Mathematical analysis of a thermodynamically consistent reduced model for iron corrosion

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MATHEMATICAL ANALYSIS OF A THERMODYNAMICALLY CONSISTENT REDUCED MODEL FOR IRON CORROSION

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ABSTRACT. We are interested in a reduced model for corrosion of iron, in which ferric cations and electrons evolve in a fixed oxide layer subject to a self-consistent electrostatic potential. Reactions at the boundaries are modeled thanks to Butler-Volmer formulas, whereas the boundary conditions on the electrostatic potential model capacitors located at the interfaces between the materials. Our model takes inspiration in existing papers, to which we bring slight modifications in order to make it consistent with thermodynamics and its second principle. Building on a free energy estimate, we establish the global in time existence of a solution to the problem without any restriction on the physical parameters, in opposition to previous works. The proof further relies on uniform estimates on the chemical potentials that are obtained thanks to Moser iterations. Numerical illustrations are finally provided to highlight the similarities and the differences between our new model and the one previously studied in the literature.

Keywords: corrosion modeling, drift-diffusion system, entropy method, existence, Moser iterations

Mathematics Subject Classification (MSC): 35Q79 – 35M33 – 35A01 – 35B35

1. INTRODUCTION

1.1. **General framework of the study.** At the request of the French nuclear waste management agency ANDRA, investigations are carried out in order to evaluate the long-term safety of the geological repository of radioactive waste. The context is the following: the waste is confined in a glass matrix, placed into steel canisters and then stored in a claystone layer at a depth of several hundred of meters. The long-term safety assessment of the geological repository has to take into account the degradation of the carbon steel used for the waste overpacks and the cell disposal liners, which are in contact with the claystone formation. The study of the corrosion processes that arise at the surface of the steel canisters and of the cell disposal liners takes part in the modelling and simulation of the repository. This has motivated the introduction of the Diffusion Poisson Coupled Model (DPCM) by Bataillon *et al.* in [3].

The DPCM describes the oxidation of a metal covered by an oxide layer (magnetite) in contact with the claystone. It consists in a system of drift-diffusion equations on the density of charge carriers (electrons, Fe^{3+} cations and oxygen vacancies) coupled with a Poisson equation on the electric potential. Boundary conditions of Robin-Fourier type are prescribed by the electrochemical reactions and the potential drops at the interfaces with the claystone and with the metal. They induce additional couplings in the system and involve numerous physical parameters. The system also includes equations governing the motion of the boundaries.

Up to now, no existence result has been established for the general DPCM [3]. However, a few mathematical results on some simplified versions have been obtained. The well-posedness of a two-species (electrons and ferric cations) model set on a fixed domain has been established in [14] for the stationary case and in [15] for the evolutive case. Some numerical methods for the simulation

of DPCM have been introduced in [4] and implemented in the code CALIPSO. The numerical experiments proposed in [3, 4] have highlighted the long-time behaviour of the model: after a transient period, the size of the oxide layer stays constant, while both interfaces move at the same velocity and the densities of charge carriers as the electrical potential have stationary profiles. This corresponds to a traveling wave solution to DPCM. The existence of a traveling wave solution has been proved first on a simplified version of DPCM in [13]. Recently in [6], the existence is also established for the original DPCM thanks to a computer-assisted proof.

The description of the transport of charge carriers in the oxide layer proposed by the DPCM is similar to the transport of charge carriers in a semiconductor device as proposed by van Roosbroeck [34]. The differences come first from some reaction terms due to recombination-generation in the continuity equations and mainly from the boundary conditions, which are of Dirichlet-Neumann type in the semiconductor setting. The mathematical analysis of the drift-diffusion-Poisson system of equations for semiconductor devices is the subject of a series of seminal papers by Gajewski and Gröger [18, 19, 20]. The strategy of proof proposed by Gajewski and Gröger relies strongly on the underlying variational structure of the model, in agreement with thermodynamics. One keypoint is a convex functional which can be interpreted as a free energy from the viewpoint of thermodynamics . This strategy has been further used in many papers dealing for instance with electro-reaction-diffusion processes [21, 25, 26], spin-polarized drift-diffusion models [22], electronic models for solar cells [23, 24],...

In order to obtain some mathematical results for the DPCM with a similar strategy, it is crucial to understand the impact of the moving boundary equations and of the boundary conditions on the structure of the system. Actually, the derivation of the DPCM proposed in [3] does not rely on energetic considerations. As a consequence, its thermodynamic stability is unclear and neither a satisfactory well-posedness result nor the assessment of the long-time behavior of the system have been established so far. This paper was thought as a first step towards the derivation and the analysis of a thermodynamically consistent DPCM model. Here, we restrict our attention to a simplified setting with only two species (electrons and iron cations), the goal being to get consistent couplings between the boundary conditions and the bulk equations. Since oxygen vacancies are not considered in our simplified setting, the boundaries are fixed throughout this paper. The derivation of a thermodynamically consistent counterpart to the full DPCM model will be the purpose of a future work.

1.2. **From the original two-species DPCM to the new model.** Let us start by introducing the original two-species DPCM, which is set on the fixed domain $(0,1) \subset \mathbb{R}$. It is already a challenge on this simplified model to manage the complexity of the boundary conditions in order to establish the dissipative behaviour of the associate system of partial differential equations.

We will denote by u_1 the density of ferric cations, u_2 the density of electrons and v_0 the electric potential. We consider a scaled model, which involves only dimensionless constants and scaled parameters, detailed below. The original DPCM in this case can be written, for $t \geq 0$,

$$\text{(1a)} \qquad \partial_t u_1 + \partial_x J_1 = 0 \quad \text{with} \quad J_1 = -d_1(\partial_x u_1 + z_1 u_1 \partial_x v_0) \qquad \text{in } (0,1),$$

$$\text{(1b)} \qquad \partial_t u_2 + \partial_x J_2 = 0 \quad \text{with} \quad J_2 = -d_2(\partial_x u_2 + z_2 u_2 \partial_x v_0) \qquad \text{in } (0,1),$$

$$\text{(1c)} \qquad -\lambda^2 \partial_{xx}^2 v_0 = z_1 u_1 + z_2 u_2 + \rho_{\text{hl}} \qquad \text{in } (0,1),$$

with the following boundary conditions:

(2a) $$-J_1(0) = k_1^0 u_1(0) e^{\frac{z_1}{2} v_0(0)} - m_1^0 (\overline{u}_1 - u_1(0)) e^{-\frac{z_1}{2} v_0(0)},$$

(2b) $$J_1(1) = m_1^1 u_1(1) e^{\frac{z_1}{2}(v_0(1) - V)} - k_1^1 (\overline{u}_1 - u_1(1)) e^{-\frac{z_1}{2}(v_0(1) - V)},$$

(2c) $$-J_2(0) = k_2^0 u_2(0) e^{\frac{z_2}{2} v_0(0)} - m_2^0 e^{-\frac{z_2}{2} v_0(0)},$$

(2d) $$J_2(1) = m_2^1 u_2(1) - k_2^1 \overline{u}_2^{\mathrm{met}} \log \left(1 + e^{z_2(V - v_0(1))} \right),$$

(2e) $$v_0(0) - \alpha_0 \partial_x v_0(0) = \Delta \Psi_0^{\mathrm{pzc}},$$

(2f) $$v_0(1) + \alpha_1 \partial_x v_0(1) = V - \Delta \Psi_1^{\mathrm{pzc}}.$$

The system (1)-(2) is supplemented with initial conditions on u_1 and u_2:

(3) $$u_1(t = 0) = u_1^{\mathrm{in}}, \quad u_2(t = 0) = u_2^{\mathrm{in}}.$$

Let us comment the different parameters arising in the system:

- λ^2 is the scaled Debye length, α_0 and α_1 are positive dimensionless parameters related to the differential capacitances of the interfaces;
- ρ_{hl} is the net charge density of the ionic species in the host lattice, assumed to be constant in space, $\rho_{\mathrm{hl}} = -5$;
- z_i is the (dimensionless) charge of the ith species. In our setting, $z_1 = +3$ and $z_2 = -1$;
- d_1 and d_2 are the scaled diffusion coefficients. In practice the scaling is relative to the characteristic time of cations, $d_1 = 1$ and $d_2 \gg 1$;
- $\overline{u}_1$ is the maximum occupancy for octahedral cations in the host lattice;
- $\overline{u}_2^{\mathrm{met}}$ is the electron density of state of the metal (Friedel model);
- $(k_i^\Gamma, m_i^\Gamma)_{i=1,2, \Gamma \in \{0,1\}}$ are interface kinetic functions. We assume that these functions are constant and strictly positive;
- $\Delta \Psi_0^{\mathrm{pzc}}$, $\Delta \Psi_1^{\mathrm{pzc}}$ are respectively the outer and inner voltages of zero charge, V is the applied potential.

Existence of a global weak solution for a system close to (1)–(3) has been established in [15]. The main difference relies in the definition of the boundary conditions (2c) and (2d) for the electrons. Moreover the result is obtained under restrictive assumptions on the parameters, the physical sense of which being unclear. Let us highlight the misfit of model (1)–(3) with respect to Onsager's reciprocal relation [32, 33] or its generalization beyond the linear setting [29]. Since inertia is not intended to play a role in our model, one expects the fluxes to be proportional to the driving forces, which can be decomposed into chemical and electrical contributions:

$$J_i = -\sigma_i \partial_x \xi_i, \quad \text{for } i = 1, 2,$$

where $\sigma_i > 0$ denotes the mobility of the ith species (which may depend on u_i), and where

(4) $$\xi_i = v_i + z_i v_0, \quad \text{for } i = 1, 2,$$

denotes the electrochemical potential, v_i being the chemical potential of species i. The expressions for the fluxes in (1a) and (1b) then suggest that

(5) $$\sigma_i = d_i u_i \quad \text{and} \quad v_i = \log u_i + \text{constant}, \quad \text{for } i = 1, 2.$$

As a consequence, (1a) and (1b) are compatible with thermodynamics, provided that u_i and v_i are linked through Boltzmann statistics.

On the other hand, one expects the boundary fluxes to depend on the electrochemical potential drop. Let us denote by ξ_i^Γ the electrochemical potential on the other side of the interface Γ (*i.e.* in

the solution if $\Gamma = 0$ and in the metal if $\Gamma = 1$), while $\xi_i(\Gamma)$ is the trace on Γ of the electro-chemical potential ξ_i defined in the oxide layer $(0, 1)$. More precisely, one expects that

$$(6) \qquad J_i(\Gamma) \cdot \nu^\Gamma = r_i^\Gamma g_i^\Gamma (\xi_i(\Gamma) - \xi_i^\Gamma), \qquad \text{for } i = 1, 2, \text{ and } \Gamma \in \{0, 1\},$$

where ν^Γ denotes the normal to Γ ($\nu^0 = -1$ and $\nu^1 = 1$), while r_i^Γ is positive and possibly depends on u_i and g_i^Γ is a non-decreasing function such that $g_i^\Gamma(0) = 0$, so that

$$(7) \qquad \forall y \in \mathbb{R}, \ y \, g_i^\Gamma(y) \geq 0, \quad \text{for } i = 1, 2, \text{ and } \Gamma \in \{0, 1\}.$$

As a consequence of (7), boundary conditions of type (6) are dissipative in the sense that

$$(8) \qquad J_i(\Gamma) \cdot \nu^\Gamma (\xi_i(\Gamma) - \xi_i^\Gamma) \geq 0.$$

Denoting

$$\kappa_1^0 = 2\sqrt{k_1^0 m_1^0}, \qquad \kappa_1^1 = 2\sqrt{k_1^1 m_1^1}, \qquad \xi_1^0 = \log \frac{m_1^0}{k_1^0}, \qquad \xi_1^1 = \log \frac{k_1^1}{m_1^1} + z_1 V,$$

we can rewrite the boundary conditions for the cations (2a) and (2b) as

$$J_1^\Gamma \cdot \nu^\Gamma = \kappa_1^\Gamma \sqrt{u_1(\Gamma)(\overline{u}_1 - u_1(\Gamma))} \sinh\left(\frac{1}{2} \left(\log \frac{u_1(\Gamma)}{\overline{u}_1 - u_1(\Gamma)} + z_1 v_0(\Gamma) - \xi_1^\Gamma \right) \right).$$

It appears then natural to define the chemical and electrochemical potentials of the cations by

$$(9) \qquad v_1 = \log \frac{u_1}{\overline{u}_1 - u_1} \quad \text{and} \quad \xi_1 = v_1 + z_1 v_0$$

in order to satisfy (6) with

$$(10) \qquad r_1^\Gamma = \kappa_1^\Gamma \sqrt{u_1(\Gamma)(\overline{u}_1 - u_1(\Gamma))} \text{ and } g_1^\Gamma(y) = \sinh\left(\frac{y}{2} \right).$$

In other words, the cations should rather obey a Blakemore statistics, see [5, 16], than Boltzmann statistics as suggested by (5).

Similarly, we can rewrite the boundary condition (2c) as

$$-J_2(0) = \kappa_2^0 \sqrt{u_2(0)} \sinh\left(\frac{1}{2} (\log u_2(0) + z_2 v_0(0) - \xi_2^0) \right)$$

by setting

$$\kappa_2^0 = 2\sqrt{k_2^0 m_2^0}, \qquad \xi_2^0 = \log \frac{m_2^0}{k_2^0}.$$

Under this form, the electron flux $J_2(0)$ clearly enters the framework of (6) for

$$(11) \qquad r_2^0 = \kappa_2^0 \sqrt{u_2(0)} \quad \text{and} \quad g_2^0(y) = \sinh\left(\frac{y}{2} \right)$$

and

$$v_2 = \log(u_2) \quad \text{and} \quad \xi_2 = v_2 + z_2 v_0.$$

Boltzmann statistics is encoded here, in accordance to what was prescribed in the bulk (5).

