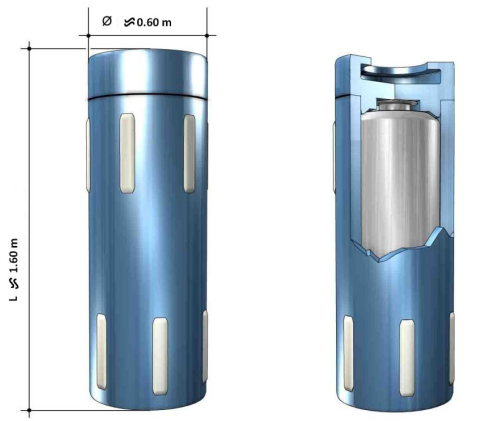
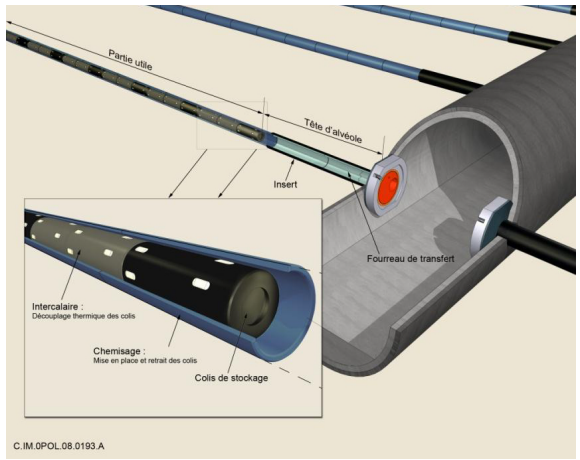
Towards a thermodynamically consistent model for the corrosion of iron

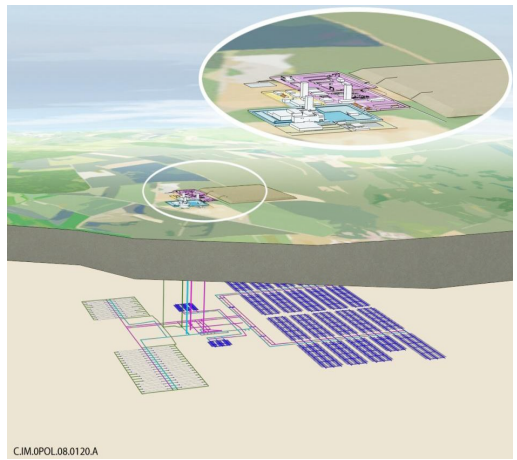
Christian Bataillon Clément Cancès Claire Chainais-Hillairet
Benoît Merlet Federica Raimondi Juliette Venel

Project team RAPSODI, Inria Lille - Nord Europe

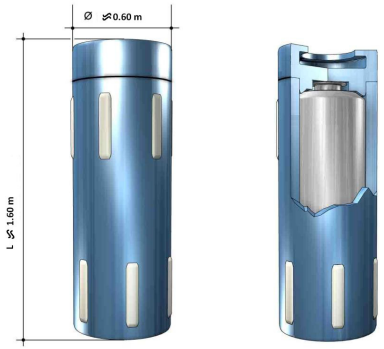
Motivation: nuclear waste repository in deep underground

