of ions follows the well-known drift regime [45]. Under the influence of an electric field E , an ion of charge q experiences an electric force $\mathbf{F}_e$ proportional to the field E :

$$\mathbf{F}_e = q\mathbf{E} \quad (10)$$

which is opposed by viscous friction $\mathbf{F}_f$:

$$\mathbf{F}_f = \mathbf{f} \times \mathbf{v} \quad (11)$$

where f is the friction coefficient and v is the ion velocity. Within an extremely short time, these forces balance:

$$\mathbf{F}_e + \mathbf{F}_f = \mathbf{0}, \quad (12)$$

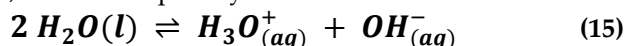
so the ion moves at a constant drift velocity v_d proportional to E :

$$\mathbf{v}_d = \mu\mathbf{E}, \quad (13)$$

where μ is the ionic mobility in ($\text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$). Although no kinetic energy accumulates in this steady state, the field continuously injects energy that is entirely dissipated by viscous friction at a rate corresponding to field-supplied power per ion P in ($\text{J}\cdot\text{s}^{-1}$), given by

$$P = \mathbf{F}_e \times \mathbf{v}_d = q\mu E^2. \quad (14)$$

Liquid water always contains minority ions H_3O^+ and OH^- at very low concentration $10^{-7} \text{ mol}\cdot\text{L}^{-1}$ at 25 °C, due to autoprotolysis:



with an equilibrium constant $K_w = 10^{-14}$ at 25 °C. When an electric field is applied to liquid water, these minority ions are the only species that undergo field-directed motion and dissipate power, whereas neutral H_2O molecules may merely reorient their dipoles. For BPM-relevant strong fields (E

$\geq 10^8 \text{ V}\cdot\text{m}^{-1}$), the per-ion dissipated power of H_3O^+ and OH^- is non-negligible and potentially chemically relevant at the molecular scale. Order-of-magnitude estimates support this plausibility:

At 25 °C, $\mu_{\text{H}_3\text{O}^+} = 3.62 \times 10^{-7} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ and $\mu_{\text{OH}^-} = 2.05 \times 10^{-7} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ [46].

For a typical BPM-field $E = 10^8 \text{ V}\cdot\text{m}^{-1}$, with $q = 1.6 \times 10^{-19} \text{ C}$ for both ions H_3O^+ and OH^- , the drift powers, using Eq. (14) are:

$$P_{\text{H}_3\text{O}^+} \approx 5.79 \times 10^{-10} \text{ J}\cdot\text{s}^{-1} \text{ and } P_{\text{OH}^-} \approx 3.28 \times 10^{-10} \text{ J}\cdot\text{s}^{-1}.$$

The molar Gibbs free energy of dissociation ΔG_d (forward reaction in Eq. 15) is obtained from the equilibrium constant K_w as:

$$\Delta G_d = -RT \times \ln(K_w) \quad (16)$$

At 25 °C, $\Delta G_d = 79.9 \text{ kJ}\cdot\text{mol}^{-1}$, meaning that the theoretical energy required to dissociate one mol of water is 79,9 kJ [47]. The per-molecule dissociation threshold energy E_d (in J) required to dissociate one water molecule is obtained from the molar Gibbs free energy of dissociation ΔG_d by:

$$E_d = \frac{\Delta G_d}{N_A} \quad (17)$$

where $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ is Avogadro's number. At 25 °C, $E_d \approx 1.33 \times 10^{-19} \text{ J}$.

Thus, under $E = 10^8 \text{ V}\cdot\text{m}^{-1}$ each single H_3O^+ and OH^- ion can, in theory, dissipate enough energy each second to induce:

$$\frac{P_{\text{H}_3\text{O}^+}}{E_d} = 4.35 \times 10^9 \text{ and } \frac{P_{\text{OH}^-}}{E_d} = 2.46 \times 10^9 \text{ potential dissociation events per second, respectively.}$$

In the specific context of BPMs under reverse bias, once the junction is depleted of mobile counter-ions, the residual current is carried by the minority autoprotolysis ions H_3O^+ and OH^- [5,14]. Because enhanced water dissociation is observed after this minority-carrier regime is established, it is natural to consider WD as a consequence of that pre-existing drift—the real process through which the field supplies power to the system.

Scaling up to a fully hydrated BPM with a surface area $A = 1 \text{ cm}^2$ and a junction $\delta = 1 \text{ nm}$, the volume of the junction is $V_j = 10^{-13} \text{ m}^3$. With concentrations of liquid water in the junction and the minority autoprotolysis ions of $c_{\text{H}_2\text{O}} = 55.5 \text{ mol}\cdot\text{L}^{-1}$ and $c_{\text{ions}} = 10^{-7} \text{ mol}\cdot\text{L}^{-1}$, respectively. The total power dissipated by all the ions H_3O^+ and OH^- present in the junction's volume V_j can be expressed as:

$$P_{\text{total}} = n_i q (\mu_{\text{H}_3\text{O}^+} + \mu_{\text{OH}^-}) E^2 \times V_j, \quad (18)$$

where n_i in (m^{-3}) is the volumetric density of ions H_3O^+ and OH^- , given by :

$$n_i = c_i \times N_A, \quad (19)$$

where c_i is the concentrations of ions. The n_i are equal (i.e. $n_{\text{H}_3\text{O}^+} = n_{\text{OH}^-} = 6.022 \times 10^{19} \text{ m}^{-3}$), since they have the same concentration. The volume V_j contains 3.3×10^{15} water molecules and 6.022×10^6 H_3O^+ and OH^- ions each. The total dissipated power for $E = 10^8 \text{ V}\cdot\text{m}^{-1}$ is $P_{\text{total}} \approx 5.46 \times 10^{-3} \text{ J}\cdot\text{s}^{-1}$. The corresponding number of potential dissociations events per second is $\frac{P_{\text{total}}}{E_d} = 4.1 \times 10^{16}$, meaning that the entire water content of the junction could, in theory, dissociate in less than one second. Furthermore, given the thermal conductivity of water ($\kappa \approx 6 \times 10^{-3} \text{ J}\cdot\text{s}^{-1}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$) and the nanometric thickness of the junction ($\delta = 1 \text{ nm}$), a simple steady-state heat-flux estimate using the expression [48]:

$$P_{\text{total}} = \frac{\kappa \times A \times \Delta T}{\delta/2}, \quad (20)$$

gives a temperature rise $\Delta T \approx 5 \times 10^{-8} \text{ K}$, showing that Joule heating is negligible at the junction scale, and the system can be treated as effectively isothermal under the conditions considered. In this isothermal limit, the power dissipated by the drift of autoprotolysis ions corresponds, in the sense of non-equilibrium thermodynamics, to the internal entropy production $d_i S$ according to [49]:

$$P_{\text{diss}} = T (d_i S / dt). \quad (21)$$

Thus, the dissipated power in the nanometric junction is interpreted as local entropy production, which can drive microscopic molecular rearrangements and provides a physically consistent basis for relating dissipation to field-assisted water dissociation.

Building on the estimates above, our working hypothesis is that the dissipated power of the drifting autoprotolysis ions (H_3O^+ , OH^-) under strong electric fields is more than sufficient to drive new water-dissociation events per second. Thus, the sudden increase of the WD rate observed in BPMs at high electric field is an indirect ion-mediated consequence of power dissipation rather than a direct field action on neutral water molecules. Therefore, in the BPM junction the intense electric field raises the effective probability of dissociation, by amplifying the frequency of activation attempts powered by drift dissipation above the dissociation energy E_d . Accordingly, we postulate that the WD rate constant $k_d(E)$ is proportional to the ratio of the total dissipated power P_{total} over E_d : $k_d(E) \propto \frac{P_{total}}{E_d}$.

