The generalized Poisson-Nernst-Planck system with nonlinear interface conditions

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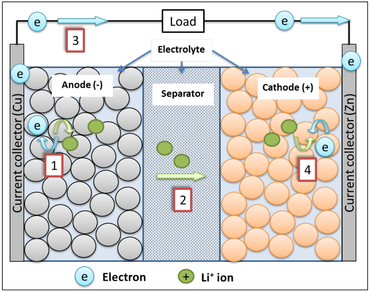
Motivation

Electro–kinetic phenomena in bio–molecular or electro–chemical models
Specific interest concerns lithium ion batteries

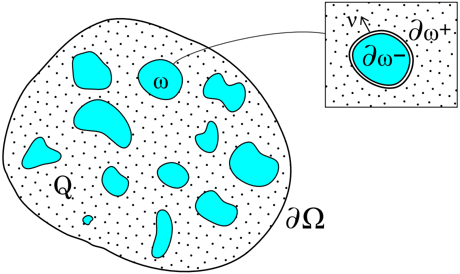


Sources: Wikipedia, University of Oxford: Energy and Power Group

Overwiew

- Modeling
  - Discontinuous solution in a two-phase medium
  - Nonlinear reactions at the face interface
  - Taking pressure into account
    (as a consequence of the Navier–Stokes equations)
  - Mass and volume balances
  - Positivity of concentrations
- Well–posedness
  - Generalized formulation coupled with dual entropy variables and constraints
  - Existence theorem based on the reduced formulation without constraints
  - A priori energy and entropy estimates
  - Weak maximum principle
  - Uniqueness in a special case
  - Lyapunov stability

Geometry



Q pore phase, ω solid phase, $\partial\omega$ interface with a jump $[\![\cdot]\!] = \cdot|_{\partial\omega^+} - \cdot|_{\partial\omega^-}$

$\Omega = Q \cup \omega \cup \partial\omega$ two-phase domain

Spatial dimension $d \in \{1, 2, 3\}$

PNP | The generalized Poisson–Nernst–Planck system. 1

For charge species $i = 1, \dots, n$ in $(0,T) \times (Q \cup \omega)$:

$$\text{The Fick's law of diffusion:} \quad \frac{\partial c_i}{\partial t} - \operatorname{div} J_i = 0 \tag{1a}$$

$$\text{with diffusion fluxes:} \quad J_i = \sum_{j=1}^{n} c_j (\nabla \mu_j)^\top m_i D^{ij} \tag{1b}$$

in particles $(0,T) \times \omega$:

$$\text{electro-chemical potentials:} \quad \mu_i = k_B \Theta \ln(\beta_i c_i) \tag{1c}$$

$$\text{the Ohm's law:} \quad -\operatorname{div}((\nabla \varphi)^\top A) = 0 \tag{1d}$$

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c_i $\left(mol/m^3\right)$ concentrations of charged species with the charge numbers z_i,
J_i $\left(mol/(m^2 \cdot s)\right)$ diffusion fluxes,
D^{ij} $\left(m^2/(J \cdot s)\right)$ diffusivity matrices in $\mathbb{R}^{d \times d}$,
φ (V) electrostatic potential,
μ_i (J) (quasi–Fermi) electro-chemical potentials,
A (F/m) electric permittivity in $\mathbb{R}^{d \times d}$,
$m_i \geqslant 0$, $k_B \geqslant 0$, $\Theta \geqslant 0$, $\beta_i \geqslant 0$ are constant

PNP | The generalized Poisson–Nernst–Planck system. 2

In pore $(0,T)\times Q$:

quasi–Fermi electro-chemical potentials:

$$\mu_i = k_B \Theta \ln(\beta_i c_i) + \frac{1}{N_A}\Big(\frac{1}{C}p + z_i\varphi\Big) \tag{2a}$$

the force balance: $$\nabla p = -\Big(\sum_{k=1}^{n} z_k c_k\Big)\nabla\varphi \tag{2b}$$

the Gauss's flux law: $$-\operatorname{div}((\nabla\varphi)^{\top}A) = \sum_{k=1}^{n} z_k c_k \tag{2c}$$

C (mol/m^3) summary concentration,
p (Pa) pressure,
$N_A \geqslant 0$ constant

PNP | Boundary and initial conditions

Dirichlet conditions:

$$c_i = c_i^D, \quad i = 1, \dots, n, \quad \text{on} \quad (0,T) \times \partial\Omega \tag{3a}$$

$$\varphi = \varphi^D \quad \text{on} \quad (0,T) \times \partial\Omega \tag{3b}$$