Yet, it seems impossible to recast the boundary condition (2d) for the electrons at the oxide/metal interface $\Gamma = 1$ into the framework (6). This led us to propose the following modification of the boundary condition (2d):

$$(12) \qquad J_2(1) = m_2^1 u_2(1) - k_2^1 e^{z_2(V - v_0(1))},$$

which enters the framework of (6) by setting

$$(13) \qquad r_2^1 = \kappa_2^1 u_2(1), \qquad \kappa_2^1 = m_2^1, \quad \xi_2^1 = \log \frac{k_2^1}{m_2^1} + z_2 V \quad \text{and} \quad g_2^1(y) = 1 - e^{-y}.$$

Our concern related to the boundary condition (2d) having been solved by changing it into (12), the last misfit to be solved is related to the Blakemore statistics (9) for the cation which is not consistent with the bulk equation (1a). On the other hand, the Butler-Volmer laws (2a) and (2b) suggest some vacancy diffusion involving a nonlinear mobility σ_1, whereas interstitial diffusion corresponding to some linear mobility σ_1 has been prescribed so far in the bulk for the cations by (5). Here, we suggest to fully adopt the vacancy diffusion process, yielding

$$(14) \qquad \sigma_1 = d_1 \frac{u_1(\overline{u}_1 - u_1)}{\overline{u}_1},$$

with v_1 being related to u_1 through the Blakemore statistics (9). With this choice, the diffusion remains linear, but the convection due to the electric potential becomes nonlinear:

$$(15) \qquad \partial_t u_1 + \partial_x J_1 = 0, \qquad J_1 = -\sigma_1 \partial_x(v_1 + z_1 v_0) = -d_1 (\partial_x u_1 + z_1 \frac{u_1(\overline{u}_1 - u_1)}{\overline{u}_1} \partial_x v_0).$$

For the electrons, we stick to band conduction leading to linear mobility σ_2 and to Boltzmann statistics:

$$(16) \qquad \sigma_2 = d_2 u_2, \qquad v_2 = \log u_2.$$

so that (1b) remains unchanged.

1.3. **Main results and outline of the paper.** Our aim in this paper is to prove the existence of a weak solution under very general assumptions to the new DPCM introduced above, where (1a) has been changed into (15) with σ_1 defined by (14), and where the oxide/metal interface condition (2d) has been modified into (12). In Section 2, we fix the mathematical setting: we recall the notations and the system of partial differential equations we consider; we also collect the general assumptions and give a weak formulation (P) to the model. The main result, namely the global in time existence of a solution, is then stated in Theorem 2.2. Section 3 is devoted to physically motivated estimates and more general a priori estimates on a solution to (P). Before dealing with (P), we introduce a family of regularized problems (P_M) (with $M > 0$) in Section 4 and we prove their solvability as stated in Proposition 4.1. Finally, in Section 5, we establish some lower and upper bounds for the solution to (P_M) which do not depend on the regularization level M (when sufficiently large). These estimates lead to the existence of a solution to (P).

2. MATHEMATICAL SETTING AND MAIN RESULT

In this section we give the precise setting of the problem we are concerned with.

2.1. **Notation.** In addition to the notation already introduced in Section 1.2, we denote by $\overline{u}_2$ the reference occupancy for electrons (equal to 1 in practice), and by u_0 the total charge density in the oxide layer. The outer electro-chemical potentials of iron cations and electrons at the interfaces are denoted by ξ_i^Γ, $i = 1, 2$, $\Gamma \in \{0, 1\}$, which are assumed to not depend on time. Finally,

$$f^0 = \frac{\lambda^2}{\alpha_0} \Delta \Psi_0^{\text{pzc}}, \qquad f^1 = \frac{\lambda^2}{\alpha_1}(V - \Delta \Psi_1^{\text{pzc}}) \quad \text{and} \quad \beta^\Gamma = \frac{\lambda^2}{\alpha_\Gamma}, \quad \text{for } \Gamma \in \{0, 1\}$$

are some given values related respectively to the interface potentials and to the differential capacitance of the boundaries. Then, we consider the corrosion model as a system of partial differential

equations whose unknowns are the charge densities (u_0, u_1, u_2) and the electrical/chemical potentials (v_0, v_1, v_2). It writes in $(0, +\infty) \times (0, 1)$, for $i = 1, 2$:

(17a) $$\partial_t u_i + \partial_x J_i = 0,$$

(17b) $$\text{with} \quad J_i = -\sigma_i(v_i)\partial_x \xi_i, \quad \xi_i = z_i v_0 + v_i,$$

(17c) $$-\lambda^2 \partial_{xx} v_0 = u_0,$$

(17d) $$\text{with} \quad u_0 = \sum_{i=1,2} z_i u_i + \rho_{hl}.$$

The boundary conditions are defined on $(0, +\infty) \times \Gamma$ with $\Gamma \in \{0, 1\}$ by:

(18a) $$J_i \cdot \nu^\Gamma = r_i^\Gamma(v_i) g_i^\Gamma(\xi_i - \xi_i^\Gamma),$$

(18b) $$\lambda^2 \partial_x v_0 \cdot \nu^\Gamma + \beta^\Gamma v_0 = f^\Gamma.$$

Moreover, as it has been explained in the introduction, we may consider the following relations between the densities and the chemical potentials:

(19) $$v_1 = \log\left(\frac{u_1}{\bar{u}_1 - u_1}\right) \quad \text{and} \quad v_2 = \log\left(\frac{u_2}{\bar{u}_2}\right),$$

or in an equivalent manner:

(20) $$u_1 = \bar{u}_1 \frac{e^{v_1}}{1 + e^{v_1}} \quad \text{and} \quad u_2 = \bar{u}_2 e^{v_2}.$$

This corresponds to a Blakemore statistics for the cations and to a Boltzmann statistics for the electrons.

Each mobility σ_i for $i = 1, 2$ has been given in (14) and (16) as a function of u_i, but it can finally be considered as a function of v_i as it will be detailed below. Similarly, the function r_i^Γ appearing in the boundary conditions introduced in Section 1.2 can be written as functions of the chemical and electro-chemical potentials of the form (18a).

2.2. Assumptions on the data.
We give here in details the hypotheses we assume throughout the paper.

(H_1) $\lambda > 0$, $\rho_{hl} \in \mathbb{R}$ and for $\Gamma \in \{0, 1\}$, $\beta^\Gamma > 0$ and $f^\Gamma \in \mathbb{R}$.

(H_2) The densities are related to the chemical potentials through

$$u_i = \bar{u}_i e_i(v_i) \quad \text{for } i = 1, 2,$$

where the functions e_i are defined on $\mathbb{R}$ by

$$e_1(z) = \frac{e^z}{1 + e^z} \quad \text{and} \quad e_2(z) = e^z$$

and the reference densities $\bar{u}_1, \bar{u}_2$ are positive numbers.

(H_3) The mobilities are related to the chemical potentials through $\sigma_i(v_i) = d_i \bar{u}_i e_i'(v_i)$ with $d_i > 0$ for $i = 1, 2$. This means that

$$\sigma_1(z) = d_1 \bar{u}_1 \frac{e^z}{(1 + e^z)^2} \quad \text{and} \quad \sigma_2(z) = d_2 \bar{u}_2 e^z.$$

(H$_4$) The positive functions $r_i^\Gamma : \mathbb{R} \to (0, +\infty)$, for $i = 1, 2$ and $\Gamma \in \{0, 1\}$, are defined by

$$\begin{cases} r_1^\Gamma(v_1) = \kappa_1^\Gamma \overline{u}_1 \dfrac{e^{\frac{1}{2}v_1}}{1 + e^{v_1}}, \ \Gamma \in \{0, 1\}, \\[2ex] r_2^0(v_2) = \kappa_2^0 \sqrt{\overline{u}_2} e^{\frac{1}{2}v_2}, \\[2ex] r_2^1(v_2) = \kappa_2^1 \overline{u}_2 e^{v_2}, \end{cases}$$

with κ_i^Γ positive constants. The outer electro-chemical potentials ξ_i^Γ for $i = 1, 2$ and $\Gamma \in \{0, 1\}$ are given real numbers. The functions g_i^Γ for $i = 1, 2$ and $\Gamma \in \{0, 1\}$ are respectively defined by

(21)
$$\begin{cases} g_1^\Gamma(y) = \sinh\left(\dfrac{y}{2}\right), \ \Gamma \in \{0, 1\}, \\[2ex] g_2^0(y) = \sinh\left(\dfrac{y}{2}\right), \\[2ex] g_2^1(y) = 1 - e^{-y}. \end{cases}$$

Note that all the functions g_i^Γ are increasing and vanish at 0 so that (7) holds true.

(H$_5$) The initial profiles u_i^{in}, $0 \le i \le 2$, are such that

$$u_0^{\mathrm{in}} = \sum_{i=1,2} z_i u_i^{\mathrm{in}} + \rho_{\mathrm{hl}},$$

and such that the corresponding chemical potentials are bounded, *i.e.*,

$$v_i^{\mathrm{in}} = e_i^{-1}\left(\frac{u_i^{\mathrm{in}}}{\overline{u}_i}\right) \in L^\infty(0, 1), \quad \text{for } i = 1, 2.$$

This is equivalent to requiring that u_1^{in} is bounded away from 0 and $\overline{u}_1$, whereas u_2^{in} is bounded away from 0.

2.3. **Notion of solution.** In order to give a variational formulation to our system, we introduce the spaces

$$\begin{aligned} V &= H^1(0, 1) \times H^1(0, 1) \times H^1(0, 1), \\ H &= H^1(0, 1) \times L^2(0, 1) \times L^2(0, 1), \\ W &= H^1(0, 1) \times L^2(0, 1) \times L^\infty(0, 1), \end{aligned}$$

equipped with their standard norms. The system is to be regarded as an initial boundary value problem for the main unknown vector (v_0, v_1, v_2) of potentials and the corresponding dual vector (u_0, u_1, u_2) of densities. Then we introduce the operators $E : W \to H^*$ and $A : H \times V \to V^*$ (where X^* is the topological dual space of X) defined by:

$$\langle Ew, \tilde{v} \rangle = \int_0^1 \left(\lambda^2 \partial_x w_0 \partial_x \tilde{v}_0 + \sum_{i=1,2} \overline{u}_i e_i(w_i) \tilde{v}_i \right) dx + \sum_{\Gamma \in \{0,1\}} \left[(\beta^\Gamma w_0 - f^\Gamma) \tilde{v}_0 \right] (\Gamma),$$

$$\langle A(w, v), \tilde{v} \rangle = \sum_{i=1,2} \int_0^1 \sigma_i(w_i) \partial_x \xi_i \partial_x \tilde{\xi}_i dx + \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma(w_i) g_i^\Gamma(\xi_i - \xi_i^\Gamma) \tilde{\xi}_i \right] (\Gamma),$$

where $w = (w_0, w_1, w_2) \in H$, $v = (v_0, v_1, v_2) \in V$, $\tilde{v} = (\tilde{v}_0, \tilde{v}_1, \tilde{v}_2) \in V$,

$$\xi_i = z_i v_0 + v_i \quad \text{and} \quad \tilde{\xi}_i = z_i \tilde{v}_0 + \tilde{v}_i, \quad \text{for } i = 1, 2.$$

Then, the weak formulation of problem (17), (18) reads

$$(P) \quad \begin{cases} \text{Find } (u, v) \text{ such that} \\ u \in H^1_{\text{loc}}(\mathbb{R}_+; V^*), \quad v \in L^2_{\text{loc}}(\mathbb{R}_+; V) \cap L^\infty_{\text{loc}}(\mathbb{R}_+ \times [0, 1]), \\ \dot{u}(t) + A(v(t), v(t)) = 0, \quad u(t) = Ev(t), \text{ for a.e. } t \in \mathbb{R}_+, \quad u(0) = u^{\text{in}}. \end{cases}$$

Remark 2.1. Standard arguments show that if (u, v) is a pair of smooth functions, then (u, v) solves (P) if and only if it satisfies (17)–(20). More precisely, on the one hand, the condition $u = Ev$ expresses both the relations $u_i = \bar{u}_i e_i(v_i)$ for $i = 1, 2$ as well as the boundary value problem (17c), (18b) relating the electrostatic potential v_0 to the charge density. On the other hand, $\dot{u} + A(v, v) = 0$ is a weak formulation of the advection diffusion equations (17a), (17b), (18a). Moreover, if (u, v) solves (P), testing $\dot{u} + A(v, v) = 0$ against the functions of the form $\tilde{w} = (y_0, -z_1 y_0, -z_2 y_0)$ for $y_0 \in C^1_c(0, 1)$, we obtain

$$\partial_t \left(u_0 - \sum_{i=1,2} z_i u_i \right) = 0 \quad \text{in } \mathcal{D}'(\mathbb{R}_+ \times (0, 1)).$$

Using the initial condition, we get that any solution (u, v) to (P) satisfies

$$u_0 = \sum_{i=1,2} z_i u_i + \rho_{\text{hl}}.$$

The aim of this paper is to prove an existence result for problem (P):

Theorem 2.2. *Under assumptions* (H_1)–(H_5), *there exists at least one solution to problem* (P).

Uniqueness is so far an open problem. A natural yet not straightforward approach would consist in extending to our context the method proposed in [17].