3.1.1. Analytical Formulation of $k_d(E)$

We interpret the WD rate constant k_d as a frequency of energy delivery relative to the activation barrier. Let the power density w ($\text{J}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$), deposited by all field-driven ions H_3O^+ and OH^- be

$$w = n_{\text{H}_3\text{O}^+} \times P_{\text{H}_3\text{O}^+} + n_{\text{OH}^-} \times P_{\text{OH}^-},$$

where $n_{\text{H}_3\text{O}^+}$ and n_{OH^-} are respectively the volumetric density of H_3O^+ and OH^- , $P_{\text{H}_3\text{O}^+}$ and P_{OH^-} are, respectively, the dissipated power by H_3O^+ and OH^- . Since the concentrations of H_3O^+ and OH^- in pure water are equal (i.e. $c_{\text{ions}} = c_{\text{H}_3\text{O}^+} = c_{\text{OH}^-} = 10^{-7} \text{ mol}\cdot\text{L}^{-1}$), their volumetric density is also equal ($n_{\text{ions}} = n_{\text{H}_3\text{O}^+} = n_{\text{OH}^-}$). Thus,

$$w = n_{\text{ions}} \times (P_{\text{H}_3\text{O}^+} + P_{\text{OH}^-}). \quad (23)$$

Dividing by the threshold dissociation energy per event E_d gives a volumetric event rate R_{vol} ($\text{s}^{-1}\cdot\text{m}^{-3}$):

$$R_{vol} = \frac{w}{E_d}. \quad (24)$$

The per-molecule (pseudo-first order) rate constant $k_d(E)$ in (s^{-1}) is then obtained by normalizing by the number density of water molecules $n_{\text{H}_2\text{O},l}$:

$$k_d(E) = \frac{R_{vol}}{n_{\text{H}_2\text{O},l}} = \left(\frac{n_{\text{ions}}}{n_{\text{H}_2\text{O},l}} \right) \times \frac{(P_{\text{H}_3\text{O}^+} + P_{\text{OH}^-})}{E_d}. \quad (25)$$

Since

$$\left(\frac{n_{\text{ions}}}{n_{\text{H}_2\text{O},l}} \right) = \left(\frac{c_{\text{ions}} \times N_A}{c_{\text{H}_2\text{O},l} \times N_A} \right) = \left(\frac{c_{\text{ions}}}{c_{\text{H}_2\text{O},l}} \right) \quad (26)$$

and replacing $P_{\text{H}_3\text{O}^+}$ and P_{OH^-} by their respective formulas, i.e.

$$P_{\text{H}_3\text{O}^+} = q\mu_{\text{H}_3\text{O}^+}E^2, \quad (27)$$

and

$$P_{\text{OH}^-} = q\mu_{\text{OH}^-}E^2 \quad (28)$$

we obtain the final expression of $k_d(E)$, as :

$$k_d(E) = \left(\frac{c_{\text{ions}}}{c_{\text{H}_2\text{O},l}} \right) \times \frac{q \times (\mu_{\text{H}_3\text{O}^+} + \mu_{\text{OH}^-})}{E_d} \times E^2, \quad (29)$$

where,

$k_d(E)$: Dissociation rate constant of water molecules as a function of the field E in (s^{-1}),

c_{ions} : Concentration of H_3O^+ and OH^- ions in water ($10^{-7} \text{ mol}\cdot\text{L}^{-1}$ at 25°C),

$c_{\text{H}_2\text{O},l}$: Concentration of free liquid water ($55.5 \text{ mol}\cdot\text{L}^{-1}$ at 25°C),

q : Absolute electric charge of H_3O^+ and OH^- ions ($q = 1.6 \times 10^{-19} \text{ C}$),

$\mu_{\text{H}_3\text{O}^+}$: Ionic mobility of the hydronium ion H_3O^+ ($3.62 \times 10^{-7} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ at 25°C),

μ_{OH^-} : Ionic mobility of the hydroxide ion OH^- ($2.05 \times 10^{-7} \text{ m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ at 25°C),

E : The electric field in the BPM junction in ($\text{V}\cdot\text{m}^{-1}$),

E_d : Threshold dissociation energy per water molecule in (J), ($E_d = 1.33 \times 10^{-19} \text{ J}$ at 25°C).

This formulation reveals k_d 's simple quadratic dependence on electric field E , representing a significant departure from previously proposed exponential models. It provides a clear analytical link between physicochemical parameters—elementary charge, ion mobility, dissociation energy,

and molar concentrations—and the dissociation rate, without relying on empirical constants or catalytic assumptions. This analytical form enables a direct estimation of the dissociation rate k_d as a function of the electric field E applied at the BPM junction.

We note that mobilities of H_3O^+ and OH^- in water are obtained from [50]:

$$\mu = \Lambda_0 / F, \quad (30)$$

where Λ_0 is the limiting molar conductivity at infinite dilution in ($\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$) and F is the Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$). It was shown that Λ_0 is independent of the field strength [51], so are the mobilities. In addition, studies reported a negligible influence of high electric fields on the viscosity η of solvents [52,53]; as per Stokes–Einstein relation $\mu \propto 1/\eta$ [46], the effect is also negligible on μ .

Furthermore, Eq. (29) carries an implicit temperature dependence (T) via three parameters: μ , which increases with T via η [54], and c_{ions} and E_d , which also increase with T via the Nernst relation (Eq. 16) [55]. Overall, the model relies solely on measurable, field-independent quantities at constant temperature. By substituting standard values at 25°C into Eq. (29), we obtain the following simplified expression for the water dissociation rate:

$$k_d(E) = 1.23 \times 10^{-15} \cdot E^2. \quad (31)$$

This equation will be used for comparison benchmarks with SWE at 25°C in section 3.2.1.

3.1.2. Junction J-V Relation Derived from $k_d(E)$

Under reverse bias, the current in a BPM primarily results from the migration of ions generated by water dissociation at the junction, which is captured by Eq. (1). Let U_j denote the junction voltage drop across the active region of thickness δ . Assuming a quasi-uniform field in the junction:

$$E = \frac{U_j}{\delta}. \quad (32)$$

By replacing E of Eq. (29) with its Eq. (32) expression and inserting Eq. (29) for $k_d(E)$ into Eq. (1), we obtain

$$J = \frac{F \times f \times q \times c_{\text{ions}} \times (\mu_{\text{H}_3\text{O}^+} + \mu_{\text{OH}^-})}{\delta \times E_d} \times U_j^2, \quad (33)$$

where,

$$f = \frac{c_{\text{H}_2\text{O},j}}{c_{\text{H}_2\text{O},l}} \quad (34)$$

is the ratio of the effective water concentration in the junction $c_{\text{H}_2\text{O},j}$ to the concentration $c_{\text{H}_2\text{O},l}$ of free liquid water. The parameter f is a dimensionless factor representing the water volume fraction in the BPM junction [56–58], which varies from 0 (no water) to 1 (fully hydrated junction). Let

$$K = \frac{F \times f \times q \times c_{\text{ions}} \times (\mu_{\text{H}_3\text{O}^+} + \mu_{\text{OH}^-})}{\delta \times E_d}, \quad (35)$$

then Eq. (33) simplifies to :

$$J = K \times U_j^2, \quad (36)$$

where K is in ($\text{mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-2}$), if J and U_j are in ($\text{mA}\cdot\text{cm}^{-2}$) and volts (V), respectively.

Assuming a homogeneous BPM with a nanometric junction $\delta=1 \text{ nm}$, fully hydrated ($f = 1$), and standard physical constants at 25°C , Eq. (36) gives

$$J \approx 660 \times U_j^2 \quad (37)$$

We emphasize that Eq. (36) is a junction-level law; in experiments, what is controlled is the external cell voltage E_{cell} . The experimental determination of U_j from E_{cell} is described in the experimental section.

3.2. Theoretical Results

3.2.1. $k_d(E)$ Enhancement and Comparison with SWE

Figure 1 shows the resulting curve $k_d(E)$ at 25°C from Eq. (31), at a $0\text{--}100 \text{ s}^{-1}$ y-axis scale. Note that this scale compresses the low-field region: although Eq. (31) yields a strictly quadratic onset from

$E=0$, $k_d(E)$ remains $< 1 \text{ s}^{-1}$ up to $E \approx 2.8 \times 10^7 \text{ V}\cdot\text{m}^{-1}$, so the curve appears nearly flat at this scale (a zoom reveals the monotonic rise).

