

# Mathematical modelling and simulation of corrosion in an underground repository

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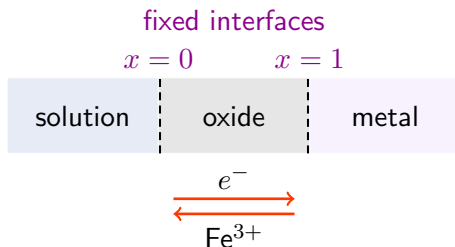
## PART II :

First results on a new model,  
the variational Diffusion Poisson Coupled Model

# Outline of Part II

- 1 Towards a thermodynamically consistent model
- 2 Free energy, a priori estimates and existence result
- 3 The three-species model on a moving domain
- 4 Numerical scheme for the vDPCM

# The two-species model as a starting point



## Notations

- $u_1, u_2$  : charge densities of  $Fe^{3+}$  and  $e^-$  (charges :  $z_1, z_2$ )
- $v_0$  : electrostatic potential
- $J_1, J_2$  : current densities

## DPCM : a drift-diffusion system of equations

$$\begin{cases} \partial_t u_i + \partial_x J_i = 0, & J_i = -d_i (\partial_x u_i + z_i u_i \partial_x v_0) \\ -\lambda^2 \partial_{xx}^2 v_0 = \sum_{i=1,2} z_i u_i + \rho_{hl} \end{cases}$$

## With no-flux boundary conditions (just an exercise...)

$$\begin{aligned}\partial_t u_i + \partial_x J_i &= 0, & J_i &= -d_i(\partial_x u_i + z_i u_i \partial_x v_0) \\ -\lambda^2 \partial_{xx}^2 v_0 &= \sum_{i=1,2} z_i u_i + \rho_{hl}\end{aligned}$$

Free energy : definition

$$\Psi(t) = \int_0^1 \sum_{i=1,2} (u_i \log u_i - u_i + 1) + \frac{\lambda^2}{2} \int_0^1 (\partial_x v_0)^2.$$

Free energy dissipation

$$\Psi'(t) = \sum_{i=1,2} \int_0^1 \partial_t u_i \log u_i + \lambda^2 \int_0^1 \partial_t (\partial_x v_0) \partial_x v_0$$

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$$\begin{aligned}\partial_t u_i + \partial_x J_i &= 0, & J_i &= -d_i(\partial_x u_i + z_i u_i \partial_x v_0) \\ -\lambda^2 \partial_{xx}^2 v_0 &= \sum_{i=1,2} z_i u_i + \rho_{hl}\end{aligned}$$

Free energy : definition

$$\Psi(t) = \int_0^1 \sum_{i=1,2} (u_i \log u_i - u_i + 1) + \frac{\lambda^2}{2} \int_0^1 (\partial_x v_0)^2.$$

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$$\Psi'(t) = \sum_{i=1,2} \int_0^1 \partial_t u_i (\log u_i + z_i v_0)$$

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$$\Psi(t) = \int_0^1 \sum_{i=1,2} (u_i \log u_i - u_i + 1) + \frac{\lambda^2}{2} \int_0^1 (\partial_x v_0)^2.$$

Free energy dissipation

$$\begin{aligned}\Psi'(t) &= \sum_{i=1,2} \int_0^1 \partial_t u_i (\log u_i + z_i v_0) \\ &= \sum_{i=1,2} \int_0^1 -\partial_x J_i (\log u_i + z_i v_0)\end{aligned}$$



## With no-flux boundary conditions (just an exercise...)

$$\begin{aligned}\partial_t u_i + \partial_x J_i &= 0, & J_i &= -d_i u_i \partial_x (\log u_i + z_i v_0) \\ -\lambda^2 \partial_{xx}^2 v_0 &= \sum_{i=1,2} z_i u_i + \rho_{hl}\end{aligned}$$