3. FREE ENERGY AND A PRIORI ESTIMATES

Before going into the details of the proof of Theorem 2.2, we give in this section an explicit expression for the total free energy, assuming that a solution to problem (P) exists. Then we show that our model is thermodynamically consistent in the sense that the free energy of a solution decreases over time. Furthermore, this leads to some *a priori* estimates for the solution which turn to be crucial in the proof. To this end we follow some ideas from [21]. Define

$$\varphi_i(v) = \int_0^v e_i(y) dy \quad \text{for } v \in \mathbb{R}, \ i = 1, 2,$$

and

$$\psi_i(u) = \int_{e_i(0)}^u e_i^{-1}(z) dz \quad \text{for } u \in [0, 1] \text{ if } i = 1 \text{ and } u \geq 0 \text{ if } i = 2.$$

For the specific choice of nonlinearities of (H_2), this provides

$$\begin{cases} \varphi_1(v) = \log(1 + e^v) - \log 2, \\ \psi_1(u) = u \log u + (1 - u) \log(1 - u) + \log 2, \end{cases} \quad \text{and} \quad \begin{cases} \varphi_2(v) = e^v - 1, \\ \psi_2(u) = u \log u - u + 1. \end{cases}$$

The non-negative convex functions ψ_i satisfy $\psi_1(1/2) = \psi_2(1) = 0$ and are extended by $+\infty$ outside of their domain of definition.

We define the Landau free energy of $v \in V$ by

$$\Phi(v) = \int_0^1 \left(\frac{\lambda^2}{2} |\partial_x v_0|^2 + \sum_{i=1,2} \overline{u}_i \varphi_i(v_i) \right) dx + \sum_{\Gamma \in \{0,1\}} \left(\frac{\beta^\Gamma}{2} v_0^2 - f^\Gamma v_0 \right) (\Gamma).$$

Its conjugate, the Helmholtz free energy, is defined for $u \in V^*$ by

$$\Psi(u) = \sup_{v \in V} \left\{ \langle u, v \rangle - \Phi(v) \right\},$$

where $\langle \, , \, \rangle$ stands for the duality pairing of V^* and V.

Note that if $\varphi_i(v_i)$, $i = 1, 2$, are not in L^1, the values $\Phi(v)$ and $\Psi(u)$ are interpreted as $+\infty$. Moreover, Φ and Ψ turn out to be strictly convex functionals and $\Phi(0) = 0$, hence for every $v \in V$ the subdifferential of Φ contains at most one element. More precisely one checks that $\partial \Phi = \{Ev\}$. Then standard computations show that

$$(22) \qquad \Psi(u) = \int_0^1 \left(\frac{\lambda^2}{2} |\partial_x v_0^*|^2 + \sum_{i=1,2} \overline{u}_i \psi_i \left(\frac{u_i}{\overline{u}_i} \right) \right) dx + \sum_{\Gamma \in \{0,1\}} \left[\frac{\beta^\Gamma}{2} |v_0^*|^2 \right] (\Gamma),$$

with v_0^* solving the Poisson equation with Robin-Fourier boundary conditions

$$\lambda^2 \int_0^1 \partial_x v_0^* \partial_x \tilde{v} \, dx + \sum_{\Gamma \in \{0,1\}} \left[(\beta^\Gamma v_0^* - f^\Gamma) \, \tilde{v} \right] (\Gamma) = \int_0^1 u_0 \tilde{v} \, dx, \quad \forall \tilde{v} \in H^1(0,1).$$

The Helmholtz free energy of an isolated system is expected to be a Lyapunov functional. Here, we have fluxes across the interfaces $\Gamma \in \{0,1\}$ which may contribute positively to the variations of $\Psi(u)$. In order to get an isolated system (and hence a Lyapunov functional), then one introduces some very elementary model for the charge carriers leaving the oxide. More precisely, we assign the energy ξ_1^0 (resp. ξ_1^1) to each unit of cations entering the solution (resp. the metal) from the oxide. Similarly the energy of one unit of electrons leaving the oxide is set to ξ_2^Γ, $\Gamma \in \{0,1\}$. Therefore the free energy associated to elements leaving the oxide layer to the solution and the metal are respectively defined by

$$\Psi^\Gamma(t) = \sum_{i=1,2} \int_0^t \left[(J_i \cdot \nu^\Gamma) \xi_i^\Gamma \right] (\Gamma) d\tau, \qquad \Gamma \in \{0,1\}.$$

Finally, the total free energy Ψ^{tot} is given by

$$(23) \qquad \Psi^{\text{tot}}(t) = \Psi(u(t)) + \sum_{\Gamma \in \{0,1\}} \Psi^\Gamma(t).$$

We prove in the following proposition the decay of the total free energy Ψ^{tot} over time. This estimate, which encodes the second principle of thermodynamics, is the key *a priori* estimate on which our analysis builds. Here and in what follows, the space $H^1(0,1)$ is equipped with the norm

$$(24) \qquad \|w\|_{H^1(0,1)} = \left(\int_0^1 |\partial_x w|^2 dx + \sum_{\Gamma \in \{0,1\}} |w(\Gamma)|^2 \right)^{1/2}.$$

Proposition 3.1. *Assume that* (H_1)–(H_5) *hold and let* (u, v) *be a solution of problem* (P). *For* $0 \leq s \leq t$,

$$\Psi^{tot}(t) - \Psi^{tot}(s) = - \sum_{i=1,2} \int_s^t \int_0^1 \sigma_i(v_i) |\partial_x \xi_i|^2 dx d\tau$$

$$- \sum_{i=1,2} \int_s^t \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma(v_i) g_i^\Gamma(\xi_i - \xi_i^\Gamma)(\xi_i - \xi_i^\Gamma) \right] (\Gamma) d\tau.$$

In particular, there holds

$$(25) \qquad \Psi^{tot}(t) \leq \Psi^{tot}(s) \leq \Psi(0) < \infty.$$

As a consequence, for all $T > 0$, *there exists* $c_T > 0$ *depending on the data of the problem and on* T *such that*

$$(26) \qquad \|v_0\|_{L^\infty((0,T);H^1(0,1))} + \sum_{i=1,2} \left\| \psi_i \left(\frac{u_i}{\overline{u}_i} \right) \right\|_{L^\infty((0,T);L^1(0,1))} \leq c_T.$$

In particular this implies that $u_i/\overline{u}_i$ *belongs to the domain of* ψ_i *for almost every* (x, t), *i.e.* $0 \leq u_1 \leq \overline{u}_1$ *and* $u_2 \geq 0$.

Proof. Let (u, v) be a solution to problem (P). Then for almost every $t \in \mathbb{R}_+$,

$$u(t) = Ev(t) \in \partial \Phi(v(t)),$$

which is equivalent to

$$v(t) \in \partial \Psi(u(t))$$

since Φ and Ψ are the Legendre transform of each other. Thus, for $0 \leq s \leq t$,

$$\Psi(u(t)) - \Psi(u(s)) = \int_s^t \langle \dot{u}(\tau), v(\tau) \rangle \, d\tau = - \int_s^t \langle A(v(\tau), v(\tau)), v(\tau) \rangle \, d\tau$$

and consequently due to the definition (23) of Ψ^{tot}

$$(27) \qquad \Psi^{tot}(t) - \Psi^{tot}(s) = - \sum_{i=1,2} \int_s^t \int_0^1 \sigma_i(v_i) |\partial_x \xi_i|^2 dx d\tau$$

$$- \sum_{i=1,2} \int_s^t \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma(v_i) g_i^\Gamma(\xi_i - \xi_i^\Gamma)(\xi_i - \xi_i^\Gamma) \right] (\Gamma) d\tau \leq 0,$$

thanks to (7). Also note that $\Psi^{tot}(t)$ is finite for every $t \in \mathbb{R}_+$ when (u, v) is a solution of (P) since $\Psi^{tot}(0) = \Psi(u^{in})$ is finite thanks to Assumption (H_5), then we obtain the validity of (25). Then one readily checks (calculations are detailed in the time discrete case in Section 4, see (47)) that the Helmholtz free energy corresponding to the oxide layer only remains bounded, but not uniformly w.r.t. time, *i.e.* $\Psi(u(t)) \leq c_T$ for $t \in [0, T]$. This implies (26) in view of (22). $\qquad \square$

4. EXISTENCE RESULT FOR A REGULARIZED PROBLEM (P_M)

In order to obtain the existence result for problem (P) stated in Theorem 2.2, we first introduce a regularized problem. It is denoted by (P_M) and it is obtained from (P) by cutting off all the nonlinearities applied to the chemical potentials v_1, v_2 at a certain level M. This section is devoted to the solvability of such a regularized problem, which is given in Proposition 4.1. Via a discretization of time, we construct a sequence of approximate solutions to problem (P_M). Then, accurate a priori estimates and compactness arguments ensure the existence of at least one solution to problem (P_M).

In the next section, for such a solution, several a priori estimates will be proved independently on the level M. Consequently, a solution to (P_M) will be also a solution to (P) when choosing the level M sufficiently large.

This technique was originally introduced in a series of seminal papers by Gajewski and Gröger [18, 19, 20]. The main differences with respect to those works consist in a different expression of the total free energy and in the presence of nonlinear Robin boundary conditions we have to deal with. Let $M > 0$ be a fixed parameter chosen large enough to ensure

$$(28) \qquad M \geq \max_{i=1,2} \|v_i^{\text{in}}\|_{L^\infty(0,1)}.$$

We introduce the usual truncation function at level M given by

$$T_M(z) = \max(-M, \min(M, z)) = \begin{cases} z & \text{if } |z| \leq M, \\ \pm M & \text{if } \pm z > M. \end{cases}$$

We also define by $E_M : H \to H^*$ and $A_M : H \times V \to V^*$ the operators defined by

$$\langle E_M v, \tilde{v} \rangle = \int_0^1 \left(\lambda^2 \partial_x v_0 \partial_x \tilde{v}_0 + \sum_{i=1,2} \overline{u}_i e_i(T_M v_i) \tilde{v}_i \right) dx + \sum_{\Gamma \in \{0,1\}} \left[(\beta^\Gamma v_0 - f^\Gamma) \tilde{v}_0 \right] (\Gamma)$$

and

$$(29) \quad \langle A_M(w,v), \tilde{v} \rangle = \int_0^1 \sum_{i=1,2} \sigma_i(T_M w_i) \partial_x \xi_i \partial_x \tilde{\xi}_i \, dx + \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma(T_M w_i) g_i^{\Gamma,\mu}(\xi_i - \xi_i^\Gamma) \tilde{\xi}_i \right] (\Gamma),$$

where $\xi_i = z_i v_0 + v_i$ and $\tilde{\xi}_i = z_i \tilde{v}_0 + \tilde{v}_i$, $i = 1, 2$. For technical reasons that will appear later on in the proof, we also have to modify the nonlinear Robin boundary conditions (21). More precisely, for $i = 1, 2$ and $\mu > 0$ (yet another parameter to be tuned later on), $g_i^{\Gamma,\mu}$ denotes the following approximation of g_i^Γ:

$$(30) \qquad g_i^{\Gamma,\mu}(\xi) = \begin{cases} g_i^\Gamma(\xi) & \text{if } |\xi| \leq \mu, \\ g_i^\Gamma(\pm\mu) + (\xi \mp \mu)(g_i^\Gamma)'(\mu) & \text{if } \pm \xi > \mu. \end{cases}$$

where the functions g_i are the ones introduced in (H$_4$). The functions $g_i^{\Gamma,\mu}$ turns out to be Lipschitz continuous functions coinciding with g_i on the interval $[-\mu; \mu]$ and being linear outside of it. Since g_1^Γ and g_2^0 are even functions, $g_1^{\Gamma,\mu}$ and $g_2^{0,\mu}$ belong to $C^1(\mathbb{R})$, while $g_2^{1,\mu}$ is merely $C^{0,1}(\mathbb{R})$. Then for some arbitrary finite time horizon $T > 0$, our regularized problem writes

$$(P_M) \qquad \begin{cases} \text{Find } (u,v) \text{ such that} \\[4pt] u \in H^1((0,T); V^*), \quad v \in L^2((0,T); V), \\[4pt] \dot{u}(t) + A_M(v(t), v(t)) = 0, \quad u(t) = E_M v(t), \text{ for a.e. } t \in (0,T), \quad u(0) = u^{\text{in}}. \end{cases}$$

The next result provides the existence of (at least) one solution, still denoted by (u,v), to problem (P_M).

Proposition 4.1. *Under assumptions* (H_1)–(H_5) *and if*

$$
\mu \leq M - \max_{i=1,2} \left(|z_i|c_1 + |\xi_i^\Gamma| \right) \tag{31}
$$

with c_1 introduced hereafter in (48), then there exists a solution (u,v) to problem (P_M). Moreover, v_0 satisfies

$$
\|v_0\|_{L^\infty((0,T);H^1(0,1))} \leq c_1 \tag{32}
$$

and there exists $c_2 > 0$ depending on T and on the data but not on M such that

$$
\|\partial_x v_0\|_{L^\infty((0,T)\times(0,1))} \leq c_2. \tag{33}
$$

The remainder of this section is devoted to the proof of Proposition 4.1. We proceed in four steps. First we construct a sequence of time discrete approximations $(P_{M,n})_{n\geq 1}$ of problem (P_M), the solutions of which being denoted by $(u_n, v_n)_{n\geq 1}$. Then we derive some estimates for such solutions. In the third step we invoke compactness arguments to pass to the limit as $n \to +\infty$ and recover a time continuous solution (u,v) to model (P_M). The last step is devoted to the proof of the regularity estimate (33).

Step 1. Let us fix $T \in [0,+\infty)$ a finite but arbitrary time horizon, and set $I = (0,T]$. For $n \geq 1$, we define the time step $k_n = T/n$ and the time intervals $I_n^j = ((j-1)k_n, jk_n]$, for $j = 1,....,n$.