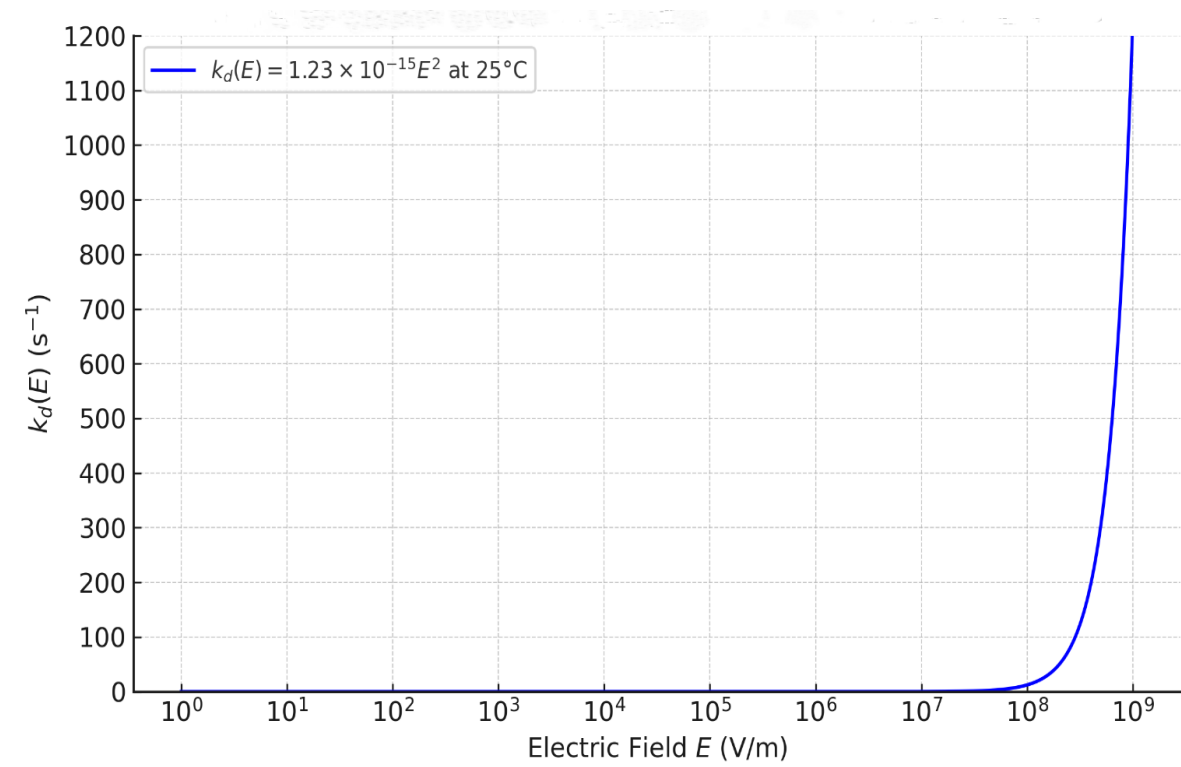


Figure 1. Curve of the evolution of $k_d(E)$ according to $k_d(E) = 1.23 \times 10^{-15} \cdot E^2$.

The profile closely resembles typical BPM J – V behavior where an initial low-conductivity region is followed by a sharp increase beyond a threshold. The crossover where $k_d(E) = k_d(0)$ occurs at $E^* \approx 1.43 \times 10^5 \text{ V}\cdot\text{m}^{-1}$. For a nanometric BPM junction ($\delta=1 \text{ nm}$), this field corresponds to a voltage of 0.14 mV . At fields below E^* , the overall dissociation is governed by the thermal constant $k_d(0)$. From E^* up to $\sim 2.8 \times 10^7 \text{ V}\cdot\text{m}^{-1}$ ($U_j \approx 28 \text{ mV}$ for $\delta=1 \text{ nm}$), $k_d(E)$ exceeds $k_d(0)$ but remains $< 1 \text{ s}^{-1}$; rates are still weak, indicating a non-activated regime where the field is insufficient to trigger significant dissociation. A sharp transition emerges above $10^8 \text{ V}\cdot\text{m}^{-1}$, corresponding to voltages $U_j \gtrsim 0.1 \text{ V}$ in the nanometric junction, marking the onset of an activated regime where the field supplies enough power to accelerate dissociation. To quantify this transition, values of $k_d(E)$ and the amplification ratio $k_d(E)/k_d(0)$ across the activated field range are reported in Table 1:

Table 1. Values of k_d as a function of E , according to equation (31) of our model.

Electric Field, E ($\text{V}\cdot\text{m}^{-1}$)	WD rate, $k_d(E)$ (s^{-1})	Ratio increase, $k_d(E)/k_d(0)$
1×10^8	12.3	4.92×10^5
5×10^8	307	1.23×10^7
8×10^8	787	3.15×10^7
1×10^9	1230	4.92×10^7
2×10^9	4920	1.97×10^8

These values show consistent increases in $k_d(E)/k_d(0)$, from $\sim 5 \times 10^5$ to $\sim 2 \times 10^8$, over the field range 10^8 – $2 \times 10^9 \text{ V}\cdot\text{m}^{-1}$, aligning with experimental requirements for sustaining current densities of 10 to several hundred mA/cm^2 . The quadratic form thus captures the field activation effect realistically:

the progression is rapid yet stable, avoiding numerical divergence and remaining compatible with electrochemical integration through Eq. (1).

To further contextualize our model, we compare it with the SWE model. Table 2 presents the $k_d(E)/k_d(0)$ ratios for each model at two representative fields (10^8 and 2×10^9 V·m⁻¹), corresponding to 0.1 V and 2 V across a 1 nm-thick BPM junction. For SWE model, both the constant permittivity ($\epsilon_r=78$) and field-dependent permittivity cases are considered ($\epsilon_r=78$ to 16 for $E=10^8$ to 2×10^9 V·m⁻¹). Two more scenarios with fixed ϵ_r (10 and 5) are considered to account for possible nanoconfinement effects.

Table 2. Comparison of $k_d(E)/k_d(0)$ values obtained with our model and SWE model.

Model	$k_d(E)/k_d(0)$ for $E = 10^8$ V·m ⁻¹	$k_d(E)/k_d(0)$ for $E = 2\times10^9$ V·m ⁻¹	Commentary
SWE (bulk $\epsilon_r=78$)	3.67	4.07×10^4	Too slow
SWE (ϵ_r variable)	3.67	8.05×10^{11}	Improved but unstable
SWE ($\epsilon_r=10$)	3.07×10^2	3.43×10^{15}	Divergence
SWE ($\epsilon_r=5$)	8.61×10^3	6.18×10^{22}	Extreme divergence
Our quadratic model	4.92×10^5	1.97×10^8	Gradual, realistic increase

The results highlight the fundamental disparities between the models. In SWE model, small field variations cause drastic shifts in k_d . At $E=10^8$ V·m⁻¹, SWE remains weak across both ϵ_r choices, whereas the quadratic law already yields $\sim 5\times10^5$. The SWE model with constant ϵ_r shows a limited increase ($< 5\times10^4$) at 2×10^9 V·m⁻¹, which is insufficient for supporting BPM current densities. Its variable- ϵ_r version improves predictions but introduces instability, with a sharp divergence at 2×10^9 V·m⁻¹. Nanoconfinement effects does not alter the qualitative conclusion that SWE either underestimates activation at 10^8 V·m⁻¹ or becomes unstable at higher fields. By contrast, our quadratic model exhibits a large yet controlled amplification, without runaway divergence over the same field window $E \in [10^8\text{--}2\times10^9]$ V·m⁻¹, providing a robust basis for BPM-relevant modeling.

3.2.2. Theoretical J-V Curve of a Nanometric BPM Junction Fully Hydrated

Figure 2 shows the resulting $J-U_j$ curve of a BPM nanometric junction ($\delta=1$ nm) fully hydrated ($f=1$), at 25 °C from Eq.(37).

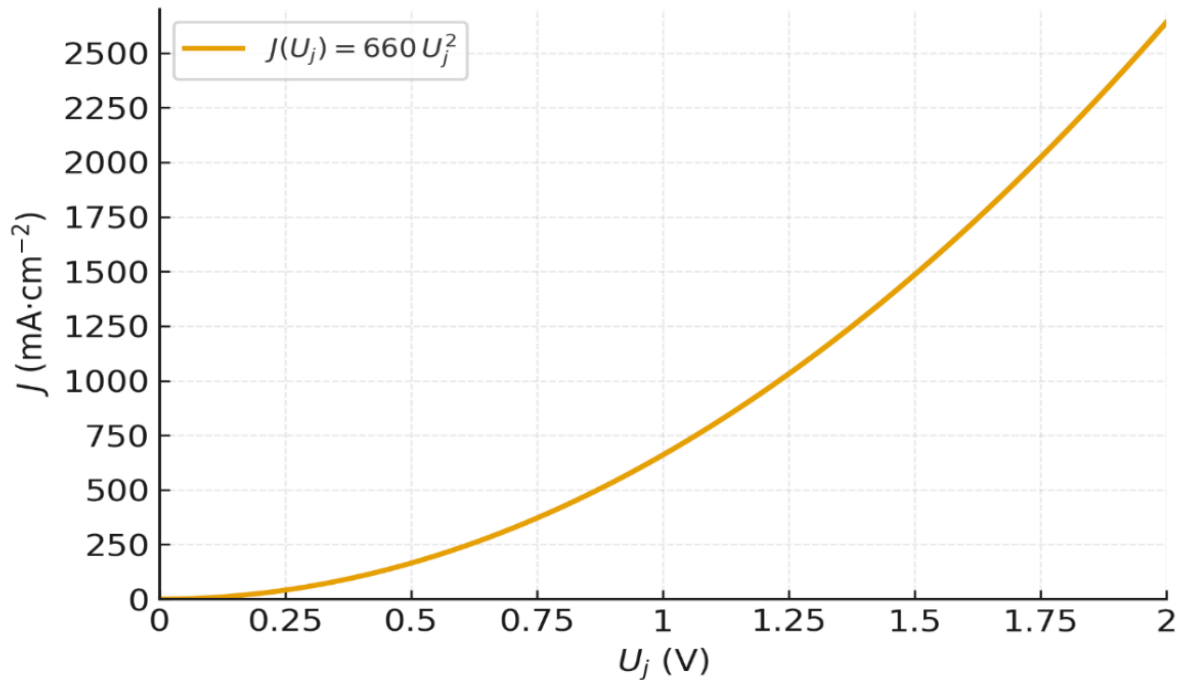


Figure 2. Theoretical $J-U_j$ curve of a nanometric BPM junction fully hydrated obtained from $J = 660 U_j^2$