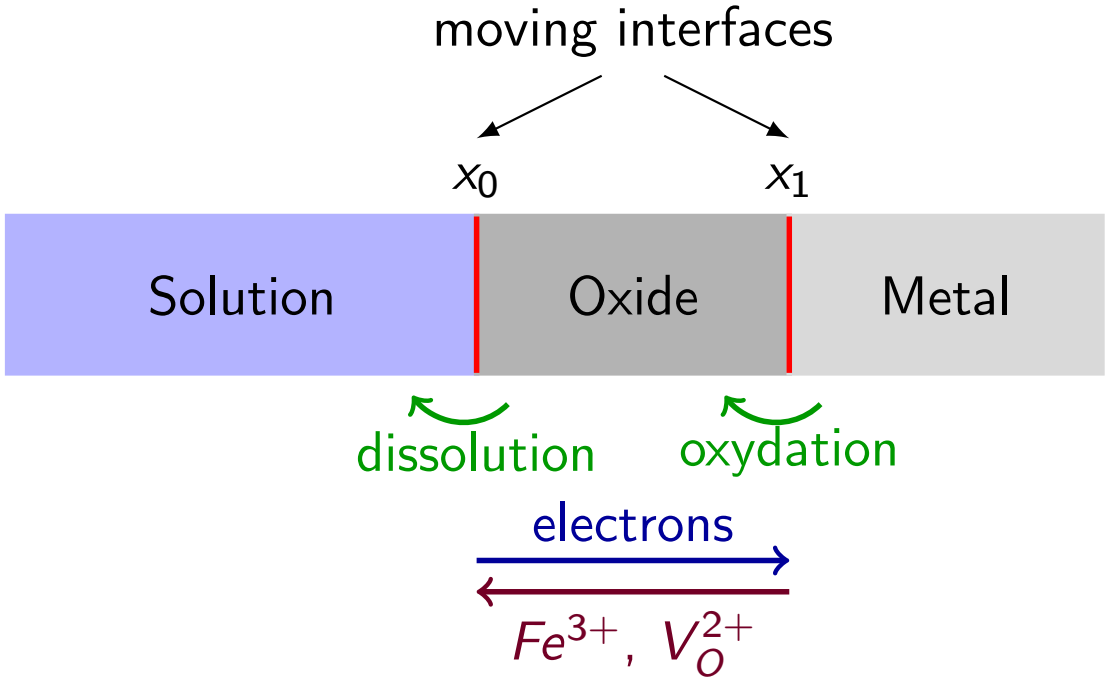






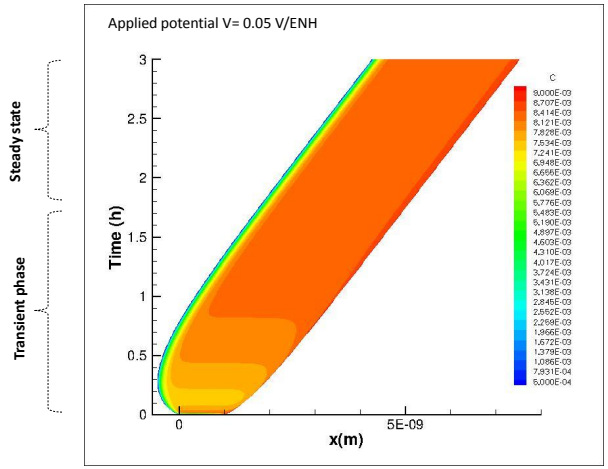
Corrosion of iron: state of the art





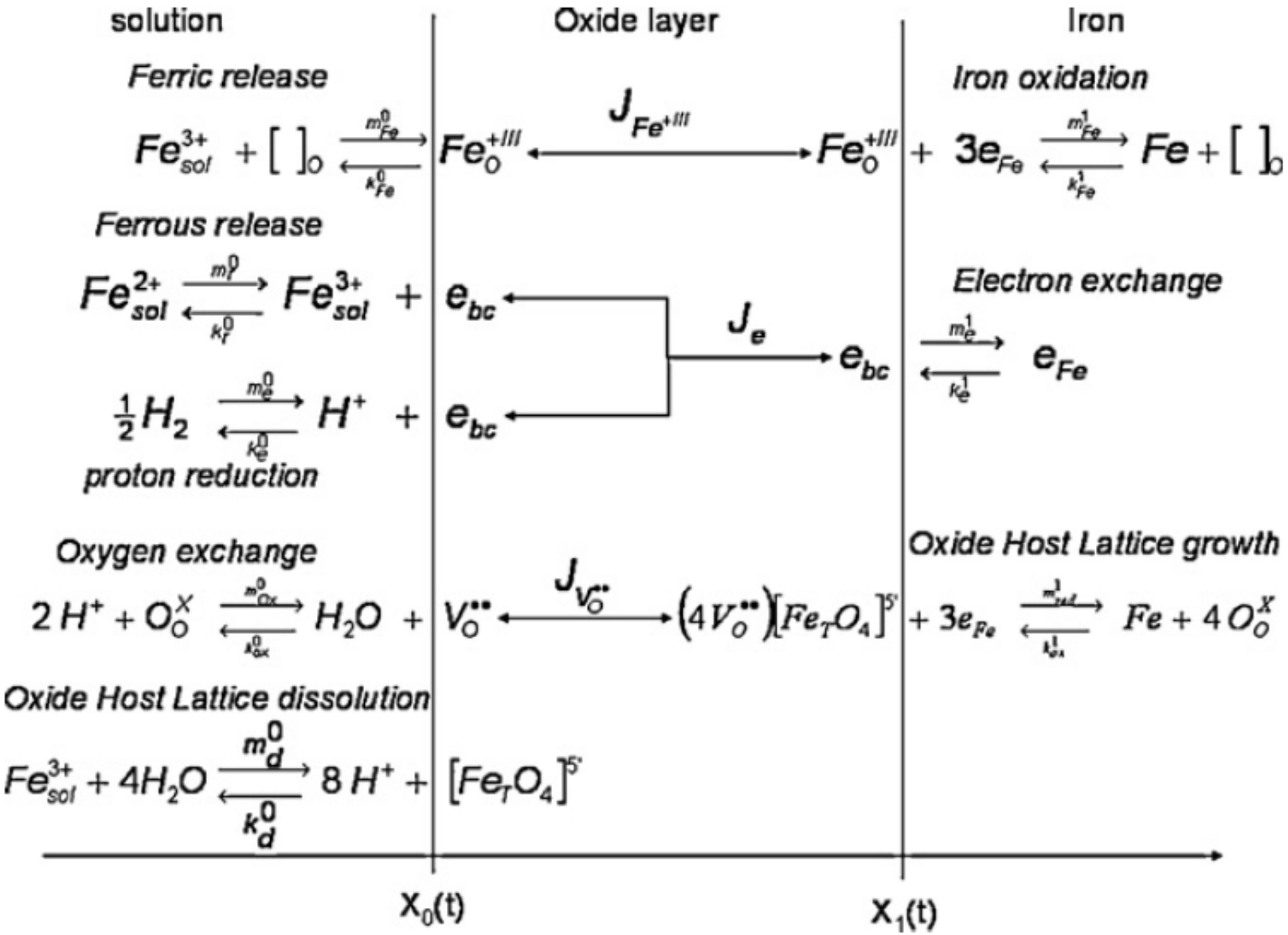
State of the art

- Reference model not based on thermodynamics [Bataillon *et al.* '10]
- Simulations without mathematical assessment [Bataillon *et al.* '12]



Chemical reaction summary

[Bataillon *et al.* '10]



Overall goal of our project within EURAD (2019-2023)