Given a Banach space X, we denote by $B_n(I;X)$ the space of functions $u : (0,T] \to X$ that are constant on each of the intervals I_n^j, $1 \leq j \leq n$. If $u \in B_n(I;X)$, we define $u^j \in X$ for $1 \leq j \leq n$ by $u = \sum u^j \mathbf{1}_{I_n^j}$. We introduce two mappings Δ_n and τ_n from $B_n(I;V^*)$ into itself defined by:

$$
(\Delta_n u)^j = \frac{1}{k_n}(u^j - u^{j-1}), \qquad (\tau_n u)^j = u^{j-1}, \qquad 1 \leq j \leq n,
$$

where $u^0 = u^{\text{in}}$ is the initial datum. We consider the discrete version of problem (P_M) corresponding to the time step k_n given by

$$(P_{M,n}) \qquad \Delta_n u_n + A_M(\tau_n v_n, v_n) = 0, \qquad u_n = E_M v_n, \quad v_n \in B_n(I;V).$$

It can be written as

$$
\frac{1}{k_n}(u_n^j - u_n^{j-1}) + A_M(v_n^{j-1}, v_n^j) = 0, \quad u_n^j = E_M v_n^j, \quad 1 \leq j \leq n, \quad u_n^0 = u^{\text{in}}. \tag{34}
$$

Thanks to arguments similar to those of Remark 2.1, there holds

$$
u_{n,0} = \sum_{i=1,2} z_i u_{n,i} + \rho_{\text{hl}}. \tag{35}
$$

The following lemma is about the well-posedness of problem $(P_{M,n})$.

Lemma 4.2. *Under assumptions* (H_1)–(H_5), *for any $M > 0$, for every $n \geq 1$, there exists a unique solution (u_n, v_n) to the problem $(P_{M,n})$.*

Proof. We use some known results on monotone operators [7, Corollaire 17] (see also [28, 8]). Let us fix $y \in H$ and define the operator $F : V \to V^*$ by

$$
F(v) = \frac{1}{k_n} E_M v + A_M(y,v).
$$

If such operator F is strongly monotone, *i.e.* if there exists $\alpha > 0$ such that

$$\langle F(v) - F(w), v - w \rangle \geq \alpha \|v - w\|^2, \qquad \forall \, v, w \in V,$$

then all the equations (34) are uniquely solvable, considered as equations with respect to v_n^j for given v_n^{j-1} (and u_n^{j-1}). This gives the unique solvability of our problem $(P_{M,n})$.

Let us check the strong monotonicity of F. Let $v, w \in V$, we compute

$$\langle F(v) - F(w), v - w \rangle$$

$$= \frac{1}{k_n} \int_0^1 \left(\lambda^2 |\partial_x(v_0 - w_0)|^2 + \sum_{i=1,2} \overline{u}_i(v_i - w_i)[e_i(T_M v_i) - e_i(T_M w_i)] \right) dx$$

$$+ \frac{1}{k_n} \sum_{\Gamma \in \{0,1\}} \left[\beta^\Gamma (v_0 - w_0)^2 \right](\Gamma) + \int_0^1 \sum_{i=1,2} \sigma_i(T_M y_i)|\partial_x(z_i(v_0 - w_0) + (v_i - w_i))|^2 \, dx$$

$$+ \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left\{ r_i^\Gamma(T_M y_i)(z_i(v_0 - w_0) + (v_i - w_i)) \right.$$

$$\left. \times \left[g_i^{\Gamma,\mu}((z_i v_0 + v_i) - \xi_i^\Gamma) - g_i^{\Gamma,\mu}((z_i w_0 + w_i) - \xi_i^\Gamma) \right] \right\}(\Gamma).$$

Using the monotonicity of the functions e_i together with the fact that

$$(x_1 - x_2)(g_i^{\Gamma,\mu}(x_1) - g_i^{\Gamma,\mu}(x_2)) \geq |x_1 - x_2|^2, \qquad x_1, x_2 \in \mathbb{R},$$

we get:

$$\langle F(v) - F(w), v - w \rangle \geq \frac{1}{k_n} \int_0^1 \lambda^2 |\partial_x(v_0 - w_0)|^2 dx + \frac{1}{k_n} \sum_{\Gamma \in \{0,1\}} \left[\beta^\Gamma (v_0 - w_0)^2 \right](\Gamma)$$

$$+ \sum_{i=1,2} \int_0^1 \sigma_i(T_M y_i)|\partial_x(z_i(v_0 - w_0) + (v_i - w_i))|^2 dx$$

$$+ \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma(T_M y_i)|z_i(v_0 - w_0) + (v_i - w_i)|^2 \right](\Gamma).$$

Moreover, defining $c > 0$ as $c = \min(\lambda^2, \min_{\Gamma \in \{0,1\}} \beta^\Gamma)$ and using that the functions $y \mapsto \sigma_i(T_M y)$ and $y \mapsto r_i^\Gamma(T_M y)$ are bounded from below by some positive constant c_M depending only on the data of the continuous problem and on M, we deduce:

$$(36) \qquad \langle F(v) - F(w), v - w \rangle \geq \frac{c}{k_n} \|v_0 - w_0\|_{H^1(0,1)}^2 + c_M \sum_{i=1,2} \|z_i(v_0 - w_0) + (v_i - w_i)\|_{H^1(0,1)}^2.$$

For $i = 1, 2$, we notice that the following alternative holds:

- either $\|z_i(v_0 - w_0)\|_{H^1(0,1)} \leq \frac{1}{2}\|v_i - w_i\|_{H^1(0,1)}$, which implies, by triangular inequality,

$$\|z_i(v_0 - w_0) + (v_i - w_i)\|_{H^1(0,1)}^2 \geq \frac{1}{4}\|v_i - w_i\|_{H^1(0,1)}^2,$$

- or $\|z_i(v_0 - w_0)\|_{H^1(0,1)} > \frac{1}{2}\|v_i - w_i\|_{H^1(0,1)}$, so that

$$\|v_0 - w_0\|_{H^1(0,1)}^2 \geq \frac{1}{4|z_i|^2}\|v_i - w_i\|_{H^1(0,1)}^2.$$

Therefore, we obtain

$$\langle F(v) - F(w), v - w \rangle \geq \frac{c}{2k_n} \|v_0 - w_0\|_{H^1(0,1)}^2 + \sum_{i=1,2} \min(\frac{c_M}{4}, \frac{c}{8k_n|z_i|^2}) \|v_i - w_i\|_{H^1(0,1)}^2.$$

This proves the strong monotonicity of F and therefore the lemma. $\qquad\square$

Step 2. With the sequence $(u_n, v_n)_{n \geq 1}$ at hand, we derive some estimates, uniform w.r.t. n.

Lemma 4.3. *Assume that assumptions* (H_1)–(H_5) *hold true. Let* $n \geq 1$, *and let* (u_n, v_n) *be the unique solution to problem* $(P_{M,n})$ *given by Lemma 4.2. We define*

$$U_n(t) = u^{\mathrm{in}} + \int_0^t (\Delta_n u_n)(s)\, ds, \quad 0 \leq t \leq T,$$

with $\Delta_n u_n(s) = u_n(s) - u_n(s - k_n)$ *for* $s \in (k_n, T]$ *and* $\Delta_n u_n = u_n(s) - u^{\mathrm{in}} = u_n^1 - u^{\mathrm{in}}$ *for* $s \in (0, k_n]$
(U_n *is the piecewise affine extension on I of* $jk_n \mapsto u_n^j$*).*
   There exists $c_{M,T} \geq 0$ *depending on M and T but not on n such that*

$$\sup_{n \in \mathbb{N}} \left\{ \|v_n\|_{L^2(I;V)} + \|\Delta_n u_n\|_{L^2(I;V^*)} + \|U_n\|_{C(I;V^*)} \right\} \leq c_{M,T}.$$

Proof. Along the proof $c \geq 0$ is a constant that may depend on the data but not on n or M and whose value may change from line to line. Similarly we denote by c_M, c_T, $c_{M,T}$ the constants that may depend on M, T or both.
Let us set

$$\varphi_{i,M}(v) = \int_0^v e_i(T_M y)\,dy, \quad v \in \mathbb{R},$$

and then let us define the functionals Φ_M and Ψ_M by

$$\Phi_M(v) = \int_0^1 \left(\frac{\lambda^2}{2}|\partial_x v_0|^2 + \sum_{i=1,2} \overline{u}_i \varphi_{i,M}(v_i) \right) dx + \sum_{\Gamma \in \{0,1\}} \left[\frac{\beta^\Gamma}{2}v_0^2 - f^\Gamma v_0 \right](\Gamma), \quad \text{for } v \in V,$$

and

$$\Psi_M(u) = \sup_{v \in V}\{\langle u, v \rangle - \Phi_M(v)\}, \quad \text{for } u \in V^*.$$

Notice that Φ_M is continuous, convex and coercive. Testing (34) with v_n^j, for $1 \leq j \leq n$, provides

$$(37) \qquad \langle u_n^j - u_n^{j-1}, v_n^j \rangle + k_n \langle A_M(v_n^{j-1}, v_n^j), v_n^j \rangle = 0.$$

Since $v_n^j \in \partial\Psi_M(u_n^j)$ (which is equivalent to $u_n^j \in \partial\Phi_M(v_n^j)$), and since Ψ_M is convex, there holds

$$(38) \qquad \Psi_M(u_n^{j-1}) \geq \Psi_M(u_n^j) + \langle u_n^{j-1} - u_n^j, v_n^j \rangle \overset{(37)}{=} \Psi_M(u_n^j) + k_n \langle A_M(v_n^{j-1}, v_n^j), v_n^j \rangle.$$

Moreover, $\Phi_M \leq \Phi$ hence $\Psi_M \geq \Psi$, and $\Psi_M(u^{\mathrm{in}}) = \Psi(u^{\mathrm{in}})$ when M is large enough, *i.e.* under condition (28). Therefore, summing the estimates, we deduce:

$$\Psi(u_n^J) + \sum_{j=1}^J k_n \langle A_M(v_n^{j-1}, v_n^j), v_n^j \rangle \leq \Psi(u^{\mathrm{in}}), \qquad J \in \{1, \dots, n\}.$$

Due to the boundary conditions, $\langle A_M(v, v), v \rangle$ might be negative. To circumvent this difficulty and as in Section 3, we introduce the total free energy taking into account the energy of the charge carriers that left the domain over time. For $j \in \{1, \dots, n\}$, define

$$\Psi_M^{\mathrm{tot},j} = \Psi_M(u_n^j) + \mathcal{J}_n^j$$

with

$$\mathcal{J}_n^j = \sum_{\ell=1}^j k_n \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma (T_M v_{n,i}^{\ell-1}) g_i^{\Gamma,\mu} (\xi_{n,i}^\ell - \xi_i^\Gamma) \xi_i^\Gamma \right] (\Gamma), \qquad 1 \le j \le n,$$

then one checks, using the definition of Ψ_M^{tot}, (38) and the definition of A_M that

$$\Psi_M^{\text{tot},j} - \Psi_M^{\text{tot},j-1} = \Psi_M(u_n^j) - \Psi_M(u_n^{j-1}) + k_n \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma (T_M v_{n,i}^{j-1}) g_i^{\Gamma,\mu} (\xi_{n,i}^j - \xi_i^\Gamma) \xi_i^\Gamma \right] (\Gamma)$$

$$\overset{(38)}{\le} -k_n \left\langle A_M (v_n^{j-1}, v_n^j), v_n^j \right\rangle$$

$$+ k_n \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma (T_M v_{n,i}^{j-1}) g_i^{\Gamma,\mu} (\xi_{n,i}^j - \xi_i^\Gamma) \xi_i^\Gamma \right] (\Gamma)$$

$$\overset{(29)}{\le} -k_n \sum_{i=1,2} \int_0^1 \sigma_i (T_M v_{n,i}^{j-1}) \left| \partial_x \xi_{n,i}^j \right|^2 dx$$

$$- k_n \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma (T_M v_{n,i}^{j-1}) g_i^{\Gamma,\mu} (\xi_{n,i}^j - \xi_i^\Gamma) \left(\xi_{n,i}^j - \xi_i^\Gamma \right) \right] (\Gamma).$$

The two terms in the right-hand side being non-positive, this leads to the following estimates, which are uniform w.r.t. n:

$$\max_{1 \le j \le n} \Psi^{\text{tot},j} \le \Psi(u^{\text{in}}), \tag{39}$$

$$0 \le \sum_{\ell=1}^j k_n \sum_{i=1,2} \int_0^1 \sigma_i (T_M v_{n,i}^{\ell-1}) \left| \partial_x \xi_{n,i}^\ell \right|^2 dx \le \Psi(u^{\text{in}}), \tag{40}$$

$$0 \le \sum_{\ell=1}^j k_n \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma (T_M v_{n,i}^{\ell-1}) g_i^{\Gamma,\mu} (\xi_{n,i}^\ell - \xi_i^\Gamma) \left(\xi_{n,i}^\ell - \xi_i^\Gamma \right) \right] (\Gamma) \le \Psi(u^{\text{in}}). \tag{41}$$

Since $\Psi^{\text{tot},j}$ can be negative due to the boundary flux contributions, some further work on (39) is needed to get some bound on $\Psi(u_{n,i}^j)$. Testing (34) with $(0, \hat{\xi}_1, \hat{\xi}_2)$ where $\hat{\xi}_i$ is defined for $i = 1, 2$ by $x \in [0,1] \mapsto \hat{\xi}_i(x) = \xi_i^0 + x(\xi_i^1 - \xi_i^0)$ (and then summing the first j time steps), we obtain

$$-\mathcal{J}_n^j = \sum_{i=1,2} \int_0^1 (u_{n,i}^j - u_i^{\text{in}}) \hat{\xi}_i dx + \sum_{\ell=1}^j k_n \sum_{i=1,2} (\xi_i^1 - \xi_i^0) \int_0^1 \sigma_i (T_M v_{n,i}^{\ell-1}) \partial_x \xi_{n,i}^\ell dx. \tag{42}$$

