Finite Volume Discretization of Nonlinear Diffusion in Li-Ion batteries

P. Popov[1], Y. Vutov[1], S. Margenov[1], and O. Iliev[2]

[1] Institute for Parallel Processing, Bulgarian Academy of Sciences, Sofia, Bulgaria,
[2] Fraunhofer ITWM, D-67663 Kaiserslautern, Germany

Abstract. Numerical modeling of electrochemical process in Li-Ion problems is an emerging topic of great practical interest. In this work we present a Finite Volume discretization of electrochemical diffusive processes occurring during the operation of Li-Ion batteries. The system of equations is a nonlinear, time-dependent diffusive system, coupling the Li concentration and the electric potential. The system is formulated at length-scale in which two different types of domains are distinguished, one for electrolyte and one for each electrode. The domains can be of highly irregular shape, with the electrolyte occupying the pore space of a porous solid electrode. The material parameters in each domain differ by several orders of magnitude and can be nonlinear. Moreover, special interface conditions are imposed at the boundary separating the electrolyte from an electrode. The field variables are discontinuous across such an interface and the coupling is highly nonlinear, rendering direct iteration methods ineffective for such problems. We formulate a Newton iteration for the coupled system. A series of numerical examples are presented for different type of electrolyte/electrode configurations and material parameters. The convergence of the Newton method is characterized both as function of nonlinear material parameters as well as the nonlinearity in the interface conditions.

1 Introduction

The Li-Ion battery system is described mathematically as a coupled system of differential equations for the concentration $c(\mathbf{x},t)$ $\left[\frac{mol}{cm^3}\right]$ and the electric potential $\phi(\mathbf{x},t)$ $[V]$ in the domain Ω [3, 2]. The domain is occupied by electrolyte and active particles. Their respective subdomains are denoted Ω_e and Ω_s, with $\Omega = \Omega_e \cup \Omega_s$ and $\Omega_e \cap \Omega_s = \emptyset$. The field equations can be written as:

$$\frac{\partial c}{\partial t} - \nabla \cdot \left(\alpha\left(c,\phi\right)\nabla c + \beta\left(c,\phi\right)\nabla\phi\right) = 0 \qquad \text{in } \Omega_s \text{ or } \Omega_e, \tag{1a}$$

$$-\nabla \cdot \left(\lambda(c,\phi)\nabla c + \kappa\left(c,\phi\right)\nabla\phi\right) = 0 \qquad \text{in } \Omega_s \text{ or } \Omega_e, \tag{1b}$$

where $\kappa(c,\phi)$ is the ionic conductivity, a prescribed function. The remaining coefficients are given by:

$$\alpha(c,\phi) := \nu_+ D_e(c,\phi) + \frac{RT}{\nu_+ z_+ F^2}\frac{t_+(c)\kappa_D(c,\phi)}{c}, \qquad \left[\frac{cm^2}{s}\right], \tag{2a}$$

$$\beta(c,\phi) := \kappa(c,\phi)\frac{t_+(c)}{\nu_+ z_+ F}, \qquad \left[\frac{mol}{V\cdot cm\cdot s}\right], \tag{2b}$$

$$\lambda(c,\phi) := \frac{RT}{F}\frac{\kappa_D(c,\phi)}{c}, \qquad \left[\frac{A\cdot cm^2}{mol}\right]. \tag{2c}$$

The dimensionless parameters $n=1$, $s_+=-1$, $z_+=1$, $z_-=-1$, $\nu_+=\nu_-=1$ indicate a single ionization state. Next, κ_D is defined as follows:

$$\kappa_D(c,\phi) := \kappa(c,\phi)\, t_+(c,\phi). \tag{3}$$

a detailed thermodynamic justification of this constitutive relationship is given in [1]. It should be noted that model used is different from the classical model of Newman, [2, 4], where one has:

$$\kappa_D(c,\phi) := \kappa(c,\phi)(\nu_+ + \nu_-)\left(\frac{s_+}{n\nu_+} + \frac{t_+(c)}{z_+\nu_+} - \frac{s_0 c}{n c_0}\right)\left(1 + \frac{\partial \ln f_+}{\partial \ln c}\right). \tag{4}$$

The transference function t_+ allows us to distinguish between electrolyte and active particles. In an active particle, one has $t_+ \equiv 0$. In the electrolyte, $t+$ is nonzero, typically an empirically measured function of c [4].