Derivation of a thermodynamically consistent model

- Same physical ingredients as in [Bataillon *et al.* '10, '12]
- Compatibility with thermodynamics (2^{nd} principle)

Mathematical analysis of the model

- Generalized gradient flow structure [Mielke '11]
- Existence, uniqueness
- Long-time behaviour

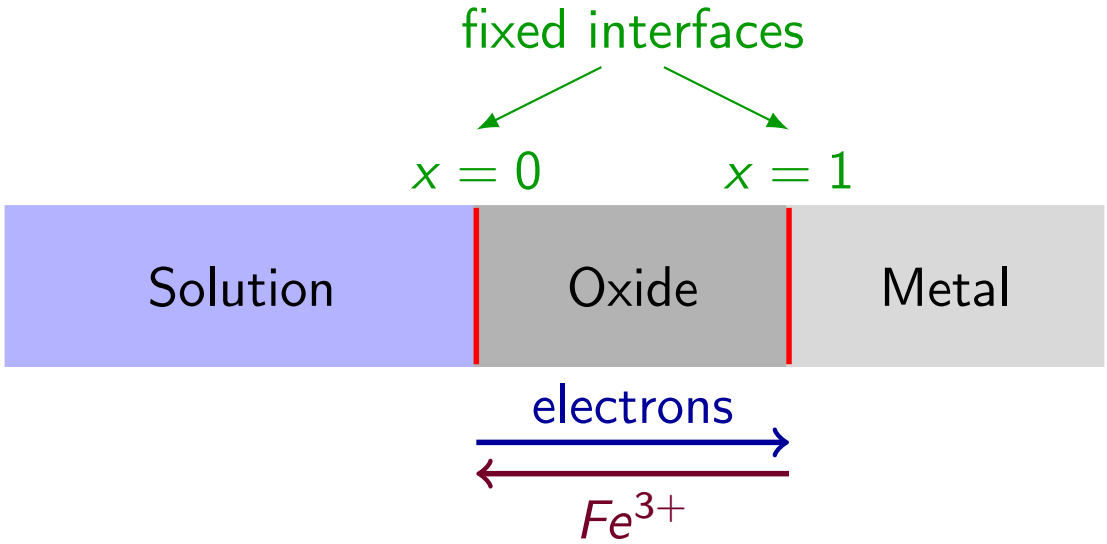
Design, analysis and implementation of relevant schemes

- Entropy production at the discrete level
- Convergence
- Long-time behaviour

A reduced model with 2 species

A reduced (toy) model

[Chainais-Hillairet & Lacroix-Violet '15]



Some notations

- u_1: concentration of iron cations Fe^{3+}
- u_2: concentration of electrons e^-
- J_1, J_2: flux of Fe^{3+} and e^-

$$\partial_t u_i + \partial_x J_i = 0$$

- μ_i: electrochemical potential

$$J_i = -\eta_i(u_i)\partial_x \mu_i, \qquad \eta_i(u_i) \geq 0$$

Electrical and chemical potentials

- z_i: charge of the i^{th} species

$$z_1 = +3, \quad z_2 = -1$$

- Electrostatic potential Ψ

$$-\lambda^2 \partial_{xx}\Psi = \sum_{i=1,2} z_i u_i + \rho_{\text{hl}} \qquad \text{in } (0,1)$$

$$\Psi - \alpha_0 \partial_x \Psi = \Delta\Psi_0^{\text{pzc}} \qquad \text{at } x = 0$$

$$\Psi + \alpha_1 \partial_x \Psi = V - \Delta\Psi_1^{\text{pzc}} \qquad \text{at } x = 1$$

- Chemical potentials $\mu_i^{\chi}(u_i)$ to be determined
- Electro-chemical potentials

$$\mu_i = \mu_i^{\chi} + z_i \Psi$$

About the boundary conditions

Ansatz: boundary fluxes are generated by differences in the chemical potentials

- for $i = 1, 2$:

$$\begin{aligned} -J_i(t,0) &= f_i^0(u_i, \mu_i(0) - \mu_i^{\mathrm{sol}}) \\ J_i(t,1) &= f_i^1(u_i, \mu_i(1) - \mu_i^{\mathrm{met}}) \end{aligned}$$

- f_i^x, $x \in \{0,1\}$, satisfies

$$\partial_\xi f_i^x(u_i, \xi) \geq 0, \qquad f_i^x(u_i, 0) = 0$$

- The electrochemical potentials outside the oxide still to be defined
  - μ_i^{sol} in the solution
  - μ_i^{met} in the metal

Iron cations Fe^{3+}

Butler-Volmer conditions

[Bataillon *et al.* '10]

Butler-Volmer fluxes

$$-J_1(t,0) = k_1^0 u_1 \, e^{\frac{z_1}{2}\Psi} - m_1^0(\overline{u}_1 - u_1)e^{-\frac{z_1}{2}\Psi}$$
$$J_1(t,1) = m_1^1 u_1 \, e^{\frac{z_1}{2}(\Psi - V)} - k_1^1(\overline{u}_1 - u_1)e^{-\frac{z_1}{2}(\Psi - V)}$$

$(\overline{u}_1 = 2)$

Butler-Volmer conditions

[Bataillon *et al.* '10]