On the one hand, due to the Young-Fenchel inequality $ab \le \psi_i(a) + \varphi_i(b)$, there holds

$$\int_0^1 (u_{n,i}^j - u_i^{\text{in}}) \hat{\xi}_i dx \le \|u_i^{\text{in}}\|_1 \max_\Gamma |\xi_i^\Gamma| + \frac{1}{2} \int_0^1 \left[\psi_i(u_{n,i}^j) + \varphi_i(2\hat{\xi}_i) \right] dx.$$

Since the functions φ_i are non-negative, we deduce

$$\sum_{i=1,2} \int_0^1 (u_{n,i}^j - u_i^{\text{in}}) \hat{\xi}_i dx \le \frac{1}{2} \Psi(u_n^j) + c. \tag{43}$$

On the other hand, the elementary Young inequality $ab \leq (\varepsilon/2)a^2 + (1/2\varepsilon)b^2$ yields

$$(44) \quad \sum_{\ell=1}^{j} k_n \sum_{i=1,2} (\xi_i^1 - \xi_i^0) \int_0^1 \sigma_i(T_M v_{n,i}^{\ell-1}) \partial_x \xi_{n,i}^\ell dx$$

$$\leq \sum_{\ell=1}^{j} k_n \sum_{i=1,2} \sigma_i(T_M v_{n,i}^{\ell-1}) \left| \partial_x \xi_{n,i}^\ell \right|^2 dx + \sum_{\ell=1}^{j} k_n \sum_{i=1,2} \frac{(\xi_i^1 - \xi_i^0)^2}{4} \int_0^1 \sigma_i(T_M v_{n,i}^{\ell-1}) dx.$$

One directly infers from the boundedness of σ_1 that

$$(45) \qquad \sum_{\ell=1}^{j} k_n \frac{(\xi_1^1 - \xi_1^0)^2}{2} \int_0^1 \sigma_1(v_{n,1}^{\ell-1}) dx \leq cT.$$

Since $\sigma_2(T_M v_{n,2}^{\ell-1}) = d_2 u_{n,2}^{\ell-1} \leq \psi_2(u_{n,2}^{\ell-1}) + \varphi_2(d_2)$, we get

$$(46) \qquad \sum_{\ell=1}^{j} k_n \frac{(\xi_2^1 - \xi_2^0)^2}{2} \int_0^1 \sigma_2(v_{n,2}^{\ell-1}) dx \leq c \left(1 + \sum_{\ell=1}^{j} k_n \Psi(u_n^{\ell-1}) \right).$$

Collecting (39) and (42)–(46), we deduce, for $1 \leq j \leq n$,

$$\Psi(u_n^j) = \Psi^{\text{tot},j} - \mathcal{J}_n^j \leq \Psi(u^{\text{in}}) + c(1+T) + \frac{1}{2}\Psi(u_n^j) + \sum_{\ell=1}^{j} k_n \Psi(u_n^{l-1}).$$

Applying a discrete Gronwall lemma after having combined the above calculations, we obtain

$$(47) \qquad\qquad\qquad \Psi(u_n^j) \leq c_T.$$

We deduce from (47) the following estimates on (u_n, v_n) which are uniform with respect to n:

$$(48) \qquad\qquad\qquad \|v_{n,0}\|_{L^\infty(I;H^1(0,1))} \leq c_1,$$

$$(49) \qquad\qquad 0 < \overline{u}_1 e_1(-M) \leq u_{n,1} \leq \overline{u}_1 e_1(M) < \overline{u}_1,$$

$$(50) \qquad\qquad 0 < \overline{u}_2 e_2(-M) \leq u_{n,2} \leq \overline{u}_2 e_2(M) < +\infty.$$

With these bounds on $u_{n1}, u_{n,2}$ and the definitions of the functions r_i^Γ and g_i^Γ, we deduce from (40) and (41) that

$$\|\xi_{n,i}\|_{L^2(I;H^1(0,1))} \leq c_M.$$

Note that the four above estimates are uniform w.r.t. n, and that the quantity c_1 appearing in (48) is the one appearing in the statement of Proposition 4.1. Besides, recalling $\xi_{n,i} = v_{n,i} + z_i v_{n,0}$ we get for $i = 1, 2$,

$$\|v_{n,i}\|_{L^2(I;H^1(0,1))} \leq c_{M,T}.$$

By continuity of $A_M : V \times V \to V^*$, we end up with

$$\|\Delta_n u_n\|_{L^2(I;V^*)} = \|A_M(v_n, v_n)\|_{L^2(I;V^*)} \leq c_{M,T},$$

and $U_n \in C(I;V^*)$ with the bound $\|U_n\|_{C(I;V^*)} \leq c_{M,T}$. $\qquad\qquad\qquad\qquad \square$

Step 3. The third step of the proof of Proposition 4.1 consists in showing the following lemma.

Lemma 4.4. *There exists a solution (u, v) to (P_M) such that, up to a subsequence,*

$$u_{n,i} \xrightarrow[n \to +\infty]{} u_i \quad \text{almost everywhere and in the } L^\infty(I \times (0,1))\text{-weak-}\star \text{ sense, for } i = 0, 1, 2,$$

$$v_{n,i} \xrightarrow[n \to +\infty]{} v_i \quad \text{weakly in } L^2(I; H^1(0,1)), \ i = 1, 2,$$

$$v_{n,0} \xrightarrow[n \to +\infty]{} v_0 \quad \text{strongly in } L^2(I; H^1(0,1)).$$

Moreover, there exists $c_T > 0$ not depending on M such that

$$\tag{51} \|\Psi(u)\|_{L^\infty(I)} \le c_T.$$

Proof. Let (u_n, v_n) be the unique solution to $(P_{M,n})$ given by Lemma 4.2. By Lemma 4.3 we have that, up to a subsequence, the following convergences hold as n goes to $+\infty$:

$$\tag{52} \begin{cases} v_{n,i} \rightharpoonup v_i & \text{weakly in } L^2(I; H^1(0,1)), \ i = 1, 2, \\ v_{n,0} \rightharpoonup v_0 & \text{in the } L^\infty(I; H^1(0,1))\text{-weak-}\star \text{ sense,} \\ U_n \rightharpoonup u & \text{weakly in } L^2(I; H^*) \text{ and } H^1(I; V^*), \\ U_n(t) \rightharpoonup u(t) & \text{weakly in } V^*, \text{ for every } t \in I, \\ \Delta_n u_n \rightharpoonup \dot{u} & \text{weakly in } L^2(I; V^*). \end{cases}$$

Note that, since $U_n(0) = u^{\text{in}}$, we have $u(0) = u^{\text{in}}$. Moreover, by definition of U_n we have

$$\tag{53} \|U_n - u_n\|_{L^2(I;V^*)} \le k_n \|\Delta_n u_n\|_{L^2(I;V^*)} \to 0, \quad \text{as } n \to +\infty.$$

Hence, for almost every t in I,

$$(U_n - u_n)(t) \xrightarrow[n \to +\infty]{} 0 \text{ in } V^* \quad \text{and} \quad u_n(t) \xrightarrow[n \to +\infty]{} u(t) \text{ weakly in } V^*.$$

By construction we have that

$$\tag{54} u_{n,i} = \bar{u}_i e_i(T_M v_{n,i}), \ i = 1, 2.$$

Then since $e_i \circ T_M$ are Lipschitz continuous, the bounds on $v_{n,i}$ ensure that $u_{n,i}$ are bounded in $L^2(I; H^1(0,1))$. We deduce then from the nonlinear Aubin-Simon compactness result [31, Proposition 1] that

$$\tag{55} u_{n,i} \to u_i \quad \text{almost everywhere in } I \times (0,1), \text{ with } u_i = \bar{u}_i e_i(T_M v_i), \ i = 1, 2,$$

which, thanks to (35), gives also $u_{n,0} \to u_0$ almost everywhere in $I \times (0,1)$ with

$$\tag{56} u_0 = \sum_{i=1,2} z_i u_i + \rho_{\text{hl}}.$$

Together with (49) and (50), this implies that

$$\tag{57} u_n \to u \quad \text{strongly in } L^2(I; L^2(0,1)) \text{ and } L^2(I; V^*),$$

due to the Lebesgue dominated convergence theorem, as well as in the $L^\infty((0,T) \times (0,1))$-weak-$\star$ sense. Moreover, in view of (53), one has

$$U_{n,i} \xrightarrow[n \to +\infty]{} u_i \text{ strongly in } L^2(I; (H^1(0,1))^*), \ i = 1, 2.$$

Since $u_{n,0} = (E_M v_n)_0$, one has

$$(58) \qquad \lambda^2 \int_0^1 \partial_x v_{n,0} \partial_x \tilde{v} dx + \sum_{\Gamma \in \{0,1\}} \left[\left(\beta^\Gamma v_{n,0} - f^\Gamma \right) \tilde{v} \right] (\Gamma) = \int_0^1 u_{n,0} \tilde{v} dx, \qquad \forall \tilde{v} \in H^1(0,1).$$

The aforementioned convergence properties are sufficient to pass to the limit $n \to +\infty$ in the above equality, leading to

$$(59) \qquad \lambda^2 \int_0^1 \partial_x v_0 \partial_x \tilde{v} dx + \sum_{\Gamma \in \{0,1\}} \left[\left(\beta^\Gamma v_0 - f^\Gamma \right) \tilde{v} \right] (\Gamma) = \int_0^1 u_0 \tilde{v} dx, \qquad \forall \tilde{v} \in H^1(0,1),$$

or equivalently $u_0 = (E_M v)_0$. Choosing $\tilde{v} = v_{n,0}$ as a test function in (58) and passing to the limit $n \to +\infty$ provides

$$\lambda^2 \int_0^T \int_0^1 |\partial_x v_{n,0}|^2 \, dx dt + \int_0^T \sum_{\Gamma \in \{0,1\}} \beta^\Gamma |v_{n,0}|^2 \, dt$$

$$= \int_0^T \int_0^1 u_{n,0} v_{n,0} dx dt + \int_0^T \sum_{\Gamma \in \{0,1\}} f^\Gamma v_{n,0} dt$$

$$\xrightarrow[n \to +\infty]{} \int_0^T \int_0^1 u_0 v_0 dx dt + \int_0^T \sum_{\Gamma \in \{0,1\}} f^\Gamma v_0 dt$$

$$= \lambda^2 \int_0^T \int_0^1 |\partial_x v_0|^2 \, dx dt + \int_0^T \sum_{\Gamma \in \{0,1\}} \beta^\Gamma |v_0|^2 \, dt$$

thanks to (59). As a consequence, $\|v_{n,0}\|_{L^2(I;H^1(0,1))}$ tends to $\|v_0\|_{L^2(I;H^1(0,1))}$, whence

$$(60) \qquad v_{n,0} \xrightarrow[n \to +\infty]{} v_0 \quad \text{strongly in } L^2(I;H^1(0,1)).$$

Next, due to (55) and to (60) combined with (49) and (50), one gets that

$$\Psi(u_n) \xrightarrow[n \to +\infty]{} \Psi(u) \quad \text{in } L^1(I).$$

Due to (47), we infer that (51) holds true.

Finally we want to show that (u,v) is a solution to problem (P_M). First we prove that

$$(61) \qquad \lim_{n \to +\infty} A_M(\tau_n v_n, v_n) = A_M(v,v) \text{ in } L^2(I;V^*).$$

Taking a test function $\tilde{v} \in V$ and setting, for $i = 1,2$, $\xi_{n,i} = v_{n,i} + z_i v_{n,0}$, $\tilde{\xi}_i = \tilde{v}_i + z_i \tilde{v}_0$, we have

$$\langle A_M(\tau_n v_n, v_n), \tilde{v} \rangle = \sum_{i=1,2} \int_0^1 \sigma_i(T_M \tau_n v_{n,i}) \partial_x \xi_{n,i} \partial_x \tilde{\xi}_i dx$$

$$+ \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} \left[r_i^\Gamma(T_M \tau_n v_{n,i}) g_i^{\Gamma, \mu}(\xi_{n,i} - \xi_i^\Gamma) \tilde{\xi}_i \right] (\Gamma).$$

By (54), (57) and the properties of the translation operator function τ_n (see for instance [9, Lemma 4.3]) we have

$$T_M \tau_n v_{n,i} \to T_M v_i \text{ strongly in } L^2(I;L^2(0,1)) \text{ and in } L^2_{\text{loc}}(I;H^s(\Gamma)), \ i = 1,2, s > \frac{1}{2},$$

implying that

(62) $$\sigma_i(T_M\tau_n v_{n,i}) \to \sigma_i(T_M v_i) \text{ strongly in } L^2(I; L^2(0,1)),\ i = 1, 2,$$

since $\sigma_i \circ T_M$ is Lipschitz continuous, and

(63) $$r_i^\Gamma(T_M\tau_n v_{n,i}) \to r_i^\Gamma(T_M v_i) \text{ strongly in } L^2(I),\ i = 1, 2,\ \Gamma \in \{0,1\}$$

thanks to the trace theorem. Moreover, by (52) we obtain

(64) $$\xi_{n,i} \rightharpoonup \xi_i \text{ weakly in } L^2(I; H^1(0,1))$$

with $\xi_i = v_i + z_i v_0$. This, together with (62) and the uniform boundedness of $\sigma_i(T_M\tau_n v_{n,i})$ and $r_i^\Gamma(T_M\tau_n v_{n,i})$ for fixed M, gives

(65) $$\lim_{n\to+\infty} \sum_{i=1,2} \int_I \int_0^1 \sigma_i(T_M\tau_n v_{n,i})\partial_x\xi_{n,i}\partial_x\tilde\xi_i\,dxdt = \sum_{i=1,2} \int_I \int_0^1 \sigma_i(T_M v_i)\partial_x\xi_i\partial_x\tilde\xi_i\,dxdt.$$