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Free energy dissipation

$$\begin{aligned}\Psi'(t) &= \sum_{i=1,2} \int_0^1 \partial_t u_i (\log u_i + z_i v_0) \\ &= \sum_{i=1,2} \int_0^1 J_i \partial_x (\log u_i + z_i v_0) \\ &= - \sum_{i=1,2} \int_0^1 d_i u_i (\partial_x (\log u_i + z_i v_0))^2 \leq 0\end{aligned}$$

## With general boundary conditions ?

Focus on one integration by parts

$$\nu^1 = 1, \nu^0 = -1$$

$$\begin{aligned} - \int_0^1 \partial_x J_i (\log u_i + z_i v_0) &= \int_0^1 J_i \partial_x (\log u_i + z_i v_0) \\ &\quad - \sum_{\Gamma=0,1} J_i(\Gamma) \cdot \nu^\Gamma (\log u_i + z_i v_0)(\Gamma). \end{aligned}$$

Can we ensure that inner and boundary terms induce dissipation ?

Some definitions for the linear convection-diffusion fluxes

- $v_i = \log u_i$  is a chemical potential (Boltzmann statistics),
- $\xi_i = v_i + z_i v_0$  is an electrochemical potential,
- $\sigma_i = d_i u_i$  is a mobility.

$$J_i = -\sigma_i \partial_x \xi_i \quad \text{general form "à la Onsager"}$$

# On the road towards an energy-dissipative model

- ▶ General form of the fluxes :  $J_i = -\sigma_i \partial_x \xi_i$
- ▶ New definition of the free energy, leading to

$$-\int_0^1 (\partial_x J_i) \xi_i = \int_0^1 J_i \partial_x \xi_i - \sum_{\Gamma=0,1} J_i(\Gamma) \cdot \nu^\Gamma \xi_i(\Gamma)$$

## Ansatz on the boundary conditions

The boundary conditions are generated by the differences of electrochemical potentials at the interfaces :

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

- each  $r_i^\Gamma$  is a positive-valued function,
- each  $g_i^\Gamma$  is an increasing function, vanishing at 0,
- the  $\xi_i^\Gamma$  are the outer electrochemical potentials,.

# Boundary conditions in the DPCM / electrons / $\Gamma = 0$

Butler Volmer law in DPCM and reformulation

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

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$$\begin{aligned} -J_2(0) &= k_2^0 u_2 e^{\frac{z_2}{2} v_0} - m_2^0 e^{-\frac{z_2}{2} v_0} \\ &= \kappa_2^0 \sqrt{u_2} \sinh \left( \frac{1}{2} (\log u_2 + z_2 v_0 - \xi_2^0) \right) \end{aligned}$$

$$\text{with } \kappa_2^0 = 2\sqrt{k_2^0 m_2^0}, \quad \xi_2^0 = \log \frac{m_2^0}{k_2^0}$$

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## (Electro-)chemical potential

$$\begin{aligned} v_2 = \log u_2 &\iff u_2 = e^{v_2} = \bar{u}_2 e_2(v_2), \bar{u}_2 = 1 \\ \xi_2 &= v_2 + z_2 v_0 \end{aligned}$$

## Mobility : band conduction (no limitation for the electrons)

$$\sigma_2 = d_2 u_2 \iff \sigma_2 = d_2 \bar{u}_2 e_2'(v_2)$$

$$J_2 = -d_2 (\partial_x u_2 + z_2 u_2 v_0)$$



# Boundary conditions in the DPCM / cations

## Butler-Volmer laws in DPCM

$$\begin{aligned} -J_1(0) &= k_1^0 u_1 e^{\frac{z_1}{2} v_0} - m_1^0 (\bar{u}_1 - u_1) e^{-\frac{z_1}{2} v_0}, \\ J_1(1) &= m_1^1 u_1 e^{\frac{z_1}{2} (v_0 - V)} - k_1^1 (\bar{u}_1 - u_1) e^{-\frac{z_1}{2} (v_0 - V)} \end{aligned}$$