The curve features a smooth, continuous increase in current, with no apparent threshold. At low voltages, the current remains low but non-zero, reflecting a gradual activation of dissociation. As the voltage increases, the field intensifies, and the current increases quadratically. This curve defines a theoretical upper bound (homogeneous, fully hydrated 1 nm junction; uniform field; no interfacial resistance). It thus serves as a universal benchmark for interpreting experiments and diagnosing losses (partial hydration $f < 1$, thicker effective junction $\delta > 1\text{ nm}$, ohmic drops and electrode overpotentials), which are analyzed in Section 4 and discussed later. It should be noted that $U_j = 1\text{ V}$ already gives a theoretical current of $J = 660\text{ mA}\cdot\text{cm}^{-2}$. At $U_j = 1.75\text{ V}$, we approach $2\text{ A}\cdot\text{cm}^{-2}$, which corresponds to the typical current of PEM electrolyzers. It can also be noted that the current density of $J = 100\text{ mA}\cdot\text{cm}^{-2}$ corresponds to a voltage of $U_j = 0.38\text{ V}$, i.e. a field $E = 3.8 \times 10^8\text{ V}\cdot\text{m}^{-1}$, for a 1 nm BPM junction. The corresponding $k_d(E)/k_d(0)$ ratio obtained by our model is 7×10^6 , a value fully consistent with BPM observations from Section 1. This agreement further supports the predictive strength and physical consistency of our quadratic model.

4. Materials and Experimental Methods

4.1. Membrane and Electrodes

A commercial bipolar membrane (Fumasep® FBM, acquired from FuelCell Store) was cut to samples of 1.0 cm^2 active area. The acidic-side working electrode was Pt foil (1.0 cm^2), and the alkaline-side working electrode was Ni foam (1.0 cm^2), both obtained from Sigma Aldrich (Oakville, Canada). They were cleaned using acetone, deionized water, alcohol and deionized water before use. These electrodes are commonly used for BPM water electrolysis characterisation [11,59].

4.2. Electrolytes, Cell Type and Components

Experiments were performed in an H-cell, (Stony Lab, Nesconset, New York USA) with two liquid compartments separated by the BPM. The acidic compartment contained H_2SO_4 (pH=0) 0.5 M and the alkaline compartment contained NaOH 1.0 M (pH=14). The inter-electrode spacing was 10 cm (non-zero-gap); the electrode–membrane distance was 5 cm on each side. Unless stated otherwise,

measurements were conducted at 25 °C. We emphasize that this is an electrolysis configuration (acid|BPM|alkali), not an electrodialysis stack.

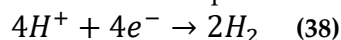
4.3. Electrochemical Instrumentation and Measurement Protocols

Linear sweep voltammetry (LSV) was performed in a two-electrode configuration on the full BPM cell, using a Solartron 1287A potentiostat/galvanostat (Scribner, North Carolina, USA). The cell voltage E_{cell} was swept at 5 mV·s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed with a VersaSTAT 4A (Ametek, Oak Ridge, Tennessee, USA), using a small-signal sinusoidal perturbation (10 mV_{rms}) over a log-spaced frequency sweep from 1 MHz down to 0.1 Hz. For the two-compartment BPM cell, global series resistance R_s was obtained from the high-frequency real-axis intercept of the Nyquist plot; values are reported in Ω·cm² after normalization by 1.0 cm² geometric area. Data and extraction details are provided in Section 5. LSVs were collected as raw curves and, when specified, as iR_s -corrected curves using the R_s obtained from EIS.

4.4. Three-Electrode Configuration Characterization of the Hydrogen Evolution Reaction (HER) and of the Oxygen Evolution Reaction (OER)

To quantify electrode kinetics independently of the membrane cell, we performed three-electrode configuration measurements for the hydrogen evolution reaction (HER) and for the oxygen evolution reaction (OER) in their respective electrolytes. In this study the hydrogen gas pressure is 1 atmosphere ($P_{H_2} = P_{O_2} = 1$ atm). The following half-reactions are considered in their respective compartment with their equilibrium potentials referenced to the Reversible Hydrogen Electrode (RHE) which potentials at standards conditions are, respectively, $E_{HER}^0 = 0$ V vs RHE for the HER at pH=0, and $E_{OER}^0 = 1.23$ V vs RHE for the OER at pH=14 [47]:

In the acidic compartment the following Hydrogen Evolution Reaction (HER) occurs:



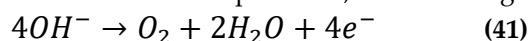
The dependence of the equilibrium potential of the reaction with the pH is:

$$E_{HER}^{eq} = E_{HER}^0 - 0.059 \times pH = -0.059pH \quad (39)$$

Here, pH = 0, $P_{H_2} = 1$ and T = 298 K which are standards conditions. Then:

$$E_{HER}^{eq} = 0.00 \text{ V vs SHE} \quad (40)$$

In the alkaline compartment, the following Oxygen Evolution Reaction (OER) occurs



The dependence of the equilibrium potential of the reaction with the pH is :

$$E_{HER}^{eq} = E_{OER}^0 - 0.059 \times pH = 1.23 - 0.059pH \quad (42)$$

In this compartment, pH = 14

$$E_{OER}^{eq} = 0.401 \text{ V vs SHE} \quad (43)$$

For HER in 0.5 M H₂SO₄, the reference electrode was Hg/HgSO₄; for OER in 1.0 M NaOH, the reference electrode was Hg/HgO. All potentials were converted to RHE using fixed offsets (Hg/HgSO₄ (sat.) = 0.64 V vs RHE; Hg/HgO = 0.098 V vs RHE). The Solartron 1287A applied 100% iR compensation in these three-electrode tests (note that this R is not the same as the two-compartment BPM cell R_s). Overpotentials were computed as:

$$\eta_{HER} = E_{HER} - E_{HER}^{eq} \quad (44)$$

$$\eta_{OER} = E_{OER} - E_{OER}^{eq} \quad (45)$$

where E_{HER} and E_{OER} are, respectively, the applied potential to the electrode of the hydrogen evolution reaction in the acidic compartment and of the Oxygen Evolution Reaction in the alkaline compartment, during the tests. Each of the potential vs current plots displays a Tafel behaviour in a certain range of potential according to:

$$\eta_{HER} = b_1 \log \left(\frac{J_1}{J_{0,HER}} \right), \quad (46)$$

for the HER, and

$$\eta_{OER} = b_2 \log \left(\frac{J_2}{J_{0,OER}} \right), \quad (47)$$

for the OER.

The respective HER and OER Tafel slopes b_1 and b_2 and their corresponding exchange current densities $J_{0,HER}$ and $J_{0,OER}$ were obtained by linear fits of the above Tafel forms applied in the appropriate overpotential ranges where E - $\log J$ is quasi-linear. Precisely, we used:

-HER: low overvoltage window $\eta_{HER} \in [-65, -45]$ mV (cathodic currents, after taking in account the value of the reference electrodes and iR -compensation).

-OER: window $\eta_{OER} \in [+0.20, +0.35]$ V (controlled by activation regime, iR -compensated).

The numerical values of the extracted Tafel slopes and exchange current densities values are reported in Section 5, together with the corresponding polarization and Tafel plots (including the fitted windows).

4.5. BPM's Junction-Voltage Accounting

For comparison to the theoretical junction law, we computed the junction drop U_j from the external cell bias E_{cell} by removing equilibrium, series resistance and overpotentials contributions [57,58]:

$$U_j \simeq E_{cell} - E_{cell}^{rev} - iR_s - |\eta_{HER}| - \eta_{OER}, \quad (48)$$

where E_{cell}^{rev} is the reversible equilibrium voltage of the cell :

$$E_{cell}^{rev} = E_{OER}^0 - E_{HER}^0 \quad (49)$$

Since $E_{HER}^0 = 0.00$ V vs RHE and $E_{OER}^0 = 1.23$ V vs RHE, then $E_{cell}^{rev} = 1.23$ V vs RHE. The LSV-derived current densities were then compared to the model prediction Eq. (37). All fits and goodness-of-fit metrics are presented in Section 5.