We are now interested in the weak convergence of the term $g_i^{\Gamma,\mu}(\xi_{n,i} - \xi_i^\Gamma)$. The approximation $g_i^{\Gamma,\mu}$ of g_i^Γ has been tailored in (30) so that the function $g_i^{\Gamma,\mu,NL}$ defined by

$$g_i^{\Gamma,\mu,NL}(\xi) = g_i^{\Gamma,\mu}(\xi) - \left(g_i^{\Gamma,\mu}\right)'(\mu)\,\xi$$

is constant outside $[-\mu, \mu]$. In view of the uniform estimate (48) of $v_{n,0}$ and the one-dimensional Sobolev-Morrey inequality (recall the definition (24) of the $H^1(0,1)$-norm),

$$\|w\|_\infty \le \|w\|_{H^1(0,1)}, \qquad \forall w \in H^1(0,1),$$

there holds

$$\|v_{n,0}\|_\infty \le c_1, \qquad \forall n \ge 1.$$

Setting $\mu_i = M - z_i c_1 - |\xi_i^\Gamma|$ and $\mu \le \min_{i=1,2}\mu_i$, then $|\xi_{n,i} - \xi_i^\Gamma| \le \mu$ implies $|v_{n,i}| \le M$. Hence $g_i^{\Gamma,\mu}(\xi_{n,i} - \xi_i^\Gamma)$ can be written as the sum of a linear and a nonlinear functions as follows:

(66) $$g_i^{\Gamma,\mu}(\xi_{n,i} - \xi_i^\Gamma) = \left(g_i^{\Gamma,\mu}\right)'(\mu)\,(\xi_{n,i} - \xi_i^\Gamma) + g_i^{\Gamma,\mu,NL}(T_M v_{n,i} + z_i v_{n,0} - \xi_i^\Gamma).$$

By (64) we immediately get that

(67) $$\left(g_i^{\Gamma,\mu}\right)'(\mu)\,(\xi_{n,i} - \xi_i^\Gamma) \xrightarrow[n\to+\infty]{} \left(g_i^{\Gamma,\mu}\right)'(\mu)\,(\xi_i - \xi_i^\Gamma) \text{ weakly in } L^2(I).$$

As for the nonlinear one, from (55) and (60) we have that $T_M v_{n,i} + z_i v_{n,0}$ converges almost everywhere in $I \times (0,1)$ to $T_M v_i + z_i v_0$, for $i = 1, 2$. Whence, via the Lebesgue convergence dominated theorem we also obtain that

(68) $$g_i^{\Gamma,\mu,NL}(T_M v_{n,i} + z_i v_{n,0} - \xi_i^\Gamma) \xrightarrow[n\to+\infty]{} g_i^{\Gamma,\mu,NL}(T_M v_i + z_i v_0 - \xi_i^\Gamma) \text{ strongly in } L^2(I).$$

Combining (67) and (68) in (66) shows that

(69) $$g_i^{\Gamma,\mu}(\xi_{n,i} - \xi_i^\Gamma)) \xrightarrow[n\to+\infty]{} g_i^{\Gamma,\mu}(\xi_i - \xi_i^\Gamma)) \text{ weakly in } L^2(I).$$

Therefore, convergences (63) and (69) and the uniform boundedness of $r_i^\Gamma(T_M\tau_n v_{n,i})$ for fixed M lead to

$$(70) \quad \lim_{n\to+\infty} \sum_{i=1,2} \sum_{\Gamma\in\{0,1\}} \int_I \left[r_i^\Gamma(T_M\tau_n v_{n,i}) g_i^{\Gamma,\mu}(\xi_{n,i} - \xi_i^\Gamma)\tilde{\xi}_i \right](\Gamma)dt$$

$$= \sum_{i=1,2} \sum_{\Gamma\in\{0,1\}} \int_I \left[r_i^\Gamma(T_M\tau_n v_i) g_i^{\Gamma,\mu}(\xi_i - \xi_i^\Gamma)\tilde{\xi}_i \right](\Gamma)dt.$$

Then, by collecting (65) and (70), we obtain the validity of (61).

Moreover, since (u_n, v_n) is a solution to (P_{M_n}) we deduce from (52) and (61) that

$$\dot{u} + A_M(v,v) = \lim_{n\to+\infty}\{\Delta_n u_n + A_M(\tau_n v_n, v)\} = 0.$$

Eventually, due to (55) and (59), there holds $u = E_M v$, which concludes the proof of the lemma. □

Step 4. To establish Proposition 4.1, it only remains to prove the following.

Lemma 4.5. *Let (u,v) be as in Lemma 4.4. There exists $c_1 > 0$ and $c_2 > 0$ depending on the final time T and on the data of the continuous problem, but not on M, such that*

$$(71) \qquad\qquad \|v_0\|_{L^\infty(I;H^1(0,1))} \leq c_1$$

$$(72) \qquad\qquad and \ \|\partial_x v_0\|_{L^\infty(I\times(0,1))} \leq c_2.$$

Proof. The bound (71) is a direct consequence of the convergence results stated in the proof of Lemma 4.4 and of the estimate (48). We deduce from (56) and (59) that

$$-\lambda^2 \partial_{xx} v_0 = \sum_{i=1,2} z_i u_i + \rho_{\text{hl}}.$$

In view of (51), the right-hand side in the above equation is bounded uniformly w.r.t. M in $L^\infty(I;L^1(0,1))$. Therefore, $\partial_x v_0$ is bounded uniformly w.r.t. M in $L^\infty(I;W^{1,1}(0,1))$, which is continuously embedded in $L^\infty(I\times(0,1))$, hence (72). □

The proof of Proposition 4.1 is now complete.

5. Lower and upper bounds for the chemical potentials

Let (u,v) be a solution to problem (P_M). In this section we provide some $L^\infty_{\text{loc}}(\mathbb{R}_+ \times [0,1])$-estimates on v_i, $i = 1,2$, which are independent of M. As a consequence, by choosing the cutoff level sufficiently large, this will allow to prove that (u,v) is a solution to problem (P) too.

The proof is based on the Moser-Alikakos iteration technique, cf. [30, 1], which consists in establishing successively L^p-norms, for increasing values of p, of some appropriate functions of the chemical potentials.

We will first show an upper bound for v_2, then both lower bounds for v_1 and v_2, and finally an upper bound for v_1 in three separated theorems. The starting point of each bootstrapping procedure will be provided by estimating an appropriate L^2-bound to initialize the method.

In each part of the section, we use the identity

$$(73) \qquad\qquad \sigma_i(T_M v_i)\partial_x v_i \partial_x u_i = d_i(\partial_x u_i)^2$$

which holds almost everywhere on $I \times (0,1)$ and for $i = 1,2$. Indeed, on the one hand, from the chain rule and the identitities $u_i = \bar{u}_i e_i(T_M v_i)$ and $\sigma_i(z) = d_i \bar{u}_i e_i'(z)$ we have

$$(74) \qquad\qquad \sigma_i(T_M v_i)\partial_x[T_M v_i] = d_i\partial_x u_i.$$

On the other hand, since $\partial_x u_i = \partial_x[T_M v_i] = 0$ almost everywhere on $\{|v_i| \geq M\}$ and $\partial_x[T_M v_i] = \partial_x v_i$ almost everywhere else, there holds

$$\partial_x[T_M v_i]\partial_x u_i = \partial_x v_i \partial_x u_i. \tag{75}$$

Multiplying (74) by $\partial_x u_i$ and using (75) yields (73).

In the sequel, c will denote different positive constants independent of M.

5.1. Upper bound for v_2.

In order to get an upper bound for the chemical potential v_2, we first derive an upper bound for the density u_2 in the following theorem.

Theorem 5.1. *Under assumptions* (H_1)–(H_5), *let* (u, v) *a solution to problem* (P_M). *There exists a constant* $c > 0$ *independent on* M *such that*

$$\|u_2(t)\|_{L^\infty(0,1)} \leq c \quad \forall t \in I.$$

Proof. Let $p \geq 2$ and $w = (u_2 - k)_+$, where $k > 0$ will be fixed later. We use $(0, 0, pw^{p-1})$ as a test function in (P_M). We have $\dot{u}_2 \in L^2(I, [H^1(0,1)]^*)$ and $w \in L^2(I, H^1(0,1)) \cap L^\infty$, so, using a smoothing argument and classical properties of Sobolev spaces, there holds

$$\langle \dot{u}_2; pw^{p-1}\rangle_{(H^1)^*, H^1} = \langle \dot{w}; pw^{p-1}\rangle_{(H^1)^*, H^1} = \frac{d}{dt}\left[\int_0^1 w^p \, dx\right] \quad \text{in } L^1(I).$$

Therefore $\langle \dot{u}_2; pw^{p-1}\rangle + \langle A_M(v, v); pw^{p-1}\rangle = 0$ reads,

$$\frac{d}{dt}\int_0^1 w^p \, dx = -Q_1 - Q_2 - Q_3, \tag{76}$$

with

$$Q_1 = \int_0^1 \sigma_2(T_M v_2)\partial_x v_2 \partial_x(pw^{p-1}) \, dx, \qquad Q_2 = \int_0^1 \sigma_2(T_M v_2)z_2 \partial_x v_0 \partial_x(pw^{p-1}) \, dx,$$

$$Q_3 = \sum_{\Gamma \in \{0,1\}} \left[r_2^\Gamma(T_M v_2)g_2^{\Gamma,\mu}(\xi_2 - \xi_2^\Gamma)pw^{p-1}\right](\Gamma).$$

In order to estimate the boundary term Q_3, we note that $\xi_2 - \xi_2^\Gamma = v_2(\Gamma) - [\xi_2^\Gamma - z_2 v_0(\Gamma)]$ and we define successively

$$v_2^{*,\Gamma} = \xi_2^\Gamma - z_2 v_0(\Gamma), \qquad u_2^{*,\Gamma} = \bar{u}_2 e_2(T_M v_2^{*,\Gamma}) \quad \text{and} \quad w^{*,\Gamma} = (u_2^{*,\Gamma} - k)_+.$$

We can then write

$$Q_3 = p \sum_{\Gamma \in \{0,1\}} \left[r_2^\Gamma(T_M v_2)g_2^{\Gamma,\mu}(v_2 - v_2^{*,\Gamma})\left(w^{p-1} - (w^{*,\Gamma})^{p-1}\right)\right](\Gamma)$$

$$+ p \sum_{\Gamma \in \{0,1\}} \left[r_2^\Gamma(T_M v_2)g_2^{\Gamma,\mu}(v_2 - v_2^{*,\Gamma})(w^{*,\Gamma})^{p-1}\right](\Gamma) =: Q_{31} + Q_{32}.$$

Due to the monotonicity of the involved functions, it results $Q_{31} \geq 0$. Let us notice that, due to (32), $v_2^{*,\Gamma}$ is bounded independently of M. Therefore, it is possible to choose k (independent of M) such that $w^{*,\Gamma} = 0$ for $\Gamma \in \{0,1\}$ and we get $Q_{32} = 0$. Hence,

$$-Q_3 \leq 0. \tag{77}$$

For Q_1, we use (73) and the fact that $\partial_x w \partial_x u_2 = (\partial_x w)^2$ to get

$$Q_1 = p(p-1)d_2 \int_0^1 (w^{(p-2)/2}\partial_x w)^2 \, dx = \frac{4d_2(p-1)}{p}\int_0^1 |\partial_x w^{p/2}|^2 \, dx. \tag{78}$$

We treat the term Q_2 as follows. Differentiating w^{p-1} and using (74), we get

$$Q_2 = p(p-1)z_2 \int_0^1 \sigma_2(T_M v_2) \partial_x w \partial_x v_0 w^{p-2} \, dx.$$

From $u_2 = \bar{u}_2 e_2(T_M v_2)$ and the definitions $e_2(z) = e^z$ and $\sigma_2(z) = d_2 \bar{u}_2 e^z$,

$$\sigma_2(T_M v_2) = d_2 \bar{u}_2 \exp(\ln(u_2/\bar{u}_2)) = d_2 u_2,$$

so that we get

$$Q_2 = d_2 p(p-1)z_2 \int_0^1 u_2 w^{p-2} \partial_x v_0 \partial_x w \, dx.$$

In any case we have $0 \leq u_2 \leq k + w$, so we have $|Q_2| \leq Q_{21} + Q_{22}$ where

$$Q_{21} = d_2 p(p-1)|z_2| \|\partial_x v_0\|_\infty \int_0^1 w^{p-1} |\partial_x w| \, dx$$

$$Q_{22} = k d_2 p(p-1)|z_2| \|\partial_x v_0\|_\infty \int_0^1 w^{p-2} |\partial_x w| \, dx.$$

Taking into account that $\partial_x v_0$ is bounded uniformy w.r.t. M (see Lemma 4.5), that $p - 1 = (p/2 - 1) + p/2$ and that $p w^{p/2-1} \partial_x w = 2 \partial_x w^{p/2}$, and applying the Young inequality, we get

$$Q_{21} \leq d_2 \int_0^1 |\partial_x w^{p/2}|^2 \, dx + d_2(p-1)^2 |z_2|^2 \|\partial_x v_0\|_\infty^2 \int_0^1 w^p \, dx$$

$$(79) \qquad \leq d_2 \int_0^1 |\partial_x w^{p/2}|^2 \, dx + c d_2 \, p^2 \int_0^1 w^p \, dx.$$

Arguing similarly for the term Q_{22} and using additionally the Young inequality:

$$ab \leq \frac{p-2}{p} a^{\frac{p}{p-2}} + \frac{2}{p} b^{\frac{p}{2}} \quad \text{for } a, b \geq 0, \ p > 2,$$

we have

$$(80) \quad Q_{22} \leq d_2 \int_0^1 |\partial_x w^{p/2}|^2 \, dx + k^2 d_2(p-1)^2 |z_2|^2 \|\partial_x v_0\|_{L^\infty(0,1)}^2 \int_0^1 w^{p-2} \, dx$$

$$\leq d_2 \int_0^1 |\partial_x w^{p/2}|^2 \, dx + d_2 c \, p^2 \int_0^1 w^p \, dx + d_2 c \, p.$$

By collecting (76)–(80), we obtain

$$(81) \qquad \frac{d}{dt} \int_0^1 w^p \, dx + d_2 \frac{2p-4}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx \leq d_2 c_3 p^2 \int_0^1 w^p \, dx + d_2 c p, \quad \forall p > 2,$$

where c_3 and the generic constant c depends neither on M nor on p. Without loss of generality, we assume that $c_3 \geq 1/16$.