Butler-Volmer fluxes

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$(\overline{u}_1 = 2)$

Reformulation of the Butler-Volmer conditions

$$-J_1(t,0) = 2r_1^0(u_1(0))\sinh\left(\frac{1}{2}\left(\log\frac{u_1}{\overline{u}_1 - u_1} + z_1\Psi - c_1^0\right)\right)$$
$$J_1(t,1) = 2r_1^1(u_1(1))\sinh\left(\frac{1}{2}\left(\log\frac{u_1}{\overline{u}_1 - u_1} + z_1\Psi - c_1^1 - z_1 V\right)\right)$$

with $r_1^x(u_1) = \sqrt{k_1^x m_1^x u_1(\overline{u}_1 - u_1)}$, $c_1^0 = \log\frac{m_1^0}{k_1^0}$ and $c_1^1 = \log\frac{k_1^1}{m_1^1}$

Some remarks

1. $\mu_1^x(u_1) = \log\frac{u_1}{\overline{u}_1 - u_1}$
2. $m_i^x > 0$ and $k_i^x > 0$ (reversibility)
3. $\mu_i^{\mathrm{sol}} = c_i^0$, $\mu_i^{\mathrm{met}} = c_i^1 + 3V$
4. Vacancy diffusion

Drift diffusion for cations in the oxide

From the ansatz

$$\partial_t u_1 + \partial_x J_1 = 0, \qquad J_1 = -\eta_1(u_1)\partial_x \mu_1$$

Fermi-Dirac statistics

$$\mu_1 = \log \frac{u_1}{\overline{u}_1 - u_1} + z_1 \Psi$$

Vacancy diffusion

$$\eta_1(u_1) = d_1 \frac{u_1(\overline{u}_1 - u_1)}{\overline{u}_1} \quad \Longrightarrow \quad J_1 = -d_1 \left(\partial_x u_1 + z_1 \frac{u_1(\overline{u}_1 - u_1)}{\overline{u}_1} \partial_x \Psi \right)$$

Electrons e^-

Electron exchange with the solution

[Bataillon *et al.* '10]

$$
\begin{aligned}
-J_2(0,t) &= k_2^0 u_2 e^{z_2 \Psi/2} - m_2^0 e^{-z_2 \Psi/2} \\
&= 2 r_2^0(u_2(0)) \sinh\left(\frac{1}{2}\left(\log(u_2) + z_2\Psi - c_2^0\right)\right)
\end{aligned}
$$

with $r_2^0 = \sqrt{m_2^0 k_2^0 u_2}$ et $c_2^0 = \log \frac{m_2^0}{k_2^0}$.

Some remarks

1. $\mu_2^{\chi}(u_2) = \log u_2$ (Boltzmann statistics)
2. $m_2^0 > 0$ et $k_2^0 > 0$ (reversibility)
3. $\mu_2^{\text{sol}} = c_2^0$
4. Band conduction (no limitation on the number of electrons)

Drift diffusion of the electrons in the oxide

[Bataillon *et al.* '10]

From the ansatz

$$\partial_t u_2 + \partial_x J_2 = 0, \qquad J_2 = -\eta_2(u_2)\partial_x \mu_2$$

Boltzmann statistics

$$\mu_2 = \log u_2 + z_2 \Psi$$

Band conduction

$$\eta_2(u_2) = d_2 u_2 \qquad \Longrightarrow \qquad J_2 = -d_2 \left(\partial_x u_2 + z_2 u_2 \partial_x \Psi\right)$$

Electron exchanges with the metal

Unbalanced Butler-Volmer condition

$$J_2^1 = m_2^1 u_2 - k_2^1 e^{z_2 V - \Psi}$$
$$= r_2^1(u_2)\left(1 - e^{-(\mu_2 - \mu_2^{\mathrm{met}})}\right)$$

with $\kappa_2^1 = m_2^1 u_2$ and $\mu_2^{\mathrm{met}} = \log \frac{m_2^1}{k_2^1} + z_2 V$

Dissipation property

As for the other boundary fluxes,

$$J_2^1(\mu_2 - \mu_2^{\mathrm{met}}) \geq 0$$

Remark: : This property was not encoded in [Bataillon *et al.* '10]

Free energy dissipation

Unknowns and evolution processes

- u_1, u_2: concentrations in the oxide layer
- J_1, J_2: corresponding fluxes

$$\partial_t u_i + \partial_x J_i = 0 \quad \text{in } \mathbb{R}_+ \times (0,1)$$

- $\mathcal{U}_1^{\text{sol}}, \mathcal{U}_2^{\text{sol}}$: quantity of iron cations and (attached) electrons in the solution

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{U}_i^{\text{sol}} = -J_i(0)$$

- $\mathcal{U}_1^{\text{met}}, \mathcal{U}_2^{\text{met}}$: quantity of iron and electrons in the metal