## Reformulation of the Butler-Volmer laws

# Boundary conditions in the DPCM / cations

## Butler-Volmer laws in DPCM

$$\begin{aligned}-J_1(0) &= k_1^0 u_1 e^{\frac{z_1}{2} v_0} - m_1^0 (\bar{u}_1 - u_1) e^{-\frac{z_1}{2} v_0}, \\ J_1(1) &= m_1^1 u_1 e^{\frac{z_1}{2} (v_0 - V)} - k_1^1 (\bar{u}_1 - u_1) e^{-\frac{z_1}{2} (v_0 - V)}\end{aligned}$$

## Reformulation of the Butler-Volmer laws

$$-J_1(0) = \kappa_1^0 \sqrt{u_1 (\bar{u}_1 - u_1)} \sinh \left( \frac{1}{2} \left( \log \frac{u_1}{\bar{u}_1 - u_1} + z_1 v_0 - \xi_1^0 \right) \right)$$

$$\text{with } \kappa_1^0 = 2 \sqrt{k_1^0 m_1^0}, \quad \xi_1^0 = \log \frac{m_1^0}{k_1^0}$$

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## Butler-Volmer laws in DPCM

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# Boundary conditions in the DPCM / cations

## Butler-Volmer laws in DPCM

$$\begin{aligned} -J_1(0) &= k_1^0 u_1 e^{\frac{z_1}{2} v_0} - m_1^0 (\bar{u}_1 - u_1) e^{-\frac{z_1}{2} v_0}, \\ J_1(1) &= m_1^1 u_1 e^{\frac{z_1}{2} (v_0 - V)} - k_1^1 (\bar{u}_1 - u_1) e^{-\frac{z_1}{2} (v_0 - V)} \end{aligned}$$

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## Natural choice for the (electro-) chemical potentials

$$v_1 = \log \frac{u_1}{\bar{u}_1 - u_1}, \quad \xi_1 = \log \frac{u_1}{\bar{u}_1 - u_1} + z_1 v_0$$

# Drift-diffusion for the cations

Balance law for the charge density

$$\partial_t u_1 + \partial_x J_1 = 0, \quad J_1 = -d_1 \sigma_1 \partial_x \xi_1$$

(Electro-)chemical potential

$$v_1 = \log \frac{u_1}{\bar{u}_1 - u_1}$$

$$\xi_1 = v_1 + z_1 v_0$$

Mobility : vacancy mechanism

$$\sigma_1 = d_1 \frac{u_1 (\bar{u}_1 - u_1)}{\bar{u}_1}$$

# Drift-diffusion for the cations

Balance law for the charge density

$$\partial_t u_1 + \partial_x J_1 = 0, \quad J_1 = -d_1 \sigma_1 \partial_x \xi_1$$

(Electro-)chemical potential

$$v_1 = \log \frac{u_1}{\bar{u}_1 - u_1} \quad \Longleftrightarrow \quad u_1 = \bar{u}_1 \frac{e^{v_1}}{1 + e^{v_1}} = \bar{u}_1 e_1(v_1)$$

$$\xi_1 = v_1 + z_1 v_0$$

Mobility : vacancy mechanism

$$\sigma_1 = d_1 \frac{u_1(\bar{u}_1 - u_1)}{\bar{u}_1} \quad \Longleftrightarrow \quad \sigma_1 = d_1 \bar{u}_1 e'_1(v_1)$$

# Drift-diffusion for the cations

Balance law for the charge density

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$$\xi_1 = v_1 + z_1 v_0$$

Mobility : vacancy mechanism

$$\sigma_1 = d_1 \frac{u_1(\bar{u}_1 - u_1)}{\bar{u}_1} \iff \sigma_1 = d_1 \bar{u}_1 e_1'(v_1)$$

$$J_1 = -d_1 \left( \partial_x u_1 + z_1 \frac{u_1(\bar{u}_1 - u_1)}{\bar{u}_1} \partial_x v_0 \right)$$