Starting from now, let us assume that $p \geq 4$. Then we combine the following Gagliardo-Nirenberg interpolation inequality:

$$\|\chi\|_{L^2(0,1)}^3 \leq c \|\chi\|_{L^1(0,1)}^2 \left(\|\chi\|_{L^2(0,1)}^2 + \|\partial_x \chi\|_{L^2(0,1)}^2 \right)^{1/2}, \qquad \forall \chi \in H^1(0,1),$$

together with the Young inequality to get that, for $\varepsilon \leq \frac{1}{2}$,

$$\frac{1}{2} \int_0^1 \chi^2 \, dx \leq (1-\varepsilon) \int_0^1 \chi^2 \, dx \leq \frac{c}{\sqrt{\varepsilon}} \left(\int_0^1 |\chi| \, dx \right)^2 + \varepsilon \int_0^1 |\partial_x \chi|^2 \, dx.$$

We apply it with $\chi = w^{p/2}$, $\varepsilon = (p-2)/(c_3 p^3) \in (0, 1/2]$ since $p \geq 4$ and $c_3 \geq 1/16$. Then, by the choice of ε, from (81) we deduce that

$$\frac{d}{dt} \int_0^1 w^p \, dx \leq \frac{c \, p^2}{\sqrt{\varepsilon}} \left(\int_0^1 w^{p/2} \, dx \right)^2 + c_2 p \leq c \, p^3 \left[\left(\int_0^1 w^{p/2} \, dx \right)^2 + 1 \right], \qquad \forall p \geq 4.$$

We integrate the last inequality with respect to the time variable and choose k such that $w(0) = 0$ (*i.e.* $k \geq \sup u_2^{\text{in}}$) getting

$$\int_0^1 w^p(t) \, dx \leq c \, p^3 \left[\sup_{s \in I} \left(\int_0^1 w^{p/2}(s) \, dx \right)^2 + 1 \right] \quad \forall t \in I,$$

that is,

(82) $$\|w(t)\|_{L^p(0,1)}^p \leq c \, p^3 \left[\sup_{s \in I} \|w(s)\|_{L^{p/2}(0,1)}^p + 1 \right] \quad \forall t \in I \text{ and } \forall p \geq 4.$$

Taking inspiration in [23], we set for $m \in \mathbb{N}$:

$$b_m = \max \left(1, \sup_{s \in I} \|w(s)\|_{L^{2^m}(0,1)}^{2^m} \right).$$

Choosing $p = 2^m$ in (82), we obtain

$$b_m \leq c \, 2^{3m} b_{m-1}^2, \qquad m \geq 2,$$

and by induction, we get

$$b_m \leq c^{(2^{m-1}-1)} \left(2^3 \right)^{(2^m - m - 1)} b_1^{2^{m-1}} \quad \forall m \geq 1.$$

Taking the power $1/2^{m-1}$ leads to the estimate:

$$\|w(t)\|_{L^{2^m}(0,1)}^2 \leq c^{1-1/2^{m-1}} (2^3)^{2-(m+1)/2^{m-1}} \max \left(1, \sup_{s \in I} \|w(s)\|_{L^2(0,1)}^2 \right) \quad \forall t \in I.$$

Sending m to $+\infty$ we find

(83) $$\|w(t)\|_{L^\infty(0,1)} \leq c \left[\sup_{s \in I} \|w(s)\|_{L^2(0,1)} + 1 \right] \quad \forall t \in I.$$

The last step consists in obtaining a L^2-estimate of the norm of $w(s)$. To this aim, we can consider inequality (81) in the limit $p \searrow 2$:

$$\frac{d}{dt} \int_0^1 w^2 \, dx \leq c \left(1 + \int_0^1 w^2 \, dx \right).$$

We apply the Gronwall's lemma to have

$$\int_0^1 w^2(s) \, dx \leq \left(\int_0^1 w^2(0) \, dx + 1 \right) e^{cs} \leq c,$$

due to the bounds on the initial data stated in (H$_5$), independently of M. Eventually, choosing

$$k \geq \max \left\{ \|u_2^{\text{in}}\|_{L^\infty(0,1)}, |u_2^{*,0}|, |u_2^{*,1}| \right\},$$

there exists a positive constant c which *does not depend on M* such that $0 \leq u_2 \leq c$ over I. $\qquad \square$

Remark 5.2. In particular, since $u_2 = \bar{u}_2 e_2(T_M v_2) = \bar{u}_2 \exp(T_M v_2)$, Theorem 5.1 implies that

$$T_M v_2 \le e_2^{-1}\left(\frac{c}{\bar{u}_2}\right) = \log\left(\frac{c}{\bar{u}_2}\right) \quad \text{almost everywhere on } I \times (0,1),$$

hence so does v_2 by choosing $M \ge \log\left(\frac{c}{\bar{u}_2}\right)$.

5.2. **Lower bounds for v_1 and v_2.** With the following theorem we derive some lower bounds for the chemical potentials v_1 and v_2. For this, we write the chemical potentials and the mobilities appearing in the problem as functions of the corresponding carrier densities. More precisely, the chemical potentials $v_i(u_i)$, $i = 1, 2$, are given by (19), while the $\sigma_i(u_i)$ are given by (H_3) so that (73) holds.

Theorem 5.3. *Under assumptions (H_1)–(H_5), let (u,v) a solution to problem (P_M). There exists a constant $c > 0$ independent on M such that*

$$v_i \ge -c \quad \text{almost everywhere in } I \times (0,1) \text{ for } i = 1, 2.$$

Proof. Let $p \ge 2$ and $w_i = (-T_M v_i - k)_+$ for $i = 1, 2$, where $k > 0$ will be fixed later. Observe that $\nabla w_i = -\nabla[T_M v_i]$ almost everywhere on $\{w_i > 0\}$ and $\nabla w_i = 0$ almost everywhere in the rest of the domain.

We do both calculations simultaneously and to lighten the exposition we make the following abuse of notation: we drop all subscripts i except when a precise notation is required (we write w for w_i, u for u_i, $\sigma(T_M v)$ for $\sigma_i(T_M v_i)$, ξ for ξ_i, ξ^Γ for ξ_i^Γ, etc).

We have using the chain rule and $u = \bar{u}e_i(T_M v)$,

$$\frac{d}{dt}\int_0^1 w^p \, dx = p\int_0^1 w^{p-1}\partial_t w \, dx = -p\int_0^1 w^{p-1}\partial_t[T_M v] \, dx = -p\int_0^1 \frac{w^{p-1}}{\bar{u}e_i'(T_M v))}\partial_t u.$$

Since by definition, $\sigma_i(z) = d_i\bar{u}_i e_i'(z)$, this reads

$$\frac{d}{dt}\int_0^1 w^p \, dx = -pd\int_0^1 \frac{w^{p-1}}{\sigma(T_M v)}\partial_t u \, dx$$

Applying $\dot{u} + A_M(v,v) = 0$ with the test function

$$\left(0, -\frac{pd_1 w_1^{p-1}}{\sigma_1(T_M v_1)}, 0\right) \quad \text{if } i = 1, \qquad \left(0, 0, -\frac{pd_2 w_2^{p-1}}{\sigma_2(T_M v_2)}\right) \quad \text{if } i = 2,$$

we have

(84) $$\frac{d}{dt}\int_0^1 w^p \, dx = R_1 + R_2 + R_3,$$

where,

$$R_1 = pd\int_0^1 \sigma(T_M v)\partial_x v\partial_x\left(\frac{w^{p-1}}{\sigma(T_M v)}\right) dx, \qquad R_2 = pdz\int_0^1 \sigma(T_M v)\partial_x v_0\partial_x\left(\frac{w^{p-1}}{\sigma(T_M v)}\right) dx,$$

$$R_3 = pd\sum_{\Gamma\in\{0,1\}}\left[r^\Gamma(T_M v)g^{\Gamma,\mu}(\xi - \xi^\Gamma)\frac{w^{p-1}}{\sigma(T_M v)}\right](\Gamma).$$

As in the previous proof, we estimate the boundary term R_3 using the fact that $\xi - \xi^\Gamma = v(\Gamma) - [\xi^\Gamma - zv_0(\Gamma)]$. By defining $v^{*,\Gamma} = \xi^\Gamma - zv_0(\Gamma)$ and $w^{*,\Gamma} = (-v^{*,\Gamma} - k)_+$, we write

$$R_3 = pd \sum_{\Gamma \in \{0,1\}} \left[\frac{r^\Gamma(T_M v)}{\sigma(T_M v)} g^{\Gamma,\mu}(v - v^{*,\Gamma})\left(w^{p-1} - (w^{*,\Gamma})^{p-1}\right) \right](\Gamma)$$

$$+ pd \sum_{\Gamma \in \{0,1\}} \left[\frac{r^\Gamma(T_M v)}{\sigma(T_M v)} g^{\Gamma,\mu}(v - v^*)(w^{*,\Gamma})^{p-1} \right](\Gamma)$$

$$=: R_{31} + R_{32}.$$

Since r^Γ and σ are positive and $g^{\Gamma,\mu}$ is increasing, we have $R_{31} \leq 0$. By choosing k large enough so that $w^{*,\Gamma} = 0$ for $\Gamma \in \{0,1\}$, we get $R_{32} = 0$. Whence it results

(85)
$$R_3 \leq 0.$$

To treat R_1, we write

(86)
$$\partial_x \left(\frac{pw^{p-1}}{\sigma(T_M v)} \right) = \frac{p(p-1)}{\sigma(T_M v)} w^{p-2}\partial_x w + \frac{p\sigma'(T_M v)}{[\sigma(T_M v)]^2} w^{p-1}\partial_x w.$$

The term R_1 then splits as follows:

$$R_1 = -dp(p-1) \int_0^1 w^{p-2}|\partial_x w|^2 \, dx - dp \int_0^1 \frac{\sigma'(T_M v)}{\sigma(T_M v)} w^{p-1}|\partial_x w|^2 \, dx =: R_{11} + R_{12}.$$

We easily see that

$$R_{11} = \frac{-4d(p-1)}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx.$$

Next, for $i = 2$, $\sigma_2'/\sigma_2 \equiv 1$ so that $R_{12} \leq 0$ in this case. For $i = 1$, $\sigma_1'(y)/\sigma_1(y) = -\tanh(y/2)$ so $\sigma_1'(T_M v_1)/\sigma_1(T_M v_1) \geq 0$ on $\{w_1 > 0\} = \{T_M v_1 < -k\}$ and $R_{12} \leq 0$ also in this case. We conclude that

(87)
$$R_1 \leq \frac{-4d(p-1)}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx.$$

Using again (86) and $|\sigma'/\sigma| \leq 1$, we have for the remaining term $|R_2| \leq R_{21} + R_{22}$ with

$$R_{21} = dp(p-1)|z|\|\partial_x v_0\|_\infty \int_0^1 w^{p-2}|\partial_x w| \, dx,$$

$$R_{22} = dp|z|\|\partial_x v_0\|_\infty \int_0^1 w^{p-1}|\partial_x w| \, dx.$$

Writing

$$R_{21} = 2d(p-1)|z|\|\partial_x v_0\|_\infty \int_0^1 w^{p/2-1}|\partial_x w^{p/2}| \, dx.$$

and using the Cauchy–Schwarz and Young inequalities, we get

$$|R_{21}| \leq \frac{d(p-1)}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx + d(p-1)p|z|^2\|\partial_x v_0\|^2 \int_0^1 w^{p-2} \, dx$$

(88)
$$\leq \frac{d(p-1)}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx + d\,c\,p^2 \left(1 + \int_0^1 w^p \, dx\right).$$

Similarly,

$$(89) \qquad |R_{22}| \leq \frac{d(p-1)}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx + d\, c \int_0^1 w^p \, dx.$$

By collecting (85), (87), (88) and (89), we obtain

$$(90) \qquad \frac{d}{dt} \int_0^1 w^p \, dx + \frac{2d(p-1)}{p} \int_0^1 |\partial_x w^{p/2}|^2 \, dx \leq d\, cp^2 \left(1 + \int_0^1 w^p \, dx \right), \quad \forall p \geq 2.$$

As in the proof of Theorem 5.1, we deduce from this estimate that

$$\|w(t)\|_{L^\infty(0,1)} \leq c \left[\sup_{s \in I} \|w(s)\|_{L^2(0,1)} + 1 \right] \quad \forall t \in I,$$

for some constant $c > 0$ independent of M. To initialize the process, we consider (90) with $p = 2$ and apply Gronwall's lemma to deduce the bound

$$\sup\{\|w(s)\|_{L^2(0,1)} : s \in I\} \leq c,$$

for some constant c depending on the T, c_1, c_2 and the L^∞-norm of v^{in} (bounded thanks to (H$_5$)).