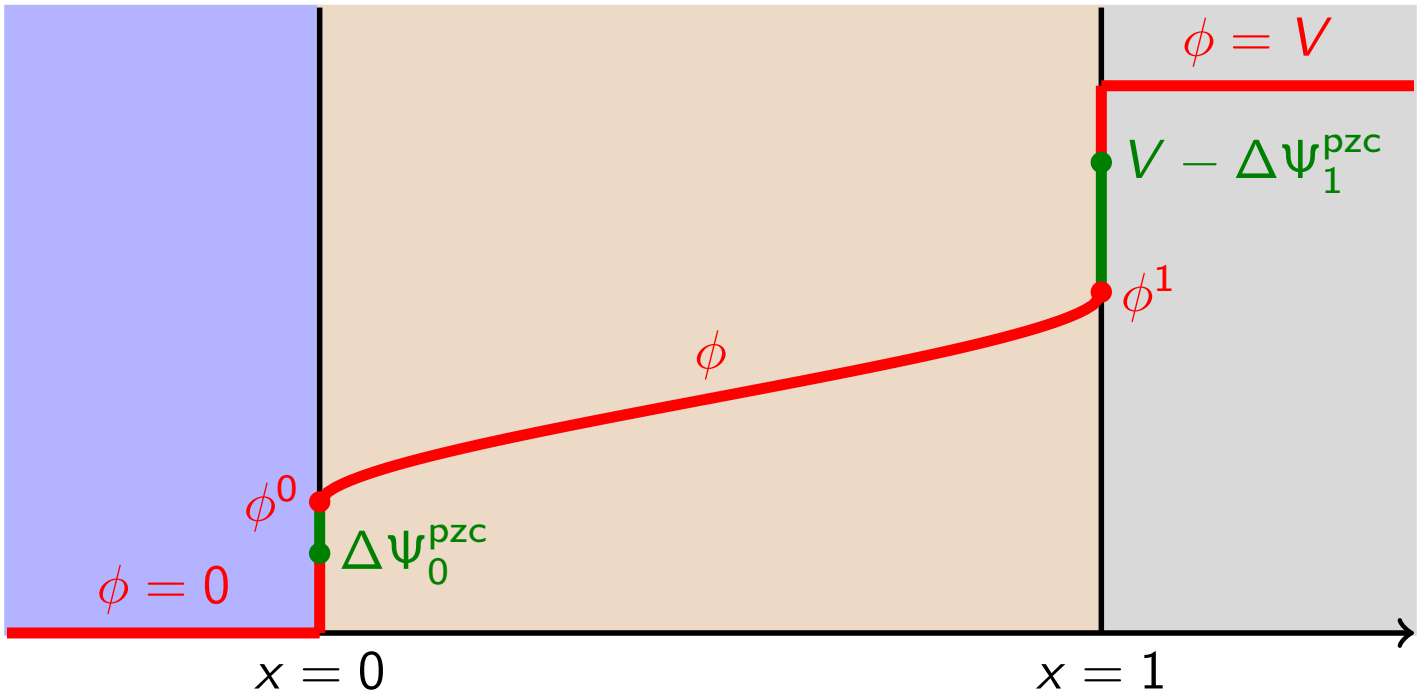
$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{U}_i^{\text{met}} = J_i(1)$$

- Self-consistent electrostatic potential Ψ (Poisson – Robin)

Electric energy

Dual electrostatic energy $\mathfrak{E}$

$$\mathfrak{E}(\phi) = \frac{\lambda^2}{2}\left(\int_0^1 |\partial_x \phi|^2 + \frac{1}{\alpha_0}\left|\phi^0 - \Delta\psi_0^{\text{pzc}}\right|^2 + \frac{1}{\alpha_1}\left|\phi^1 - V + \Delta\psi_1^{\text{pzc}}\right|^2\right)$$



Electric energy

Primal electrostatic energy $\mathcal{E}$

$$\mathcal{E}(\boldsymbol{u}) = \mathfrak{E}^*(\rho) = \sup_{\phi} \left[\int_0^1 \rho\phi - \mathfrak{E}(\phi) \right]$$

where ρ is the charge:

$$\rho = z_1 u_1 + z_2 u_2 + \rho_{\mathsf{hl}}$$

$$\mathcal{E}(\rho) = \frac{\lambda^2}{2} \int_0^1 |\partial_x \Psi|^2 + \frac{\lambda^2}{2\alpha^0} \left(|\Psi^0|^2 - |\Delta\Psi_0^{\mathsf{pzc}}|^2 \right) + \frac{\lambda^2}{2\alpha^1} \left(|\Psi^1|^2 - |V - \Delta\Psi_1^{\mathsf{pzc}}|^2 \right)$$

where the electric potential $\Psi = \frac{\delta \mathcal{E}}{\delta \rho}$ satisfies the elliptic equation

$$\begin{cases} -\lambda^2 \partial_{xx} \Psi = \rho & \text{dans } (0,1), \\ -\alpha^0 \partial_x \Psi^0 + (\Psi^0 - \Delta\Psi_0^{\mathsf{pzc}}) = 0 & \text{en } 0, \\ \alpha^1 \partial_x \Psi^1 + (\Psi^1 - V + \Delta\Psi_1^{\mathsf{pzc}}) = 0 & \text{en } 1. \end{cases}$$

Electric energy

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where ρ is the charge:

$$\rho = z_1 u_1 + z_2 u_2 + \rho_{\text{hl}} \qquad \Longrightarrow \qquad \frac{\delta \mathcal{E}}{\delta u_i} = z_i \Psi$$

$$\mathcal{E}(\rho) = \frac{\lambda^2}{2} \int_0^1 |\partial_x \Psi|^2 + \frac{\lambda^2}{2\alpha^0} \left(|\Psi^0|^2 - |\Delta\Psi_0^{\text{pzc}}|^2 \right) + \frac{\lambda^2}{2\alpha^1} \left(|\Psi^1|^2 - |V - \Delta\Psi_1^{\text{pzc}}|^2 \right)$$

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Chemical and electro-chemical free energies

Chemical energy

$$\mathcal{A}(\boldsymbol{u}) = \int_0^1 [u_1 \log u_1 + (\overline{u}_1 - u_1)\log(\overline{u}_1 - u_1) + u_2 \log u_2 - u_2 + \kappa] \geq 0$$

Oxide electrochemical energy

$$\mathcal{F}(\boldsymbol{u}) = \mathcal{A}(\boldsymbol{u}) + \mathcal{E}(\boldsymbol{u}) \geq 0$$