# Boundary conditions in the DPCM / electrons / $\Gamma = 1$

Butler Volmer law in DPCM, modification and reformulation

$$J_2(1) = m_2^1 u_2 - k_2^1 \log(1 + e^{z_2(V-v_0)})$$



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# Boundary conditions in the DPCM / electrons / $\Gamma = 1$

## Butler Volmer law in DPCM, modification and reformulation

$$\begin{aligned} J_2(1) &= m_2^1 u_2 - k_2^1 \log(1 + e^{z_2(V-v_0)}) \\ &= \kappa_2^1 u_2 \left(1 - e^{-(\xi_2 - \xi_2^1)}\right) \end{aligned}$$

### At this point

- a new definition of the current density of cations,
- a new boundary condition for the electrons at the interface with metal
- some values for the outer electrochemical potentials
- the ansatz on the boundary conditions is satisfied

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# The new model

## Equations

$$\begin{cases} \partial_t u_i + \partial_x J_i = 0 & \text{with } J_i = -\sigma_i(v_i) \partial_x \xi_i, \xi_i = v_i + z_i v_0 \\ -\lambda^2 \partial_{xx}^2 v_0 = u_0 & \text{with } u_0 = \sum_{i=1,2} z_i u_i + \rho_{hl} \end{cases}$$

## Boundary conditions

$$\begin{cases} J_i \cdot \nu^\Gamma = r_i^\Gamma(v_i) g_i^\Gamma(\xi_i - \xi_i^\Gamma) & \text{for } i = 1, 2, \Gamma = 0, 1 \\ \lambda^2 \partial_x v_0 \cdot \nu^\Gamma + \beta^\Gamma v_0 = f^\Gamma & \text{for } \Gamma = 0, 1 \end{cases}$$

## Relation charge densities / chemical potential

$$u_i = \bar{u}_i e_i(v_i) \quad (\text{Blakemore / Boltzmann statistics})$$

## Mobilities / chemical potentials

$$\sigma_i(v_i) = d_i \bar{u}_i e_i'(v_i)$$

# Free energy

## Internal energies

$$a_1(u) = u \log u + (1 - u) \log(1 - u) + \log 2, \quad A_1(u) = \bar{u}_1 a_1(u/\bar{u}_1)$$

$$a_2(u) = u \log u - u + 1, \quad A_2(u) = \bar{u}_2 a_2(u/\bar{u}_2)$$

## Helmholtz free energy

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

## Contributions of the carriers leaving the oxide

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

## Total free energy

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

# Free energy dissipation and bounds

## Energy-dissipation equality

$$\begin{aligned} \frac{d}{dt} \Psi^{tot} + \sum_{i=1,2} \int_0^1 \sigma_i(v_i) |\partial_x \xi_i|^2 dx d\tau \\ + \sum_{i=1,2} \sum_{\Gamma \in \{0,1\}} [r_i^\Gamma(v_i) g_i^\Gamma(\xi_i - \xi_i^\Gamma)(\xi_i - \xi_i^\Gamma)] (\Gamma) d\tau = 0. \end{aligned}$$

## Corollary

- Decay in time of  $\Psi^{tot}$
- Time dependent bound on the oxide energy  $\Psi$
- Bounds on the charge densities  $u_1, u_2$
- $C^1$  bound on the electrostatic potential  $v_0$

## Functional setting

$$V = H^1(0, 1) \times H^1(0, 1) \times H^1(0, 1)$$

$$W = H^1(0, 1) \times L^2(0, 1) \times L^\infty(0, 1)$$

$$H = H^1(0, 1) \times L^2(0, 1) \times L^2(0, 1)$$

$$E : W \rightarrow H^*$$

$$A : H \times V \rightarrow V^*$$

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

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

□ GAJEWSKI, GRÖGER, '86, '89



# A global existence result

## Weak solution

$$\begin{cases} u \in H_{loc}^1(\mathbb{R}_+; V^*), & v \in L_{loc}^2(\mathbb{R}_+; V) \cap L_{loc}^\infty(\mathbb{R}_+ \times [0, 1]), \\ \dot{u}(t) + A(v(t), v(t)) = 0, & u(t) = Ev(t), \text{ for a.e. } t \in \mathbb{R}_+, \\ u(0) = u^{\text{in}}. \end{cases}$$