5. Results and Discussion

Figure 3 shows the raw J vs E_{cell} curve of Fumasep® FBM obtained from LSV (two-compartment FBM cell, $\Delta pH=14$). A measurable current appears near 1.36 V (sub- $\text{mA}\cdot\text{cm}^{-2}$), while the 1 $\text{mA}\cdot\text{cm}^{-2}$ onset occurs at ≈ 1.42 V. The curve exhibits 3 salient regions: First, a linear ohmic-like rise between 1.36–1.54 V, followed by quasi-stationary plateau between 1.55 and 1.62 with an average limiting current density $J_{lim} \approx 2.19$ $\text{mA}\cdot\text{cm}^{-2}$, then a transition into an over-limiting regime beyond ~ 1.62 V, where the current leaves the shelf and increases rapidly. This morphology is the canonical BPM signature at low current densities [3,44]: an initial rise, a limiting shelf associated with internal depletion in the ion-exchange layers, then take-off as the junction field grows and water dissociation (WD) becomes dominant.

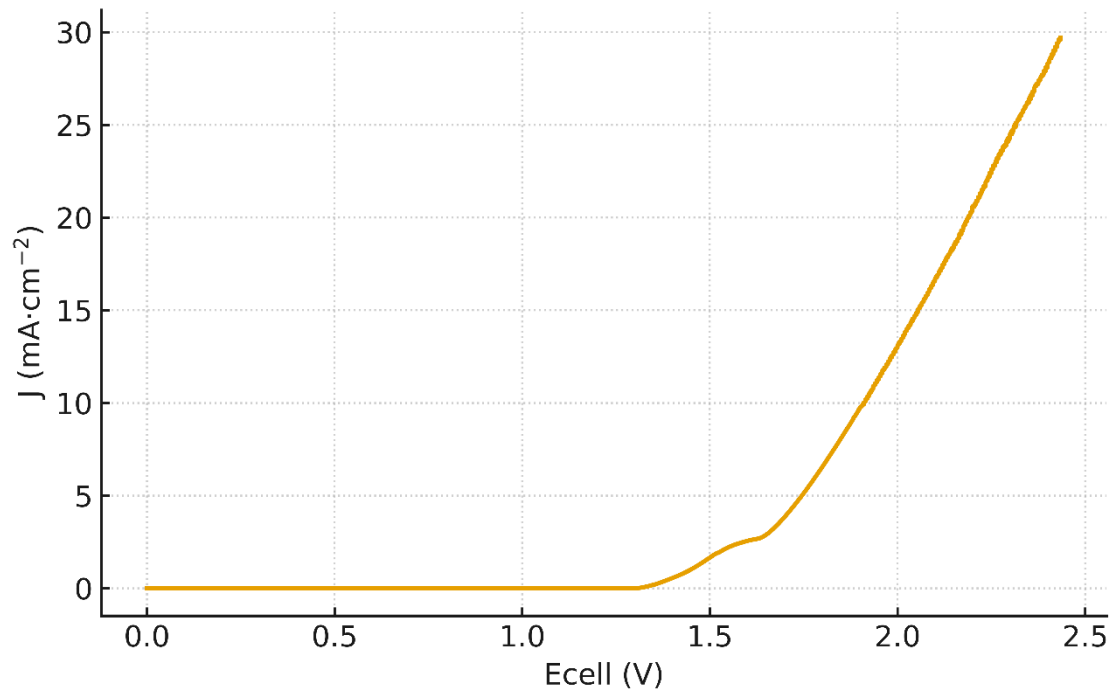


Figure 3. Raw J vs E_{cell} curve of Fumasep® FBM obtained from LSV measurement.

Importantly, a linear fit over 1.36–1.54 V (Figure 4.a) is excellent with slope $10.73 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-1}$ and $R^2 = 0.990$, indicating an ohmic behavior governed by co-ions transport. Yet, when we re-plot the same data against $E_{cell} - E_{rev}$ (Figure 5), a quadratic form fits equally well on that narrow span. This apparent paradox suggests that the low-bias current is composite: a nascent WD channel already contributes below 1 mA cm^{-2} , as emphasized by recent literature [44], while a residual co-ions transport path (imperfect permselectivity through the ion-exchange layers) adds an ohmic-like component. By contrast, the quasi-plateau 1.55–1.62 V (with $J_{lim} \approx 2.19 \text{ mA}\cdot\text{cm}^{-2}$) is not captured by a pure quadratic law (Figure 5) and marks the limiting-current shelf typical of BPMs at low current densities. For completeness, a quadratic fit restricted to 1.36–1.54 V with ($K=21.94 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-2}$, $R^2 = 0.987$) is provided in (Figure 4.b).

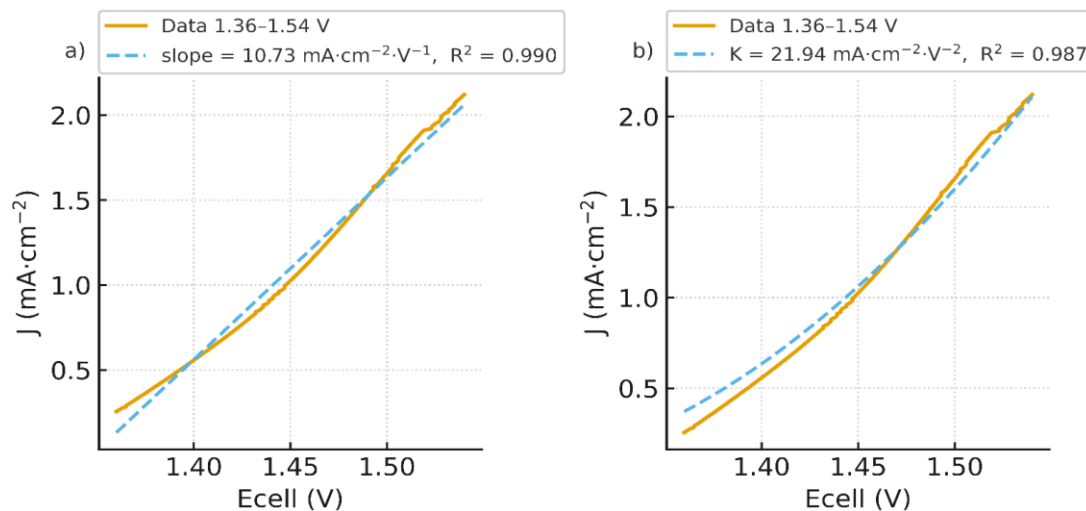


Figure 4. Fits over 1.36V-1.54V of J vs E_{cell} : a) Linear fit ; b) Quadratic fit.

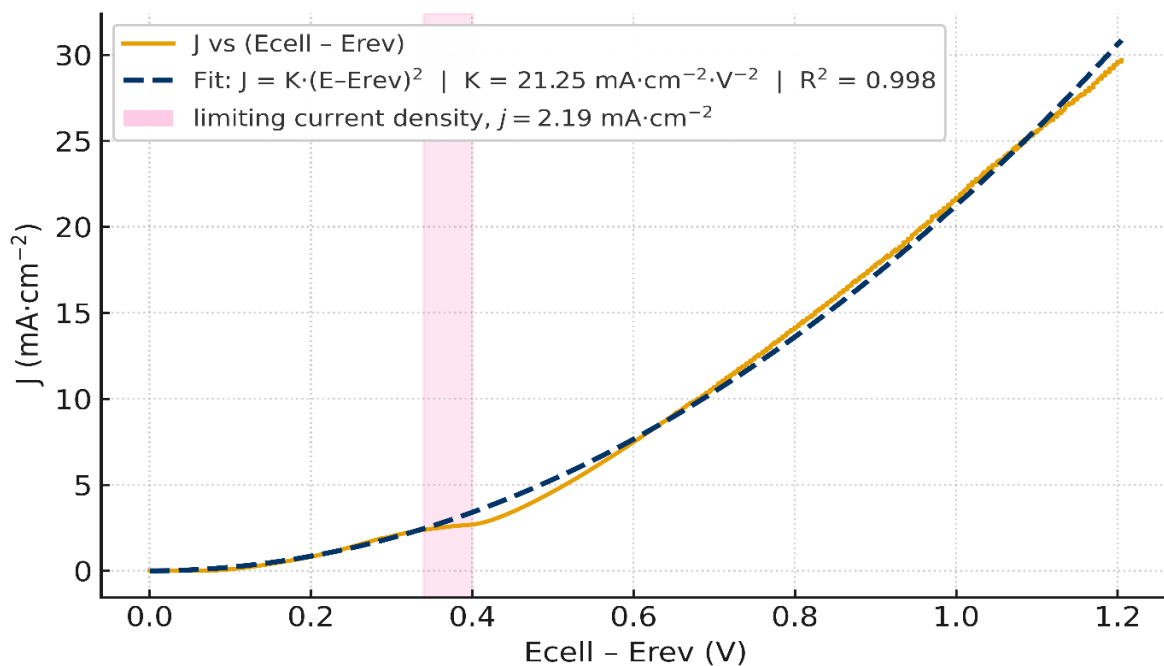


Figure 5. Variation of the current density J vs $E_{cell} - E_{cell}^{rev}$, quadratic fit J vs $(E_{cell} - E_{cell}^{rev})^2$ and limiting-current density $J = 2.19 \text{ mA}\cdot\text{cm}^{-2}$.