Total electrochemical energy

$$\mathcal{F}_{\text{tot}}(t) = \mathcal{A}(\boldsymbol{u}(t)) + \mathcal{E}(\boldsymbol{u}(t)) + \underbrace{\sum_{i=1,2} \left(\mathcal{U}_i^{\text{met}}(t)\mu_i^{\text{met}} + \mathcal{U}_i^{\text{sol}}(t)\mu_i^{\text{sol}}\right)}_{\text{contributions from outside the oxide}}$$

Free energy dissipation

Energy dissipation equality

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}_{\mathsf{tot}} + \sum_{i=1,2} \int_0^1 J_i(-\partial_x \mu_i)$$
$$+ \sum_{i=1,2} J_i(1)\left(\mu_i(1) - \mu_i^{\mathsf{met}}\right) + \sum_{i=1,2} (-J_i(0))\left(\mu_i(0) - \mu_i^{\mathsf{sol}}\right) = 0$$

Free energy dissipation

Energy dissipation equality

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}_{\mathsf{tot}} + \sum_{i=1,2}\int_0^1 J_i(-\partial_x\mu_i) + \sum_{i=1,2} J_i(1)\left(\mu_i(1) - \mu_i^{\mathsf{met}}\right) + \sum_{i=1,2}\left(-J_i(0)\right)\left(\mu_i(0) - \mu_i^{\mathsf{sol}}\right) = 0$$

Corollary

- Time-dependent bound on the oxide energy

$$0 \le \mathcal{F}(\boldsymbol{u}(t)) \le C(t) \quad \Longrightarrow \quad 0 \le u_1 \le \overline{u}_1,\ u_2 \in L^\infty_{\mathsf{loc}}(\mathbb{R}_+; L\log L(0,1))$$

- C^1 bound on the electric potential

$$\|\partial_x\Psi(t)\|_\infty \le C(t)$$

A global existence result

Theorem [C., Chainais-Hillairet, Merlet, Raimondi & Venel, *submitted*]

Assume that the initial concentration profiles satisfy

$$u_i(t=0) \geq \epsilon > 0, \qquad u_1(t=0) \leq \overline{u}_1 - \epsilon < \overline{u}_1,$$

then there exists a weak solution with

$$\mu_i \in L^2_{\mathrm{loc}}(\mathbb{R}_+; H^1(0,1)) \cap L^\infty_{\mathrm{loc}}(\mathbb{R}_+ \times [0,1])$$

In particular, (EDE) is satisfied.

Main ideas of the proof [Gajewski & Gröger '89 '96], ...

1. regularize η_i and r_i^x near $u_i = 0$ and $u_1 = \overline{u}_1$ and discretize w.r.t. time
2. existence of a solution to the regularized time discrete problem
3. limit $\Delta t \to 0 \rightsquigarrow$ existence to the regularized system
4. Moser iterations $\rightsquigarrow \|\mu_i\|_\infty \leq C \implies (u_i)_i$ solution to the initial problem

Numerical approximation

Main ingredients

Finite Volume approximation

- Fully implicit in time (Backward Euler scheme)
- TPFA finite volume scheme for the Poisson equation on Ψ
  [Herbin '95], [Eymard, Gallouët & Herbin '00]
- Scharfetter-Gummel fluxes to approximate J_2 (linear in u_2)
  [Scharfetter-Gummel '69], [Chatard '11]
- SQRA fluxes to approximate J_1 (nonlinear in u_1)
  [C. & Venel '22+ϵ]

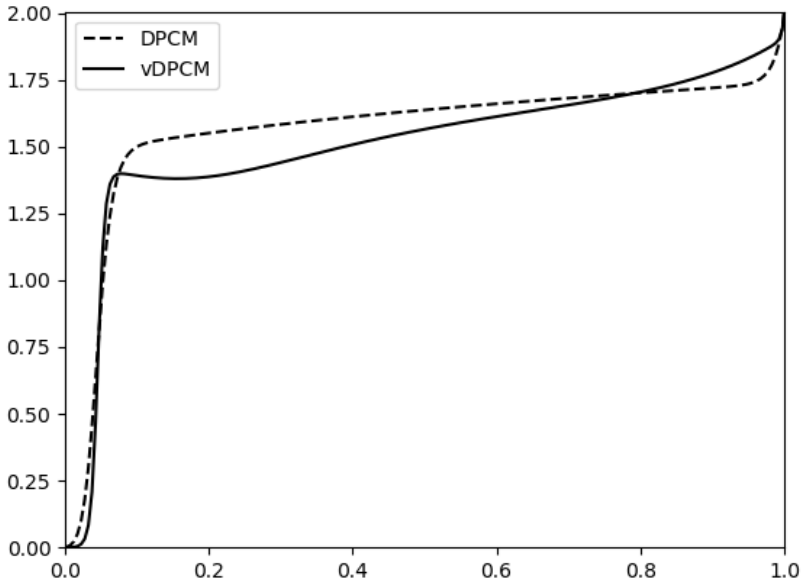
$$J_1 = -d_1 \partial_x u_1 - \eta_1(u_1) z_1 \partial_x \Psi, \qquad \eta_1(u_1) = d_1 \frac{u_1(\overline{u}_1 - u_1)}{\overline{u}_1}$$