Interface conditions:

$$[\![J_i]\!]\nu = 0, \quad -J_i\nu = g_i\big(\boldsymbol{c}, \varphi\big) \quad \text{on } (0,T) \times \partial\omega \tag{4a}$$

$$[\![(\nabla\varphi)^\top A]\!]\nu = 0, \quad -(\nabla\varphi)^\top A\nu + \alpha[\![\varphi]\!] = g \quad \text{on } (0,T) \times \partial\omega \tag{4b}$$

Initial conditions:

$$c_i = c_i^{in} \quad \text{on } Q \cup \omega \tag{5}$$

PNP | Thermodynamic properties

Positivity of concentrations:

$$c_i > 0, \quad i = 1, \ldots, n, \quad \text{in} \quad (0, T) \times (Q \cup \omega) \tag{6}$$

Volume balance:

$$\sum_{i=1}^{n} c_i = C \quad \text{in} \quad (0, T) \times (Q \cup \omega) \tag{7}$$

Mass balance:

$$\sum_{i=1}^{n} J_i = 0 \quad \text{in} \quad (0, T) \times (Q \cup \omega) \tag{8}$$

follows from volume balance (7) and diffusivity property (19)

PNP | Data of the problem

Initial data as $t = 0$

Volume balance:

$$\sum_{i=1}^{n} c_i^{in} = C \quad \text{in} \quad Q \cup \omega \tag{9}$$

Positivity:

$$c_i^{in} > 0, \quad i = 1, \ldots, n, \quad \text{in} \quad Q \cup \omega \tag{10}$$

Boundary data

Volume balance:

$$\sum_{i=1}^{n} c_i^{D} = C \quad \text{on} \quad (0, T) \times \partial\omega \tag{11}$$

Positivity:

$$c_i^{D} > 0 \quad \text{on} \quad (0, T) \times \partial\omega \tag{12}$$

Compatibility conditions:

$$c_i^{D}(0, \cdot) = c_i^{in}, \quad i = 1, \ldots, n, \quad \text{in} \quad Q \cup \omega \tag{13}$$

Nonlinear boundary data

Growth conditions:

$$\int_{\partial\omega} |g_i(\mathbf{c},\varphi)|^2\,dx \leqslant \gamma_1^i + \gamma_2^i ||\varphi||^2_{L^2(0,T;H^1(Q)\times H^1(\omega))}, \quad i = 1,\dots,n, \tag{14}$$

where $\gamma_1^i \geqslant 0$ and $\gamma_2^i \geqslant 0$

Mass balance:

$$\sum_{i=1}^{n} g_i(\mathbf{c},\varphi) = 0 \quad \text{on} \quad (0,T)\times\partial\omega \tag{15}$$

Positive production rate:

$$g_i(\mathbf{c},\varphi)[\![c_i^-]\!] = 0 \quad \text{on} \quad (0,T)\times\partial\omega, \quad \text{for all } c_i, \quad i = 1,\dots,n \tag{16}$$

where $c_i^+ := \max\{0, c_i\}$, $c_i^- := -\min\{0, c_i\}$,
such that $c_i = c_i^+ - c_i^-$, $c_i^+ \geqslant 0, c_i^- \geqslant 0$, $c_i^+ c_i^- = 0$, for $i = 1,\dots,n$.

Example of $g_i(\boldsymbol{c},\varphi)$

For example, the non trivial functions

$$\begin{aligned} g_1(\boldsymbol{c},\varphi) &= G_1\big((\boldsymbol{c}|_{\partial\omega^+})^+\big)G_1\big((\boldsymbol{c}|_{\partial\omega^-})^+\big)G_2\big((\boldsymbol{c}|_{\partial\omega^+})^+\big)G_2\big((\boldsymbol{c}|_{\partial\omega^-})^+\big), \\ g_2(\boldsymbol{c},\varphi) &= -g_1(\boldsymbol{c},\varphi) \end{aligned}$$

where $G_j(\boldsymbol{c}) := \frac{c_j}{\sum_{k=1}^n c_k}$ such that $|G_j(\boldsymbol{c})| \leqslant 1$ and $G_j(\boldsymbol{c}^+)c_j^- = 0$, fulfill all the conditions (14)–(16) with $\gamma_2^i = 0$ and $\gamma_1^i = |\partial\omega|$.