Subtracting only the equilibrium reversible voltage ($U_j \simeq E_{cell} - E_{cell}^{rev}$) yields already an excellent quadratic fit, $R^2 = 0.998$ with a prefactor $K \simeq 21.25 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-2}$, as shown in Figure 5. This supports our quadratic model and means that the cell current is mainly dominated by WD. The low prefactor compared to the theoretical $K=660$ reflects the fact that bulk ohmic loss and electrode overpotentials still remain in the trace. This supports the importance to make the ohmic loss and overvoltage correction, i.e. Eq. (48). Figure 6.a) shows the Nyquist plot obtained from the Electrochemical Impedance Spectroscopy (EIS) measurement. The area-normalized series resistance is extracted from the high-frequency real-axis intercept: $R_s = 20.19 \Omega\cdot\text{cm}^2$. Figure 6.b) shows the corresponding iR_s -corrected J vs E_{cell} curve.

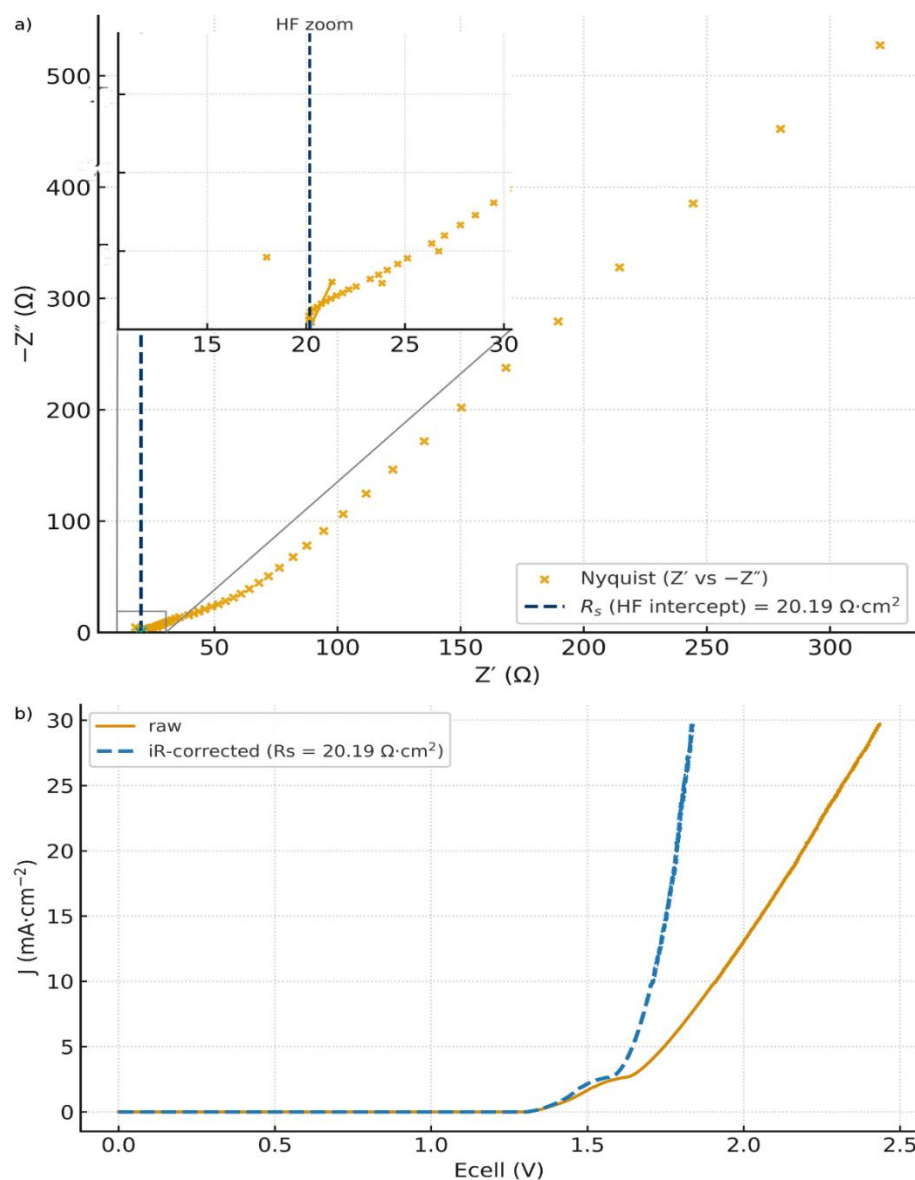


Figure 6. a) Nyquist plot from (EIS) of the FBM H-cell (VersaSTAT 4A) with Zoom on HF-intercept $R_s = 20.19$ Ω·cm²; b) Raw J vs E_{cell} curves (LSV) for the FBM H-cell together with iR_s -corrected by the cell-level $R_s = 20.19$ Ω·cm².

Independent three-electrode HER & OER polarization curves, each with its own iR -correction (not the FBM-cell R_s), are shown in Figure 7.a) and Figure 7.b), respectively. These datasets supply η_{HER} and η_{OER} used in the junction mapping.

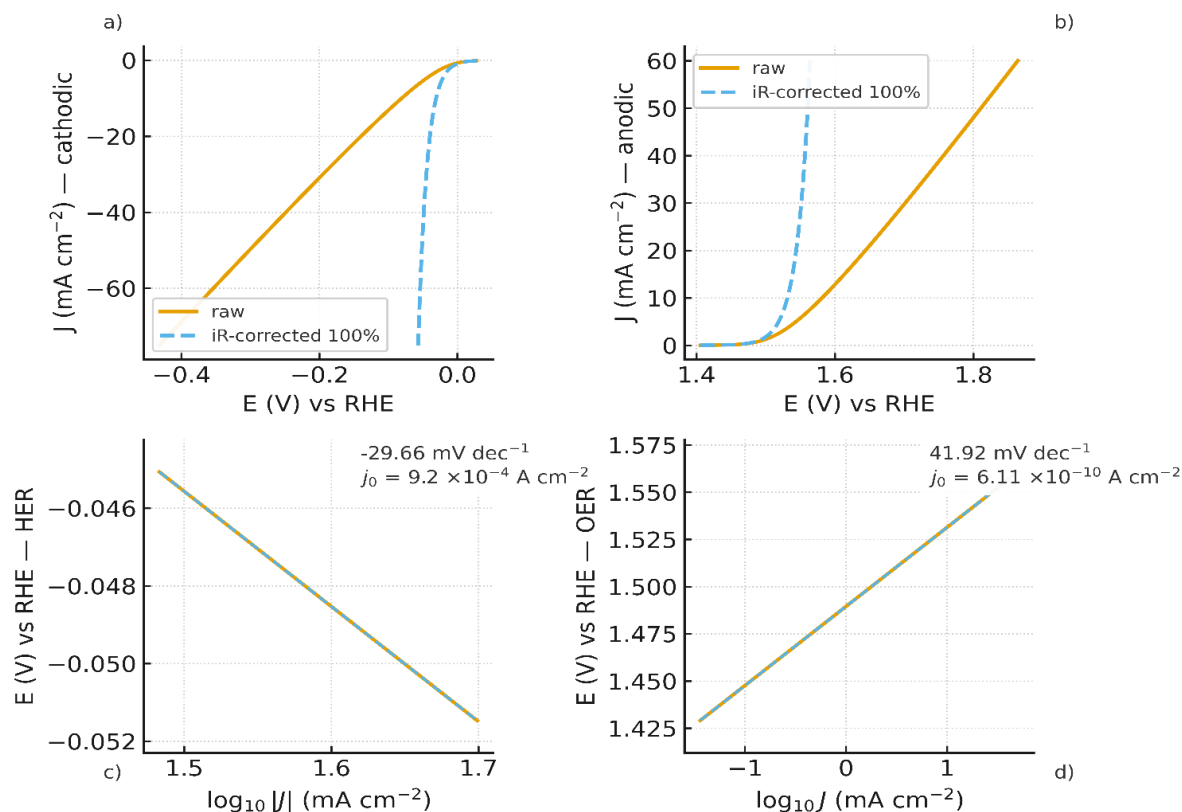


Figure 7. **a)** HER polarization curves (raw and *iR*-corrected) : Pt in 0.5 M H₂SO₄ vs Hg/HgSO₄ (reported vs RHE); **b)** OER polarization curves (raw and *iR*-corrected) : Ni-foam in 1.0 M NaOH vs Hg/HgO (vs RHE); **c)** HER Tafel plot $b_1 = -29.66 \text{ mV} \cdot \text{dec}^{-1}$; $J_{0,HER} = 9.20 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$; **d)** OER Tafel plot $b_2 = 41.92 \text{ mV} \cdot \text{dec}^{-1}$; $J_{0,OER} = 6.11 \times 10^{-10} \text{ A} \cdot \text{cm}^{-2}$.