## Theorem

Assume that the initial profiles satisfy

$$\begin{aligned} 0 < \varepsilon \leq u_1^{\text{in}} \leq \bar{u}_1 - \varepsilon, & \quad u_2^{\text{in}} \geq \varepsilon, \\ u_0^{\text{in}} = \sum_{i=1,2} z_i u_i^{\text{in}} + \rho_{hl} \end{aligned}$$

Then, there exists at least one weak solution to the corrosion model.

□ CANCÈS, C.-H., MERLET, RAIMONDI, VENEL, '23

# Main steps of the proof

- 1  $(P_M)$  : a regularized problem obtained by truncating all the nonlinearities applied to chemical potentials at a level  $M$ .
- 2  $(P_{M,n})$  : a time-discrete approximation of  $(P_M)$ 
  - existence result *via* the theory of monotone operators.
  - **compactness** of the sequences of approximate solutions and passage to the limit
  - existence of a solution to  $(P_M)$
- 3 Lower and upper bounds for the chemical potentials obtained by the Moser-Alikakos iteration technique
  - for  $M$  large enough, a solution to  $(P_M)$  is a solution.

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# What is new ?

## An additional species : oxygen vacancies

- Density of the charge species :  $u_3$ , with a charge  $z_3 = 2$ ,
- Chemical and electro-chemical potentials :

$$v_3 = \log \frac{u_3}{\bar{u}_3 - u_3} \text{ and } \xi_3 = v_3 + z_3 v_0$$

- Mobility with vacancy mechanism :

$$\sigma_3 = \frac{u_3(\bar{u}_3 - u_3)}{\bar{u}_3}$$

## A moving domain ( $X_0(t), X_1(t)$ )

- We need equations for the moving boundaries.
- The inertial frame of the oxide moves with velocity

$$v_{ox} = (1 - R_{PB})X_1'.$$

# Balance laws

## Fluxes of species

- $G_i$  : the flux in the inertial frame of the oxide,
- $J_i$  : the flux in the inertial frame of reference.

We have

$$G_i = -\sigma_i \partial_x \xi_i$$

$$J_i = G_i + \varepsilon_i u_i v_{ox} = G_i + \varepsilon_i u_i (1 - R_{PB}) X'_1$$

## Equations on the densities

$$\varepsilon_i \partial_t u_i + \partial_x J_i = 0 \quad \text{in } (X_0, X_1)$$

$$J_i(X_0) - \varepsilon_i u_i(X_0) X'_0 = -r_i^0(u_i(X_0)) g_i^0(\xi_i(X_0) - \xi_i^0), \quad 1 \leq i \leq 3$$

$$J_i(X_1) - \varepsilon_i u_i(X_1) X'_1 = r_i^1(u_i(X_1)) g_i^1(\xi_i(X_1) - \xi_i^1), \quad 1 \leq i \leq 2$$

The flux of oxygens through the interface with the metal vanishes :

$$J_3(X_1) - \varepsilon_3(u_3(X_1) - \bar{u}_3) X'_1 = 0$$

# Grand canonical potential and moving boundaries

## Definition of the grand canonical potential

$$\partial_x \Pi = \sum_{i=1}^3 u_i \partial_x \xi_i, \quad \text{in } (X_0, X_1)$$
$$\int_{X_0}^{X_1} \Pi dx = \int_{X_0}^{X_1} \left( \sum_{i=1}^3 (u_i v_i - A_i(u_i)) - \rho_{\text{hl}} \Phi - \frac{\lambda^2}{2} |\partial_x \Phi|^2 \right) dx$$

## Equations on the moving boundaries

$$X_1' = \kappa^1(\mathbf{u}(X_1), \Phi(X_1)) Z^1 (\Pi(X_1) - \bar{u}_3 \xi_3(X_1) - \Pi^1),$$

$$X_0' = -\kappa^0(\mathbf{u}(X_0), \Phi(X_0)) Z^0 (\Pi(X_0) - \Pi^0) + (1 - R_{\text{PB}}) X_1'.$$

- $(\kappa^\Gamma)_{\Gamma \in \{0,1\}}$  positive functions,
- $(Z^\Gamma)_{\Gamma \in \{0,1\}}$  nondecreasing functions.