PNP | Assumptions on matrices

Symmetric positive definiteness of A: There exist $0 < \underline{a} \leqslant \bar{a}$ such that

$$\underline{a}|\xi|^2 \leqslant \xi^\top A\,\xi \leqslant \bar{a}|\xi|^2, \quad \xi \in \mathbb{R}^d. \tag{17a}$$

Strong ellipticity condition for D^{ij}: There exist $0 < \underline{d} \leqslant \bar{d}$ such that

$$\underline{d}\sum_{i=1}^{n}|\xi_i|^2 \leqslant \sum_{i,j=1}^{n}\xi_i^\top m_i D^{ij}\,\xi_j \leqslant \bar{d}\sum_{i=1}^{n}|\xi_i|^2, \quad \xi_1,\ldots,\xi_n \in \mathbb{R}^d. \tag{17b}$$

Symmetric positive definiteness of D: There exist $0 < \underline{d} \leqslant \bar{d}$ such that

$$\underline{d}|\xi|^2 \leqslant \xi^\top D\,\xi \leqslant \bar{d}|\xi|^2, \quad \xi \in \mathbb{R}^d. \tag{18}$$

Properties of diffusivity matrices

Weak assumption:

$$\sum_{i=1}^{n} m_i D^{ij} = D, \quad j = 1,\ldots,n; \tag{19}$$

Strong assumption:

$$m_i D^{ij} = \delta_{ij} D, \quad i,j = 1,\ldots,n. \tag{20}$$

PNP | Weak formulation of the problem

Find discontinuous functions $c_1, \dots, c_n$, and φ such that

$$c_i \in L^\infty(0,T; L^2(Q) \times L^2(\omega)) \cap L^2(0,T; H^1(Q) \times H^1(\omega)), \tag{21a}$$

$$\varphi \in L^\infty(0,T; H^1(Q) \times H^1(\omega)), \tag{21b}$$

$$c_i \nabla \varphi_i \in L^2((0,T) \times (Q \cup \omega)) \quad \text{for } i = 1, \dots, n, \tag{21c}$$

which satisfy the Dirichlet boundary conditions, the initial conditions, the volume balance and positivity, as well as fulfill the following variational equations:

$$\int_0^T \int_{Q \cup \omega} \Big\{ \frac{\partial c_i}{\partial t} \bar{c}_i + \sum_{j=1}^n \Big[k_B \Theta \nabla c_j + \mathbf{1}_Q \Upsilon_j(\boldsymbol{c}) \nabla \varphi \Big]^\top m_i D^{ij} \nabla \bar{c}_i \Big\} \, dx \, dt = \int_0^T \int_{\partial\omega} g_i(\boldsymbol{c}, \varphi) [\![\bar{c}_i]\!] \, dS_x \, dt, \tag{22a}$$

$$\int_{Q \cup \omega} (\nabla \varphi^\top A \nabla \bar{\varphi} - \mathbf{1}_Q \Upsilon(\boldsymbol{c}) \bar{\varphi}) \, dx + \int_{\partial\omega} \alpha [\![\varphi]\!] [\![\bar{\varphi}]\!] \, dS_x = \int_{\partial\omega} g [\![\bar{\varphi}]\!] \, dS_x, \tag{22b}$$

for all test functions $\bar{c}_i \in H^1(0,T; L^2(Q) \times L^2(\omega)) \cap L^2(0,T; H^1(Q) \times H^1(\omega))$ and $\bar{\varphi} \in H^1(Q) \times H^1(\omega)$ such that $\bar{c}_i = 0$ on $(0,T) \times \partial\Omega$ and $\bar{\varphi} = 0$ on $\partial\Omega$

$\Upsilon_j(\boldsymbol{c}) := \dfrac{1}{N_A} c_j \Big(z_j - \dfrac{1}{C} \Upsilon(\boldsymbol{c}) \Big)$ and $\Upsilon(\boldsymbol{c}) := \sum_{k=1}^n z_k c_k$

PNP | Reduced formulation. 1

The formulation after excluding μ_i and p and reducing the constraints.

Reduced system of the equations

$$\frac{\partial c_i}{\partial t} - \operatorname{div} \sum_{j=1}^{n} \Big[k_B \Theta \nabla c_j + \mathbf{1}_Q \Gamma_j(\boldsymbol{c}^+) \nabla \varphi \Big]^\top m_i D^{ij} = 0 \quad \text{in} \quad (0,T)\times(Q\cup\omega) \tag{23}$$

$$-\operatorname{div}(\nabla \varphi^\top A) = \mathbf{1}_Q C \frac{\sum_{k=1}^n z_k c_k^+}{\sum_{k=1}^n c_k^+} \quad \text{in} \quad (0,T)\times(Q\cup\omega) \tag{24}$$

where $\Gamma_j(\boldsymbol{c}^+) := \dfrac{C}{N_A} \dfrac{c_j^+}{\sum_{k=1}^n c_k^+} \left(z_j - \dfrac{\sum_{k=1}^n z_k c_k^+}{\sum_{k=1}^n c_k^+} \right)$ are uniformly bounded:

$0 \leqslant \Gamma(c_j^+) \leqslant \dfrac{CZ}{N_A}$, where $Z = \displaystyle\sum_{i=1}^n |z_i|$

If constraints (6) and (7) hold, then $\Gamma_j(\boldsymbol{c}^+) = \Upsilon_j(\boldsymbol{c})$ and $C \dfrac{\sum_{k=1}^n z_k c_k^+}{\sum_{k=1}^n c_k^+} = \Upsilon(\boldsymbol{c})$

PNP | Reduced formulation. 2

Boundary conditions

Neumann–Robin conditions:

$$[\![J_i]\!]\nu = 0, \quad -J_i\nu = g_i(\mathbf{c}, \varphi) \quad \text{on} \quad (0,T) \times \partial\omega, \tag{25}$$

where

$$J_i = \sum_{j=1}^{n} \Big[k_B \Theta \nabla c_j + \mathbf{1}_Q \Gamma_j(\boldsymbol{c}^+) \nabla\varphi \Big]^\top m_i D^{ij};$$

$$[\![(\nabla\varphi)^\top A]\!]\nu = 0, \quad -(\nabla\varphi)^\top A\nu + \alpha[\![\varphi]\!] = g \quad \text{on} \quad (0,T) \times \partial\omega; \tag{26}$$

Dirichlet conditions:

$$c_i = c_i^D, \quad i = 1, \dots, n, \quad \text{on} \quad (0,T) \times \partial\Omega; \tag{27}$$

$$\varphi = \varphi^D \quad \text{on} \quad (0,T) \times \partial\Omega. \tag{28}$$

Initial conditions

$$c_i(0,\cdot) = c_i^{in}, \quad i = 1, \dots, n, \quad \text{as} \quad t = 0. \tag{29}$$

Existence theorem. 1

Theorem 1 (Existence of a weak solution of the reduced problem)

Let the growth conditions for reactions on the boundary

$$\int_{\partial\omega} |g_i(\boldsymbol{c}, \varphi)|^2 \, dx \leqslant \gamma_1^i + \gamma_2^i ||\varphi||_{L^2(0,T;H^1(Q)\times H^1(\omega))}, \quad i = 1, \ldots, n,$$

and the assumptions on coefficient matrices hold:

$$\underline{a}|\xi|^2 \leqslant \xi^\top A\, \xi \leqslant \bar{a}|\xi|^2, \quad \xi \in \mathbb{R}^d, \tag{30}$$

$$\underline{d} \sum_{i=1}^{n} |\xi_i|^2 \leqslant \sum_{i,j=1}^{n} \xi_i^\top m_i D^{ij}\, \xi_j \leqslant \bar{d} \sum_{i=1}^{n} |\xi_i|^2, \quad \xi_1, \ldots, \xi_n \in \mathbb{R}^d \tag{31}$$

Then there exists a weak solution of the reduced problem.

Two auxiliary lemmas

Lemma 2 (Volume conservation)

Under assumptions on the boundary and the weak assumption of the diffusivity matrices

$$\sum_{i=1}^{n} g_i(\boldsymbol{c},\varphi) = 0 \quad on \quad (0,T)\times\partial\omega, \quad \sum_{i=1}^{n} m_i D^{ij} = D, \quad j=1,\dots,n,$$

the volume constraint $\sum_{i=1}^{n} c_i = C$ *is satisfied a.e. on* $(0,T)\times(Q\cup\omega)$.

Lemma 3 (Weak maximum principle)

Under assumptions on the data

$$g_i(\boldsymbol{c},\varphi)[\![c_i^-]\!] = 0 \quad on \quad (0,T)\times\partial\omega, \quad \forall c_i, \quad i=1,\dots,n,$$

$$m_i D^{ij} = \delta_{ij} D, \quad i,j=1,\dots,n,$$

we have the positive solution $c_i \geqslant 0$ *a.e. on* $(0,T)\times(Q\cup\omega)$ *for* $i=1,\dots,n$.

From Lemma 2 and Lemma 3 it follows

Lemma 4 (Equivalence of formulations)

Under assumptions made in Lemmas 2 and 3 the complete and the reduced problems are equivalent.

Theorem 5 (Well–posedness of generalized Poisson–Nernst–Planck system)

Let assumptions on the nonlinear boundary terms hold.

1. *If the weak assumption on diffusivity matrices holds, then there exists a weak solution of the problem. By continuity,* $\boldsymbol{c} > 0$ *locally for small* $t > 0$.
2. *If additionally the strong assumption on diffusivity matrices holds, then* $\boldsymbol{c} \geqslant 0$ *globally for* $T > 0$.