Effective resolution

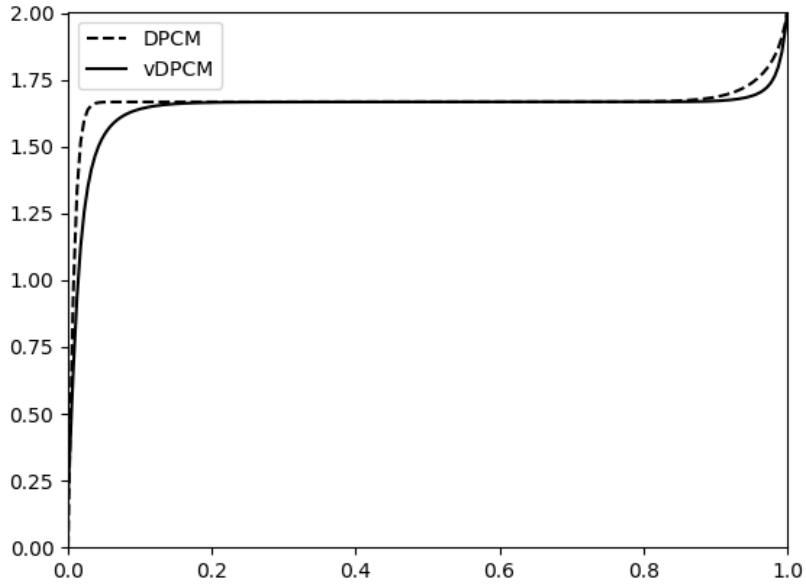
- Nonlinear system $\Phi(\boldsymbol{u}_h^n, \Psi_h^n) = 0$ solved with Newton at each time step

Numerical results

Solution profiles (cations)



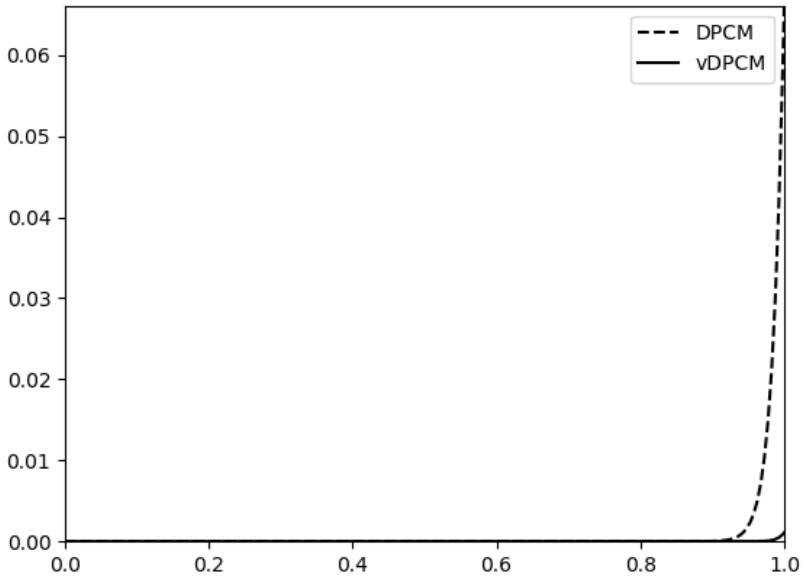
$t = 18$s (transient)



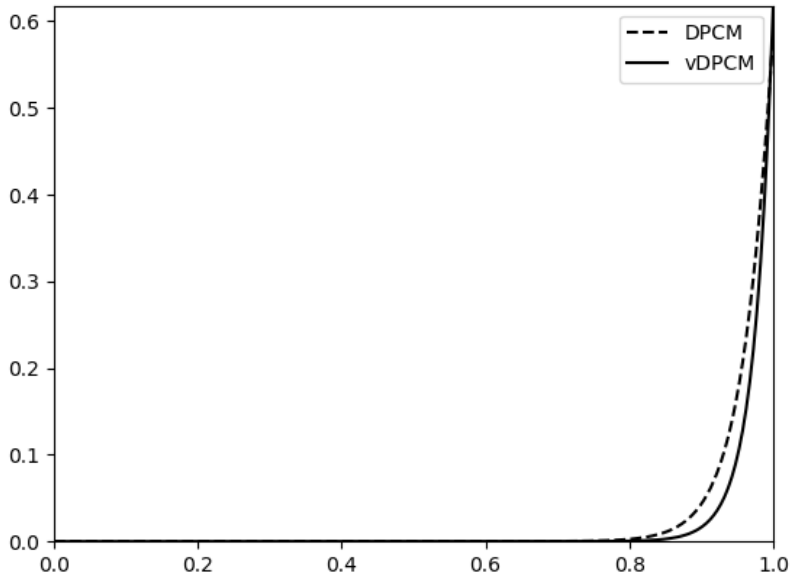
$t = 1510$s (steady steate)

Numerical results

Solution profiles (electrons)