# Free energy

Helmholtz free energy in the oxide

$$\Psi(u) = \int_{X_0}^{X_1} \left( \frac{\lambda^2}{2} |\partial_x v_0^*|^2 + \sum_{i=1}^3 A_i(u_i) dx \right) + \sum_{\Gamma \in \{0,1\}} \left[ \frac{\beta^\Gamma}{2} |v_0^*|^2 \right] (\Gamma)$$

Contributions of the carriers leaving the oxide

$$\Psi^\Gamma(t) = \sum_{i=1}^3 \int_0^t [(J_i \cdot \nu^\Gamma) \xi_i^\Gamma] (X_\Gamma) d\tau, \quad \Gamma \in \{0, 1\}.$$

Contribution of the moving boundaries

$$\Psi^{mb}(t) = (X_1(t) - X_1(0))(\Pi^1 + (1 - R_{PB})\Pi^0) - (X_0(t) - X_0(0))\Pi^0$$

Total free energy

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

# Free energy dissipation and bounds

Total free energy

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

Energy-dissipation equality

$$\frac{d}{dt} \Psi^{tot} + \mathcal{D}(t) = 0, \text{ with } \mathcal{D}(t) \geq 0.$$

And now ?

- Proof of the existence of a solution to this new model ?
- Study of the long time behaviour :
  - Existence of traveling waves ?
  - Convergence towards a traveling wave ?
- Numerical simulation of the vDPCM

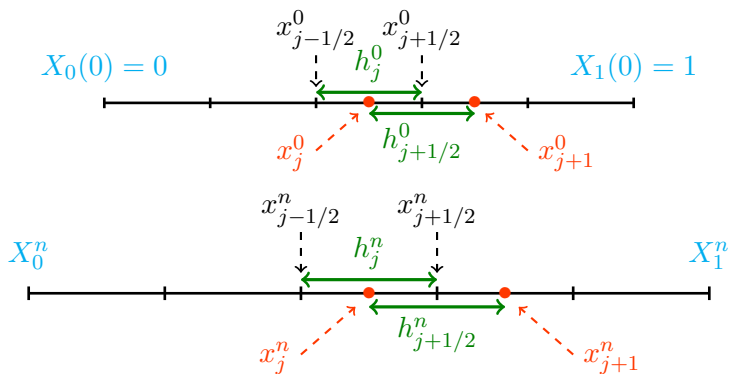


# Outline of the talk

- 1 Towards a thermodynamically consistent model
- 2 Free energy, a priori estimates and existence result
- 3 The three-species model on a moving domain
- 4 Numerical scheme for the vDPCM

# How to deal with a moving domain (in 1D)?

Notations for the mesh



$$\frac{h_j^n}{h_j^0} = \frac{h_{j+1/2}^n}{h_{j+1/2}^0} = \frac{L^n}{L^0} = L^n$$

$$x_{j+1/2}^n = X_0^n + x_{j+1/2}^0 L^n$$
$$x_j^n = \frac{x_{j-1/2}^n + x_{j+1/2}^n}{2}$$