A weak solution satisfies a priori estimates

$$||\varphi||^2_{L^\infty(0,T;H^1(Q)\times H^1(\omega))} \leqslant K_\varphi, \tag{32}$$

$$||\boldsymbol{c}||^2_{L^\infty(0,T;L^2(Q)\times L^2(\omega))} + ||\boldsymbol{c}||^2_{L^2(0,T;H^1(Q)\times H^1(\omega))} \leqslant K_c + \gamma_c K_\varphi. \tag{33}$$

Uniqueness theorem

Theorem 6 (Uniqueness of the solution of generalized Poisson–Nernst–Planck system)

Let φ be smooth such that

$$\varphi \in L^\infty((0,T)\times(Q\cup\omega))^d \text{ and } \nabla\varphi \in L^\infty((0,T)\times(Q\cup\omega))^d \tag{34}$$

and the nonlinear boundary fluxes are injective and satisfy the following assumption: there exists $\tilde{G}_i(\boldsymbol{c}^{(1)}, \boldsymbol{c}^{(2)}, \varphi^{(1)}, \varphi^{(2)}) > 0$ such that

$$\left| \int_{\partial\omega} \left(g_i(\boldsymbol{c}^{(1)}, \varphi^{(1)}) - g_i(\boldsymbol{c}^{(2)}, \varphi^{(2)})\right) [\![c_i^{(1)} - c_i^{(2)}]\!] \, dS_x \right| \leqslant \tilde{G}_i(\boldsymbol{c}^{(1)}, \boldsymbol{c}^{(2)}, \varphi^{(1)}, \varphi^{(2)}) \int_{Q\cup\omega} (c_i^{(1)} - c_i^{(2)})^2 \, dx, \quad i = 1, \dots, n, \tag{35}$$

for all $\boldsymbol{c}^{(1)} > 0$, $\boldsymbol{c}^{(2)} > 0$ such that $\sum_{i=1}^n c_i^{(1)} = \sum_{i=1}^n c_i^{(2)} = C$ and for all $\varphi^{(1)}$, $\varphi^{(2)}$.
Then a weak solution of the complete problem is unique.

Lyapunov stability

Entropy and entropy dissipation

We define the entropy as follows:

$$S : \mathbb{R}^+ \to \mathbb{R}, \quad S(t) := -k_B N_A \sum_{i=1}^{n} \int_{Q\cup\omega} c_i \ln(\beta_i c_i)\, dx.$$

We introduce the function of dissipation: $\mathcal{D} : \mathbb{R}^+ \to \mathbb{R}$,

$$\mathcal{D}(t) := -\frac{dS}{dt} = k_B N_A \sum_{i=1}^{n} \int_{Q\cup\omega} \frac{\partial c_i}{\partial t} \ln(\beta_i c_i)\, dx.$$

Theorem 7 (Lyapunov stability)

Under assumptions $m_i D^{ij} = \underline{d}\delta_{ij} I$, $A = \underline{a} I$, $\sum_{i=1}^{n} z_i c_i^D = 0$ and $c_i^D = 1/\beta_i$ on $\partial\Omega$ for the mass concentrations c_i satisfying the constraints (6) and (7), the entropy dissipation can be expressed equivalently as follows: $\mathcal{D} = \mathcal{D}_1 + \mathcal{D}_2$, where

$$\mathcal{D}_1 := \frac{\underline{d} k_B}{\underline{a}} \int_Q \Big(\sum_{i=1}^{n} z_i c_i\Big)^2 dx + 4\underline{d} k_B^2 N_A \Theta \sum_{i=1}^{n} \int_{Q\cup\omega} |\nabla(\sqrt{c_i})|^2\, dx, \tag{36}$$

$$\mathcal{D}_2 := \frac{\underline{d} k_B}{\underline{a}} \int_{\partial\omega} (g - \alpha[\![\varphi]\!]) \sum_{i=1}^{n} z_i [\![c_i]\!]\, dS_x - k_B N_A \sum_{i=1}^{n} \int_{\partial\omega} g_i(\mathbf{c}, \varphi) \left[\!\!\left[\ln\left(\frac{c_i}{c_i^D}\right) \right]\!\!\right] dS_x.$$

Results and future work

- We have derived the rigorous mathematical formulation for the physical model
- We have got existence based on the reduced model without constraints
- We have provided uniqueness in a special case
- We have obtained a priori energy and entropy estimates of the solution
- We have obtained the dissipation of the entropy

Plans:

- Homogenization of a porous medium with respect to a solid micro–particle size
- Numerical algorithms and tests

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