As a conclusion, choosing

$$k \geq \max\{\|v_1^{\text{in}}\|_{L^\infty(0,1)}, \|v_2^{\text{in}}\|_{L^\infty(0,1)}, |v_1^{*,0}|, |v_1^{*,1}|, |v_2^{*,0}|, |v_2^{*,1}|\},$$

there holds $v_i(t) \geq -c$ almost everywhere in $I \times (0,1)$ and for $i = 1,2$ with a constant $c > 0$ independent of M. $\qquad \square$

5.3. **Upper bound for v_1.** We state here an upper bound for the chemical potential v_1.

Theorem 5.4. *Under assumptions* (H$_1$)–(H$_5$), *let* (u,v) *a solution to problem* (P_M). *There exists a constant $c > 0$ independent on M such that*

$$v_1(t) \leq c, \ \forall t \in I.$$

Proof. Let $p \geq 2$ and $w = (T_M v_1 - k)_+$, with

$$k \geq \max \left\{ \|v_1^{\text{in}}\|_{L^\infty(0,1)}, |v_1^{*,0}|, |v_1^{*,1}| \right\}$$

where we have set $v_1^{*,\Gamma} = \xi_1^\Gamma - z_1 v_0(\Gamma)$ for $\Gamma \in \{0,1\}$.
We compute

$$(91) \qquad \frac{d}{dt} \int_0^1 w^p \, dx = p \int_0^1 w^{p-1} \partial_t [T_M v_1] \ dx = pd_1 \int_0^1 \frac{w^{p-1}}{\sigma_1(T_M v_1)} \partial_t u_1 \, dx.$$

Here we can apply $\dot{u} + A_M(v,v) = 0$ with the test function

$$\left(0, \frac{pw^{p-1}}{\sigma_1(T_M v_1)}, 0 \right),$$

and express the right hand side of (91) as a sum of integrals involving space derivatives of w. The proof follows exactly the same lines of that of Theorem 5.3, we do not repeat the details. $\qquad \square$

6. Conclusion

6.1. **Proof of Theorem 2.2.** In this paper, we have introduced a new corrosion model inspired from the DPCM introduced in [3]. The changes we introduced are motivated by the expected compatibility of the model with thermodynamics. Indeed, they permit to establish the decay of a free energy with a control of the dissipation of energy as stated in Section 3.

The main result of the paper is the existence of a weak solution to this new corrosion model, stated in Theorem 2.2. In Section 4, we have first established the existence of a solution to a regularized problem (P_M). Then lower and upper bounds for the chemical potentials $(v_i)_{i=1,2}$ have been proved in Section 5, so that we are now able to conclude the proof of Theorem 2.2.

Indeed, to find a solution to problem (P) it suffices to show the existence of a solution on any finite time interval of the form $I = [0, T]$, $T > 0$. Let us fix such $T > 0$ and let $M > 0$. Proposition 4.1 ensures the existence of a solution (u, v) to the regularized problem (P_M) on I. Now, Theorems 5.1, 5.3, 5.4 and Remark 5.2 guarantee the existence of bounds for $\|v_i\|_{L^\infty(I \times [0,1])}$, $i = 1, 2$ independent of M. Consequently, for M large enough, for this solution the operators A_M and E_M coincide with A and E respectively, and (u, v) turns out to be a solution to the original problem (P).

6.2. **Towards a comparison between the DPCM and the new model.** To conclude this paper, we provide a first evaluation of the changes involved by the two modifications we proposed for the model DPCM (1)–(3), leading to the new model that will be referred as vDPCM (for "variational DPCM" as we have established its variational structure). The changes are as follows:

(a) convection is made nonlinear in the cation flux of the vDPCM, defined by (14), (15), to be compared with the linear convection (1a) originally proposed in DPCM;

(b) the original boundary condition (2d) for the electrons at the interface between the oxide and the metal is replaced by (12) in vDPCM.

We aim now to provide some numerical experiments in order to highlight the impact of the changes on the numerical solutions. Numerical methods have been introduced for the simulation of the DPCM in [4] and implemented in the code CALIPSO. For the simplified two-species DPCM on a fixed domain, the numerical scheme is described and analyzed in [11] for the stationary model and in [12] for the evolutive one. It is based on a Scharfetter-Gummel approximation of the linear drift-diffusion fluxes. Because of the nonlinear convection in the cation flux pointed out in **(a)** above, one can no longer use the Scharfetter-Gummel scheme to compute the numerical fluxes corresponding to (15). For the approximation of this new flux, we use the extension proposed in [10] to the nonlinear mobility framework of the SQRA (SQuare-Root Approximation) studied in [27]. The remaining of the numerical strategy (fully implicit in time schemes, resolution based on Newton's method) is similar for both models.

In order to evaluate the impact of the changes **(a)** and **(b)**, we want to compute the numerical solution of the two models with a given set of physical parameters. Starting with physical parameters, we can derive an adimensional system of equations following the procedure detailed for instance in [6]. In order to describe the test case we use for the simulations, we will just give the values of the scaled parameters involved in (1), (2) for DPCM. They have been designed following [2], in order to ensure that the model admits a thermodynamical equilibrium ($u_1 = 2$, $u_2 = 1$ and v_0 constant) for specific values of some physical parameters. Then, the only difference for the simulation of vDPCM will be the chosen value for k_2^1 involved in (12) (instead of (2d)). We first give in Table 1 the values of the dimensionless parameters involved in the Poisson equation (1c) and

in the associated boundary conditions (2e), (2f), while Table 2 gives the values of the dimensionless parameters involved in the drift-diffusion equations and in the associated boundary conditions. Let us note that some parameters depend on the pH.

λ	ρ_{hl}	α_0	α_1	$\Delta\Psi_0^{\mathrm{pzc}}$	$\Delta\Psi_1^{\mathrm{pzc}}$
$3.247 \cdot 10^{-2}$	-5	$1.771 \cdot 10^{-1}$	$8.854 \cdot 10^{-2}$	$6.96094 \cdot 10^{-1} - \log(10)\mathrm{pH}$	-4.008

TABLE 1. Dimensionless parameters involved in the Poisson equation.

k_1^0	m_1^0	k_1^1	m_1^1
$1.0 \cdot 10^{10}$	0	$1.0 \cdot 10^{11}$	$1.49961 \cdot 10^3$

k_2^0	m_2^0	k_2^1	m_2^1
$1.3 \cdot 10^2 \cdot 10^{-\mathrm{pH}}$	$2.8025 \cdot 10^5 \cdot 10^{-\mathrm{pH}}$	$2.6804 \cdot 10^1$ (DPCM) $4.8702 \cdot 10^{-1}$ (vDPCM)	$2.6804 \cdot 10^1$

$\overline{u}_1$	d_1	$\overline{u}_2^{\mathrm{met}}$	d_2
2.005	1	0.2484	10^{17}

TABLE 2. Dimensionless parameters involved in the drift-diffusion equations.

Figure 1 shows the evolution of the steady total current $J_{\mathrm{tot}} = z_1 J_1 + z_2 J_2$, given in physical units $A \cdot m^{-2}$, with respect to the applied potential V expressed in Volts and evaluated relatively to the normal hydrogen electrode (NHE) reference. Note that because very different orders of magnitude, we rather plot $|J_{\mathrm{tot}}|$ as a function of V in semilog-y scale. The function $V \mapsto J_{\mathrm{tot}}(V)$ is decreasing and changes its sign at the so-called free corrosion potential V_{fc}. We observe that, for two different values of the pH, the solutions to the DPCM and the vDPCM have similar qualitative behaviours.

However, when focusing on the computed profiles for both models, we may better highlight the differences between the DPCM and the vDPCM. Figure 2 shows the profiles of the densities of cations and electrons and of the electrostatic potential obtained with the two models at pH=8.5 and for two different values of the applied potential (-0.4 and 0.3 Volts). In particular, we observe that the DPCM can lead to densities of cations greater than 2.005 which is the maximal physical value authorized in the oxide. In contrast and consistently with the mathematical results of our paper, vDPCM ensures that there is no overshoot. It is a direct consequence of the modification proposed for the definition of the flux of cations based on (9).

6.3. **Concluding remarks.** The above discussion on the comparison of two models is still in its infancy, and a more advanced study on the influence of the changes is needed. Besides, other thermodynamically consistent variants of the model could be considered, for instance by considering Fermi-Dirac statistics for the electrons rather than Boltzmann statistics. The main challenge is now to extend our study to the full 3-species models [3] on moving domain.
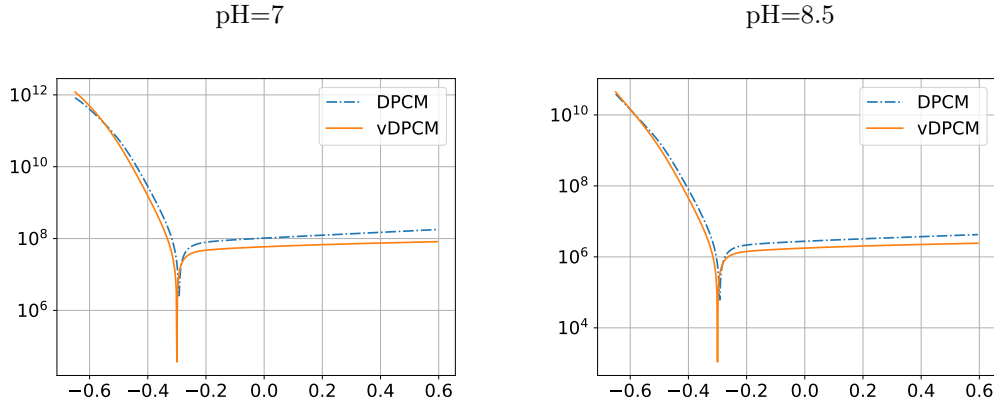
pH=7 · pH=8.5

FIGURE 1. Evolution of the total current for the steady state (in physical units $A \cdot m^{-2}$) in terms of the applied potential (in Volts) at pH = 7 and pH = 8.5

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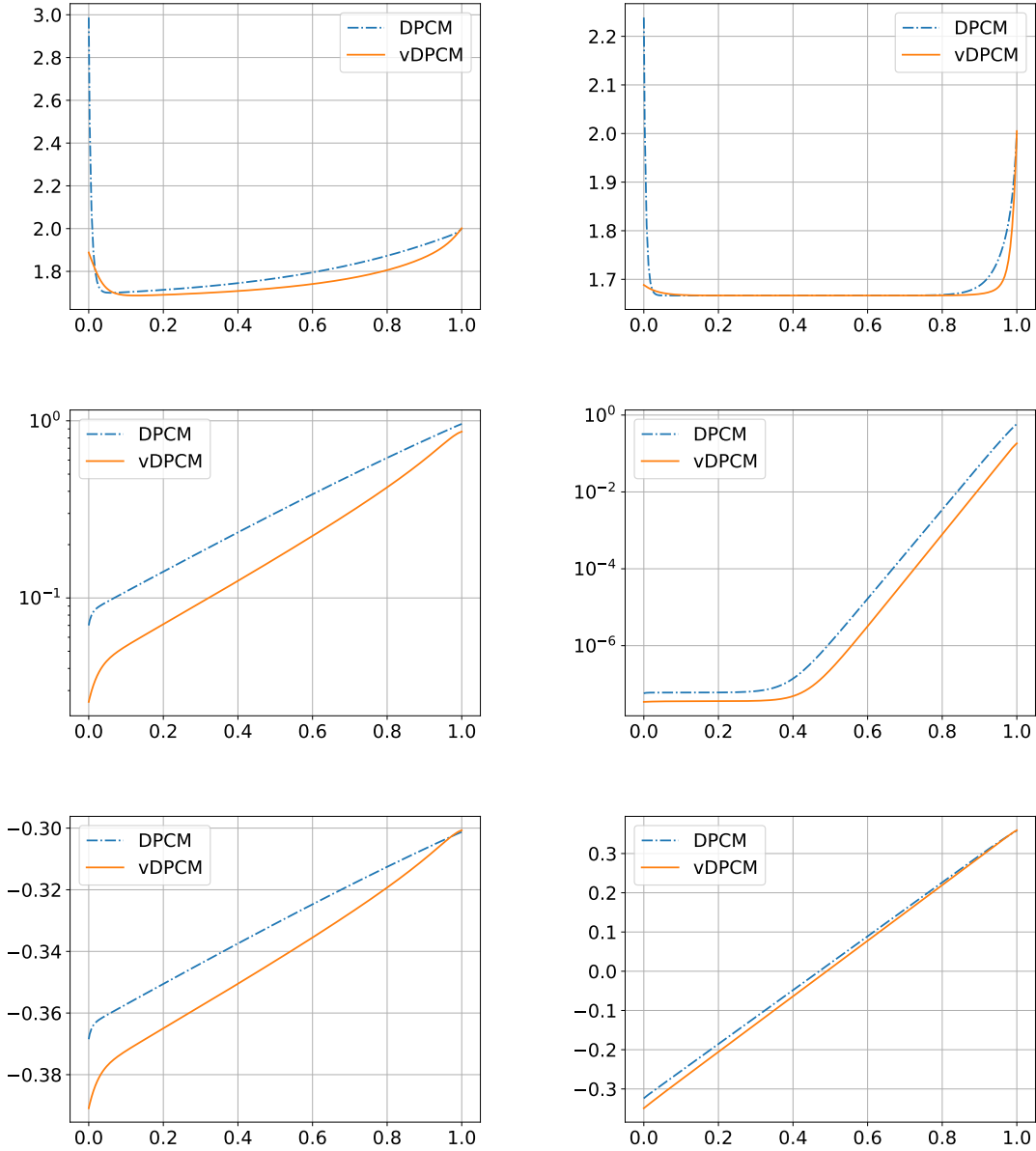
FIGURE 2. Profiles of the scaled densities of cations (top), electrons (middle) and of the electrostatic potential (bottom, in Volts, the physical unit) at the steady state for two values of the applied potential V :-0.4 Volts (left) and 0.3 Volts (right).

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