# Finite volume scheme

$$\varepsilon \partial_t u + \partial_x J = 0 \text{ in } (X_0(t), X_1(t))$$

Integration over  $(x_{j-1/2}(t), x_{j+1/2}(t))$

$$\begin{aligned} \varepsilon \frac{d}{dt} \int_{x_{j-1/2}(t)}^{x_{j+1/2}(t)} u(x, t) dx &= \int_{x_{j-1/2}(t)}^{x_{j+1/2}(t)} \varepsilon \partial_t u(x, t) dx \\ &+ \varepsilon u(x_{j+1/2}(t), t) x'_{j+1/2}(t) - \varepsilon u(x_{j-1/2}(t), t) x'_{j-1/2}(t) \\ &= -J(x_{j+1/2}(t), t) + \varepsilon u(x_{j+1/2}(t), t) x'_{j+1/2}(t) \\ &+ J(x_{j-1/2}(t), t) - \varepsilon u(x_{j-1/2}(t), t) x'_{j-1/2}(t) \end{aligned}$$

Approximation

$$\begin{aligned} h_j^n u_j^n &\approx \int_{x_{j-1/2}(t^n)}^{x_{j+1/2}(t^n)} u(x, t) dx \\ \mathcal{F}_{j+1/2}^n &\approx J(x_{j+1/2}(t^n), t^n) - \varepsilon u(x_{j+1/2}(t^n), t^n) x'_{j+1/2}(t^n) \end{aligned}$$

# Finite volume scheme

## Balance law

$$\varepsilon \frac{h_j^n u_j^n - h_j^{n-1} u_j^{n-1}}{\delta t} + \mathcal{F}_{j+1/2}^n - \mathcal{F}_{j-1/2}^n = 0$$

## Numerical fluxes

$$G = -\sigma(u) \partial_x \xi$$

$$J = G + \varepsilon u (1 - R_{\text{PB}}) X_1'$$

$$\begin{aligned} \mathcal{F}_{j+1/2}^n &\approx G(x_{j+1/2}(t^n), t^n) \\ &\quad + \varepsilon u(x_{j+1/2}(t^n), t^n) \left( (1 - R_{\text{PB}}) X_1' - x'_{j+1/2}(t^n) \right) \end{aligned}$$

We set

$$\begin{aligned} \mathcal{F}_{j+1/2}^n &= \mathcal{G}_{j+1/2}^n \\ &\quad + \varepsilon u_{j+1/2}^n \left( \frac{(1 - R_{\text{PB}})(X_1^n - X_1^{n-1}) - x_{j+1/2}^n + x_{j+1/2}^{n-1}}{\delta t} \right) \end{aligned}$$

# Numerical fluxes, interface values and canonical potential

## Definition of $\mathcal{G}_{j+1/2}$

- For the electrons, standard Scharfetter-Gummel fluxes.
- For the cations and oxygen vacancies

$$\mathcal{G}_{j+1/2} = \frac{1}{h_{j+1/2}} \left( B(z_i(\Phi_{j+1} - \Phi_j)) \frac{u_j(\bar{u} - u_{j+1})}{\bar{u}} - B(-z_i(\Phi_{j+1} - \Phi_j)) \frac{u_{j+1}(\bar{u} - u_j)}{\bar{u}} \right).$$

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□ CANCÈS, HERDA, MASSIMINI, '23

## Definition of $u_{j+1/2}$

- mean value of  $u_j, u_{j+1}$ , depending on  $\Phi_j, \Phi_{j+1}$

## Approximation of the grand canonical potential $\Pi$

# Main property of the scheme

## Total free energy

We can define :

- $\Psi_{tot}^n$  discrete counterpart of the total free energy  $\Psi^{tot}(t^n)$ ,
- $\mathcal{D}^n$  discrete counterpart of its dissipation  $\mathcal{D}(t^n)$

### Energy-dissipation inequality

$$\frac{\Psi_{tot}^n - \Psi_{tot}^{n-1}}{\delta t} + \mathcal{D}^n \leq 0, \text{ with } \mathcal{D}^n \geq 0.$$

- a first step towards the numerical analysis of the scheme
- implementation and simulation of the vDPCM

# Numerical experiments

- Still under progress !
- The code is running for a set of parameters.
- But the set of parameters has to be calibrated...

values for the grand canonical potentials ?

functions defining the displacement of interfaces ?

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À SUIVRE !...