Independent three-electrode characterizations provided a Tafel slope b_1 of $-29.66 \text{ mV} \cdot \text{dec}^{-1}$ and an exchange current density $J_{0,HER}$ of $9.2 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$ for HER on Pt (Figure 7.c). While for OER on Ni foam, a Tafel slope b_2 of $41.92 \text{ mV} \cdot \text{dec}^{-1}$ and an exchange current density $J_{0,OER}$ of $6.11 \times 10^{-10} \text{ A} \cdot \text{cm}^{-2}$ were obtained (Figure 7.d). These values are consistent with literature values for the respective HER and OER on these materials [60,61]. These values are used for the overpotential corrections in the full junction mapping which results are shown in Figure 8.

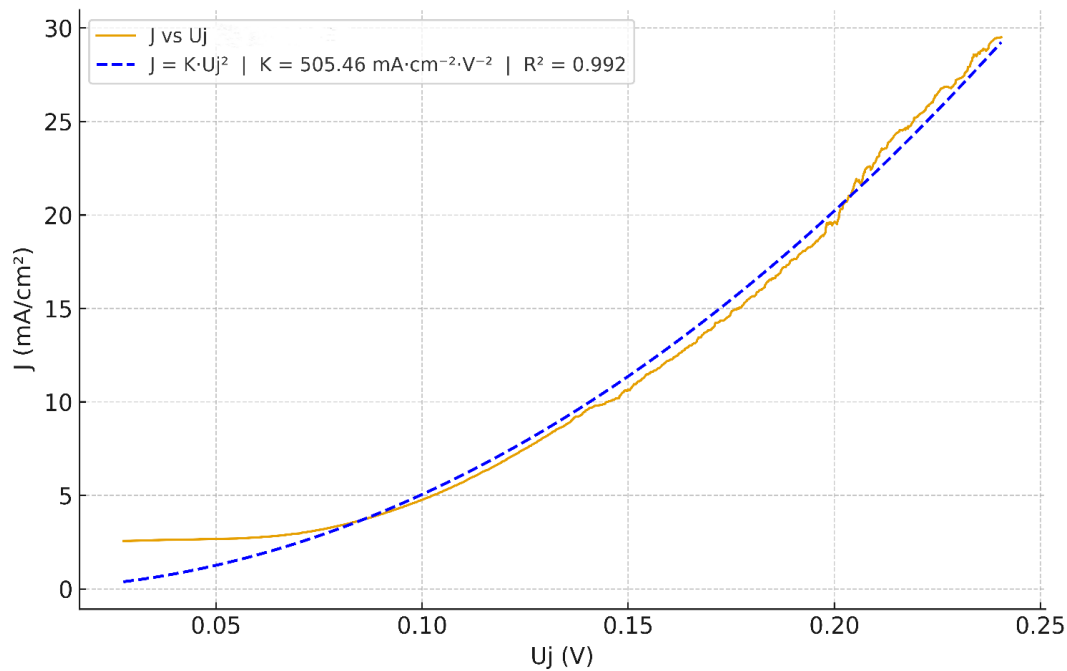


Figure 8. Quadratic fit of J vs U_j curve obtained from Eq.(33) : $U_j = E_{cell} - E_{cell}^{rev} - iR_s - |\eta_{HER}| - \eta_{OER}$.

After full junction mapping using Eq.(48), the obtained J vs U_j curve of the junction voltage collapse onto a robust quadratic law, $R^2 = 0.992$ with a much larger prefactor $K = 505.46 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-2}$, as shown in Figure 8. We notice that in a narrow window $U_j \in [0, 0.07] \text{ V}$, the current remains nearly constant at $J \approx 2.2 \text{ mA}\cdot\text{cm}^{-2}$, in excellent agreement with the limiting current measured on the raw LSV $J_{lim} \approx 2.19 \text{ mA}\cdot\text{cm}^{-2}$. This flat shoulder reflects the transport-limited baseline that precedes strong field-assisted water dissociation (WD) in BPMs; it does not contradict the junction quadratic law. Subtracting this constant baseline would force the curve through the origin and numerically reduce the zero-intercept prefactor K (a generic effect of vertical offsets in least-squares), but adds no physical information; we therefore report only the full-mapping result in Fig. 8 and interpret the small offset as the limiting baseline with minor reconstruction offsets expected at very low junction field.

The prefactor for Fumasep® FBM, $K = 505.46 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-2}$ is $\sim 76.6\%$ of the ideal $K = 660 \text{ mA}\cdot\text{cm}^{-2}\cdot\text{V}^{-2}$ estimated for a 1 nm, fully hydrated junction (§3.1.3). Since the Fumasep® FBM is homogenous [62], a $\delta \approx 1 \text{ nm}$ active region is plausible (Section 1). Hence, the observed prefactor gap can be reasonably attributed to the water volume fraction f , as reflected in Eq. (35). Beyond hydration, the gap can also be explained by a slight deviation of the effective junction thickness from the 1 nm benchmark (e.g., $\delta \gtrsim 1.1 - 1.3 \text{ nm}$, or conversely $< 1 \text{ nm}$) or a dissipation efficiency α capturing non-productive channels, without affecting the quadratic law. Overall, the FBM junction exhibit a high-quality quadratic dependence of J on U_j ($R^2 \approx 0.99$), with a high prefactor K after full junction mapping. These results provide a proof-of-principle of the quadratic $k_d(E)$ dependence anticipated by our power-dissipation model.

The above experimental results clearly indicate that our proposed model provides a novel power dissipation framework for interpreting WD enhancement under strong electric fields in BPMs with nanometric junctions. The central premise is that the dissipated power of drifting autoprotolysis ions H_3O^+ and OH^- under field, raises the propensity for heterolytic O–H bond cleavage. Thus, these rare ions act as indirect agents promoting the dissociation of new water molecules. The originality of our approach lies in expressing $k_d(E)$ as proportional to the power dissipated by migrating H_3O^+ and OH^- ions, thus directly linking field intensity to molecular bond breaking via power dissipation. A

direct consequence is a quadratic dependence of the WD rate on field strength $k_d(E) \propto E^2$, which we formalized with Eq. (29):

$$k_d(E) = \left(\frac{c_{ions}}{c_{H2O,l}} \right) \times \frac{q \times (\mu_{H3O^+} + \mu_{OH^-})}{E_d} \times E^2. \quad (29)$$

Built on fundamental physical principles, our analytical formulation is simple and requires no adjustable parameters; furthermore, it avoids the fragile/explosive behavior of exponential laws at 10^8 – 2×10^9 V·m⁻¹ yet still delivers the orders of magnitude required for BPM operation. In our comparison (Table 2), SWE is either too weak (constant ϵ_r) or numerically unstable (field-dependent ϵ_r), whereas the quadratic law gives a large but bounded amplification $k_d(E)/k_d(0) \sim 5 \times 10^5$ at 10^8 V·m⁻¹ and $\sim 2 \times 10^8$ at 2×10^9 V·m⁻¹. To our knowledge, this is the first analytical model capable of quantitatively predicting the experimental increase in $k_d(E)/k_d(0)$, as observed in literature. This alone marks a major advancement over existing models such SWE and CRM, which often rely on semi-empirical formulations or are unable to predict the correct order of magnitude of the dissociation rate enhancement.

While Onsager's formulation of SWE may yield a near-quadratic trend at low fields, this regime is outside the range relevant to BPMs with nanometric junctions, where electric fields exceed 10^8 V·m⁻¹. Moreover, in the SWE, this scaling emerges from a series expansion and is not the central feature of the model; in contrast, in our formulation it is intrinsic, directly derived from power dissipation, and remains valid over a broader range of practical fields in BPMs. Interestingly, a quadratic field dependence was briefly considered by Simons and Khanarian in their 1978 study [48], where they experimentally reported a quadratic J - V response across a neutral junction 60 nm to 1 μm thick. However, they dismissed this scenario not on theoretical grounds, but because the junction thickness in their setup was too large to sustain intense electric fields, thus making the quadratic scenario ineffective in their experimental regime. Our model revisits and justifies this scenario in modern BPMs with nanometric junctions enabling high fields, making this mechanism not only plausible but necessary to explain observed trends.