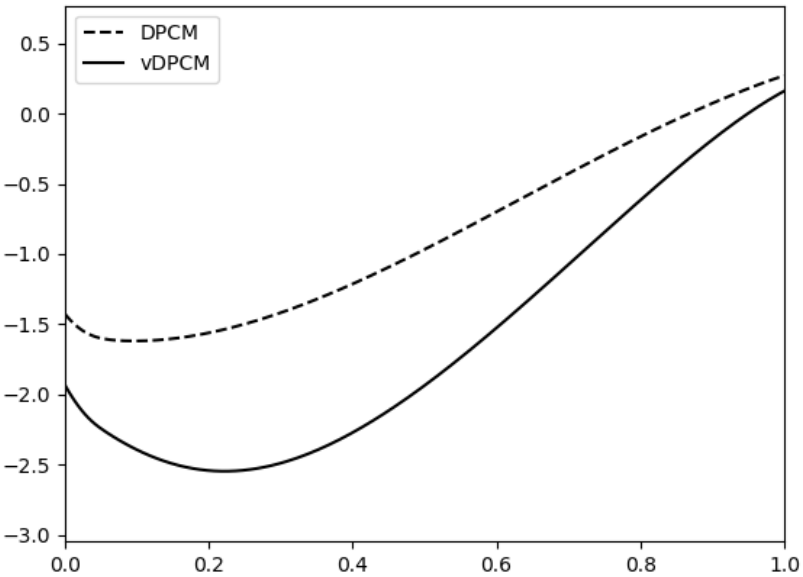
$t = 18$s (transient)



$t = 1510$s (steady steate)

Numerical results

Solution profiles (electric potential)



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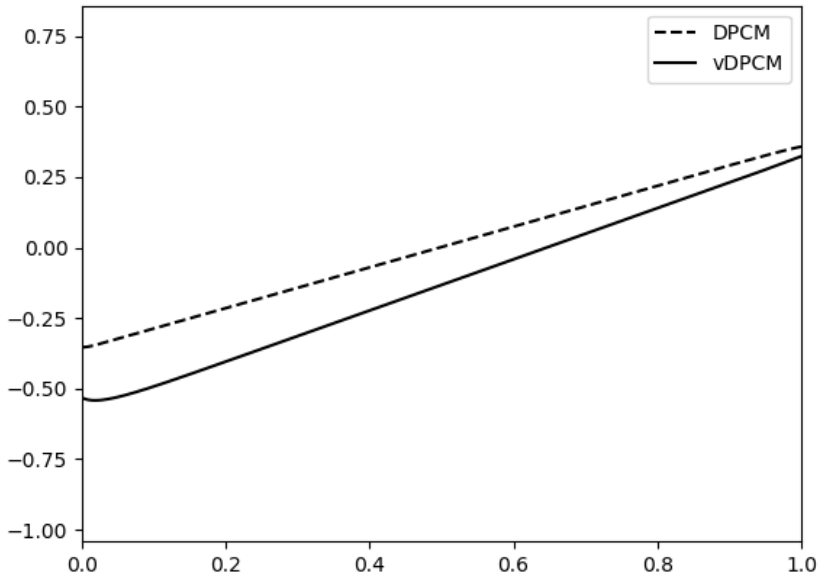

$t = 1510$s (steady steate)

Numerical results

I-V curves

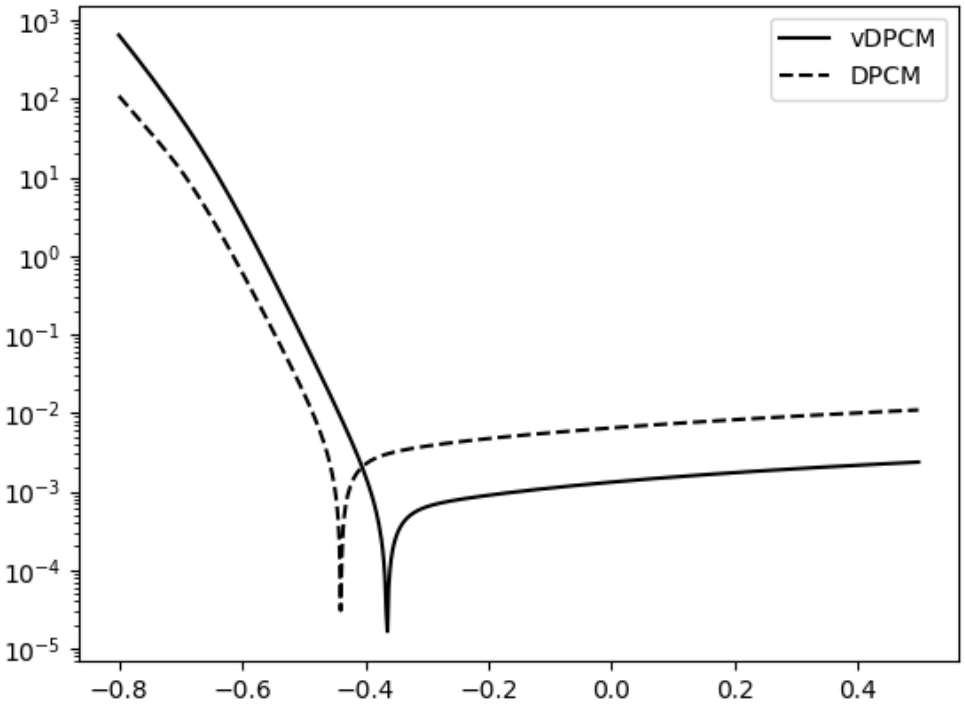

Figure: Evolution of the total current for the steady state (in physical units $A \cdot m^{-2}$) in terms of the applied potential (in Volts) at $pH = 8.5$.

Conclusions and prospects

Conclusions

- Minor modifications (mobility η_1, boundary condition for electrons at oxide/metal interface) of the original (toy) model studied in [Chainais-Hillairet & Lacroix-Violet '15] to make it free-energy diminishing
- This energetic stability allows to show an existence result without any condition on the physical parameters following [Gajewski & Gröger '89]
- Thermodynamically consistent approximation based on SQRA finite volumes

Prospects

- Numerical evaluation of the influence of these modifications on the solution
- Back to the original problem with moving boundaries