Building on the $k_d(E) \propto E^2$ result, the same quadratic law carries to the current $J \propto U_j^2$. For a fully hydrated, nanometric junction, this sets a clear upper-bound benchmark $J = 660 U_j^2$. Our experiments on Fumasep® FBM form a proof of principle that support our quadratic model. The measured J - U_j curve is already strongly quadratic before subtracting R_s and electrode overpotentials, showing that, in reverse bias, the cell current is WD-dominated. After full junction mapping (Eq. 48), the quadratic form remains while the fitted prefactor K increases; the law is robust, and reducing ohmic losses should be a priority. We attribute the remaining gap to the theoretical bound to incomplete local hydration (effective water fraction $f < 1$); improving hydration should raise K . Moreover, Eq. (33) shows that J scales not only with U_j^2 but also with $1/\delta$, inviting falsifiable tests that vary both the junction drop and the junction thickness. Finally, both theoretical and experimental results agree that WD ramps up as soon as $U_j > 0$, with no threshold, consistent with recent observations [44,63,64]. This suggests that a strong electric field in the junction is enough to trigger WD while interfacial catalysts are often unnecessary. Therefore, junction geometry and thickness that allow strong and uniform fields, complete hydration to maximize f , and parasitic-loss suppression (resistances and overpotentials) are the primary levers for pushing BPMs toward the theoretical upper-bound of our power-dissipation-based quadratic model. Overall, the Fumasep® FBM experimental results supports a quadratic, field-driven WD mechanism without added catalysts, providing proof of principle and motivating broader tests for validation.

Despite its simplicity, the model remains agnostic as to whether the injected power induces molecular collisions, vibrational excitation, hydrogen-bond destabilization, or solvent reorganization. Nonetheless, our approach is compatible with a thermodynamic interpretation of energy dissipation as entropy production [49]. This aligns with the observations of Chen et al.[65] and with the work of Rodellar et al. [43], who showed that high electric fields modulate interfacial

entropy in BPMs via the Arrhenius pre-exponential factor. The link to high-frequency interfacial capacitance suggests that the field alters vibrational modes and molecular ordering at the junction, facilitating access to the transition state for WD. Very recently, Litman and Michaelides [66] have investigated WD under strong electric fields using *ab initio* molecular dynamics and free-energy decomposition. They show that field-induced WD becomes predominantly entropy-driven due to protonic defects (autoprotolysis ions) disrupting an otherwise ordered hydrogen-bond network, in line with our interpretation of dissipated power and entropy production as key ingredients for field-assisted WD. Altogether, these results support a picture in which field-assisted WD in BPM junctions is sustained by local power dissipation and entropy-driven solvent reorganization, while the precise microscopic pathways remain to be resolved by multiscale molecular dynamics (MD) simulations or *in situ* spectroscopy.

Finally, we acknowledge limits and possible extensions of this research. The intricate chemistry and morphology of specific membranes may modulate the prefactor through mobilities, local activities, or effective E_d ; nonetheless, these variations do not undermine the functional E^2 scaling. Furthermore, saturation phenomena may emerge at fields beyond the practical BPM range ($E \sim 10^8$ – 2×10^9 V·m⁻¹). In such cases, it would be natural to incorporate a bounded efficiency factor or a mild saturation function in the prefactor—without altering the basic E^2 link. Similarly, marked dehydration or transport bottlenecks would call for couplings with water activity or layer conductivities. These are interesting directions for future work, but they lie outside the intended baseline purpose of the present model.

4. Conclusion

This work introduced a power-dissipation framework for electric field-induced water dissociation (WD) in bipolar membranes, in which minority autoprotolysis ions H₃O⁺ and OH⁻ drift under strong interfacial fields and continuously dissipate field-supplied power, thereby raising the propensity for heterolytic O–H bond cleavage. This mechanism yields a quadratic rate law $k_d(E) \propto E^2$ and an associated junction-level current law $J = K \times U_j^2$. Without adjustable parameters, the model reproduces the orders-of-magnitude enhancement $k_d(E)/k_d(0)$ across BPM-relevant fields while avoiding the numerical fragilities of exponential SWE formalisms. A proof-of-principle on a commercial Fumasep® FBM corroborates the quadratic J - U_j trend, supporting a field-driven, catalyst-free WD pathway under reverse bias. Altogether, the theory and experiment provide a compact, falsifiable baseline for WD in strong-field, reaction-limited, well-hydrated BPM nanometric junctions, and motivate broader catalyst-free validations across materials and operating windows to establish generality.

Author Contributions: Ma-El-Ainine: Contributed to the development of the model, prepared the mathematical expressions and figures, organized the structure of the manuscript, and wrote the initial version and subsequent revisions. Boukhili: Provided discussions, general guidance, and revisions that helped improve the clarity and structure of the manuscript. Savadogo: Proposed the overall research direction and provided key scientific guidance throughout the development of the study. Contributed to the interpretation of the water-dissociation mechanism within the BPM junction and suggested potential extensions of the model for future work, including the exploration of field limits and characteristic parameters of the junction. Provided major scientific feedback, contributed to structure organization and major manuscript revisions, and guided the refinement of the electrochemical discussion.

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List of Symbols (Definitions & Units)

- $k_d(E)$: Water dissociation rate constant vs field; unit s^{-1} .
- $k_d(0)$: Thermal WD rate constant (no field); s^{-1} .
- E : Electric field in the BPM junction; $V \cdot m^{-1}$.
- U_j : Junction voltage drop across active region; V.
- δ : Junction thickness; m (e.g., 1 nm benchmark).
- J : Current density at the junction; $mA \cdot cm^{-2}$.
- K : Prefactor in junction law $J = K U_j^2$; $mA \cdot cm^{-2} \cdot V^{-2}$ (when J in $mA \cdot cm^{-2}$, U_j in V).
- f : Water volume fraction in the junction (hydration); dimensionless [0,1].
- q : Elementary charge; C (e.g., 1.6×10^{-19}).
- $\mu_{H_3O^+}, \mu_{OH^-}$: Ionic mobilities; $m^2 \cdot V^{-1} \cdot s^{-1}$ (e.g., 3.62×10^{-7} , 2.05×10^{-7} at 25 °C).
- c_{ions} : Concentration of autoprotolysis ions H_3O^+/OH^- in water; $mol \cdot L^{-1}$ ($\approx 10^{-7}$ at 25 °C).
- $c_{H_2O,l}$: Concentration of free water; $mol \cdot L^{-1}$ (≈ 55.5 at 25 °C).
- $c_{H_2O,j}$: Concentration of water in the junction; $mol \cdot L^{-1}$.
- E_d : Threshold dissociation energy per water molecule; J ($\approx 1.33 \times 10^{-19}$ at 25 °C).
- J_{lim} : Limiting current density (plateau); $mA \cdot cm^{-2}$ (≈ 2.19 measured here).
- E^* : Crossover field where $k_d = k_0$; $V \cdot m^{-1}$ ($\approx 1.43 \times 10^5$).
- E_{cell} : External cell voltage applied; V.
- E_{cell}^{rev} : Reversible (equilibrium) voltage of the cell; V (see Eq. 49).
- R_s : Series resistance (two-compartment cell, area-normalized); $\Omega \cdot cm^2$ (EIS-derived).
- η_{HER}, η_{OER} : Overpotentials for HER/OER; V.
- Λ° : Limiting molar conductivity at infinite dilution; $S \cdot m^2 \cdot mol^{-1}$ (used to infer μ).
- F : Faraday constant; $C \cdot mol^{-1}$ (96 485).
- η : Viscosity (in Stokes–Einstein context for μ); $Pa \cdot s$.
- b : Tafel slope; $mV \cdot dec^{-1}$.
- j_0 : Exchange current density; $A \cdot cm^{-2}$.
- v_d : Drift velocity of ions under the field; $m \cdot s^{-1}$. (Relation: $v_d = \mu E$.)
- P : Per-ion Field-supplied power dissipated by drift; ($J \cdot s^{-1}$). (Model: $P = q \mu E^2$.)
- $P_{H_3O^+}, P_{OH^-}$: Per-ion power for H_3O^+ and OH^- ; ($J \cdot s^{-1}$).
- $n_{H_3O^+}, n_{OH^-}$: Number density of autoprotolysis ions; m^{-3} .
- V_j : Junction volume (membrane area $\times$ active thickness δ); m^3 .
- P_{total} : Total power dissipated in the junction by all ions; ($J \cdot s^{-1}$).
- w : Power density dissipated by H_3O^+/OH^- in the junction; $J \cdot s^{-1} \cdot m^{-3}$.
- ΔG_d : Molar Gibbs free energy of water dissociation; ($kJ \cdot mol^{-1}$). (Used to compute the per-molecule threshold $E_d = \Delta G_d / N_A$.)
- N_A : Avogadro constant; mol^{-1} .
- κ : Thermal conductivity of water used in the heating estimate; $W \cdot m^{-1} \cdot K^{-1}$.
- ΔT : Estimated junction temperature rise from dissipation; K.
- A : Membrane area used in estimates; m^2 (our benchmark: 1 cm^2).
- ϵ_r : Relative permittivity; dimensionless.
- T : Absolute temperature; K (reference 298 K / 25 °C).
- R : Universal gas constant ($8.314 \text{ J} \cdot mol^{-1} \cdot K^{-1}$).
- K_w : Water equilibrium constant (10^{-14} at 25 °C).

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