The system (2) is not complete without conditions on the interface $\Gamma = \partial\Omega_e \cap \partial\Omega_s$ between active particles and electrolyte. The flux of Li ions, which is implied by the model (1), is:

$$\mathbf{N} := -\left(\alpha(c,\phi)\nabla c + \beta(c,\phi)\nabla\phi\right), \tag{5}$$

and the flux of the electric potential is, i.e. the current, is

$$\mathbf{J} := -\lambda(c,\phi)\nabla c + \kappa(c,\phi)\nabla\phi. \tag{6}$$

At the interface between a solid particle and electrolyte, one has a discontinuous concentration c and potential ϕ. We denote values on the electrolyte part of the interface with subscript e and on the solid part with subscript s. The type of interface conditions to be imposed is subject to active research [2]. In this paper we follow [1], where two interface conditions, for each of the fluxes (5) and (6) are proposed. One is that the normal component of each of the fluxes is continuous across an interface. Moreover, it is required that the value of the normal component of the flux is given by a nonlinear relationship of all the variables c_e, c_s, ϕ_e, ϕ_s, that is:

$$\mathbf{N}_s\mathbf{n} = \mathbf{N}_e\mathbf{n} = \mathcal{N}(c_e, c_s, \phi_e, \phi_s), \tag{7}$$

$$\mathbf{J}_s\mathbf{n} = \mathbf{J}_e\mathbf{n} = \mathcal{J}(c_e, c_s, \phi_e, \phi_s), \tag{8}$$

where the scalar functions $\mathcal{N}$ and $\mathcal{J}$ are defined as follows:

$$\eta = \phi_s - \phi_e - U_0 \tag{9}$$

$$\mathcal{J} = k\left(\frac{c_e}{c_e^0}\right)^{\alpha_a}\left(\frac{c_s}{c_s^0}\right)^{\alpha_a}\left(1-\frac{c_s}{c_{s,max}}\right)^{\alpha_c}\left(\exp\left(\frac{\alpha_a F}{RT}\eta_s\right)-\exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)\right) \tag{10}$$

$$\mathcal{N} = \frac{\mathcal{J}}{F}. \tag{11}$$

Note that when t_+ is constant in the electrolyte (it is always constant in the active particles), the divergence of the current is identically, zero, which allows to simplify the first equation in (1). As a result, the system (1)-(2) takes the following simplified form in either subdomain:

$$\frac{\partial c}{\partial t} - \nabla\cdot\left(\nu_+ D_e\left(c,\phi\right)\nabla c\right) = 0, \tag{12a}$$

$$-\nabla\cdot\left(\lambda(c,\phi)\nabla c + \kappa\left(c,\phi\right)\nabla\phi\right) = 0. \tag{12b}$$

If D_e is not a function of ϕ, the system (12) becomes completely decoupled in each subdomain. Note however, that the interface conditions imply that the system is always coupled and always nonlinear, regardless of the coefficients.

2 Discretization

We present here the discretization of the general case, that is, the system (1) is discretized by cell centered finite volumes. Let the domain Ω be partitioned into a polygonal mesh, e.g. $\Omega = \sum_{i=1}^{N} e_i$, with each cell e_i being a polygon/polyhedron. It is further required that this mesh is suitable for finite volume discretizations, that is, all vertices of e_i lie on a circle/sphere, whose center lies in the proper interior of e_i. By integrating the first equation over $e_i \times [t_n, t_{n+1}]$ and using the divergence theorem, one gets:

$$\begin{aligned}0 &= \int_{t_n}^{t_{n+1}}\int_{e_i}\left(\frac{\partial c}{\partial t} - \nabla\cdot\left(\alpha\left(c,\phi\right)\nabla c + \beta\left(c,\phi\right)\nabla\phi\right)\right)dxdt\\ &= \int_{e_i} c(x,t_{n+1})dx - \int_{e} c(x,t_n)dx - \int_{t_n}^{t_{n+1}}\int_{\partial e_i}\left(\alpha\left(c,\phi\right)\nabla c + \beta\left(c,\phi\right)\nabla\phi\right)\cdot\mathbf{n}dA.\end{aligned} \tag{13}$$

The second equation (1b) is similarly transformed as follows:

$$0 = -\int_{t_n}^{t_{n+1}}\int_{\partial e_i}\left(\lambda(c,\phi)\nabla c + \kappa(c,\phi)\nabla\phi\right)dA. \tag{14}$$

Now, denote by x_i the circumcenter of e_i and denote by $c_i(t)$ the value of the concentration at x_i, that is, $c_i(t) = c(x_i,t)$. Similarly, let $\phi_i(t) = \phi(x_i,t)$. The volume integral in (13) can be approximated by a one-point formula. Moreover, let e_j be a neighbor of e_i and denote by f_{ij} the face common to e_i and e_j. Denote by $\mathcal{N}_i$ the index set of all same domain neighbors of e_i, that is, $\mathcal{N}_i = \{j \in \mathbb{N} | e_j \text{ and } e_i \text{ are neighbors}\}$. Using the standard midpoint flux approximations and assuming e_i and e_j share no interface faces one gets:

$$\begin{aligned} 0 = &|e_i| \left(c_i(t_{n+1}) - c_i(t_n)\right) \\ &- \int_{t_n}^{t_{n+1}} \sum_{j \in \mathcal{N}_i} |f_{ij}| \left(\alpha_{\frac{i+j}{2}} \frac{c_j(t) - c_i(t)}{d(x_i, x_j)} + \beta_{\frac{i+j}{2}} \frac{\phi_j(t) - \phi_i(t)}{d(x_i, x_j)} \right) dt, \end{aligned} \tag{15}$$

$$0 = - \int_{t_n}^{t_{n+1}} \sum_{j \in \mathcal{N}_i} |f_{ij}| \left(\lambda_{\frac{i+j}{2}} \frac{c_j(t) - c_i(t)}{d(x_i, x_j)} + \kappa_{\frac{i+j}{2}} \frac{\phi_j(t) - \phi_i(t)}{d(x_i, x_j)} \right) dt, \tag{16}$$

where $\alpha_{\frac{i+j}{2}}$, $\beta_{\frac{i+j}{2}}$, $\lambda_{\frac{i+j}{2}}$, $\kappa_{\frac{i+j}{2}}$ are the harmonic averages of the respective coefficients at the midpoints of each face. That is, given a function $\psi(x,t)$, $\psi_{\frac{i+j}{2}} := (|e_i| + |e_j|) \left(\frac{|e_i|}{\psi_i(t)} + \frac{|e_i|}{\psi_j(t)} \right)^{-1}$ is the harmonic average approximation.

In the case when e_i has an interface face, then (5) and (6) have to be incorporated. Let an element e_i now share an interface face with e_k. Then, by definition, $\mathcal{N}_i$ does not contain k. Moreover, suppose for concreteness that e_i is electrolyte and e_k is solid. Then we add the terms

$$\int_{t_n}^{t_{n+1}} |f_{ik}| \mathcal{N}(c_i(t), c_k(t), \phi_i(t), \phi_k(t)), \tag{17}$$

$$\int_{t_n}^{t_{n+1}} |f_{ik}| \mathcal{J}(c_i(t), c_k(t), \phi_i(t), \phi_k(t)) \tag{18}$$

to the RHS of (15) and (16), respectively.

Next, we employ a backward Euler method to approximate the remaining time integrals. By denoting $C_i = c_i(t_{n+1})$ and $\Phi_i = \phi_i(t_{n+1})$ this results in the system of algebraic equations for $\mathbf{C}^{n+1}, \mathbf{\Phi}^{n+1}$:

$$\begin{aligned} 0 = |e_i| \frac{C_i - c_i(t_n)}{dt} &- \sum_{j \in \mathcal{N}_i} |f_{ij}| \left(\alpha_{\frac{i+j}{2}} \frac{C_j - C_i}{d(x_i, x_j)} + \beta_{\frac{i+j}{2}} \frac{\Phi_j - \Phi_i}{d(x_i, x_j)} \right) \\ &+ \sum_{k \in \mathcal{I}_i} |f_{ik}| \mathcal{N}(C_i, C_k, \Phi_i, \Phi_k), \end{aligned} \tag{19}$$

$$\begin{aligned} 0 = &- \sum_{j \in \mathcal{N}_i} |f_{ij}| \left(\lambda_{\frac{i+j}{2}} \frac{C_j - C_i}{d(x_i, x_j)} + \kappa_{\frac{i+j}{2}} \frac{\Phi_j - \Phi_i}{d(x_i, x_j)} \right) \\ &+ \sum_{k \in \mathcal{I}_i} |f_{ik}| \mathcal{J}(C_i, C_k, \Phi_i, \Phi_k). \end{aligned} \tag{20}$$

Here $\mathcal{I}_i$ is the set of cells that share an interface with e_i, and without loss of generality, e_i is an electrolyte cell. If e_i is a solid cell, then the sign of the interface fluxes has to be reversed.

3 Linearization

Due to the strong nonlinearities involved, the Newton method is used to linearize the system (19), (20) at each time step. Denote by $\mathbf{F}\left(\mathbf{C},\boldsymbol{\Phi}\right)$ and $\mathbf{G}\left(\mathbf{C},\boldsymbol{\Phi}\right)$ the right-hand sides of (19) and (20), respectively. The Newton iteration in component form is:

$$\begin{aligned} 0 = F_i\left(\mathbf{C},\boldsymbol{\Phi}\right) &+ \sum_{j\in\mathcal{N}_i} \frac{\partial F_i}{\partial C_j}\left(\mathbf{C}^{(k)},\boldsymbol{\Phi}^{(k)}\right)\left(C_j^{(k)} - C_j^{(k+1)}\right) \\ &+ \sum_{j\in\mathcal{N}_i} \frac{\partial F_i}{\partial \Phi_j}\left(\mathbf{C}^{(k)},\boldsymbol{\Phi}^{(k)}\right)\left(\Phi_j^{(k+1)} - \Phi_j^{(k)}\right), \end{aligned} \tag{21}$$

$$\begin{aligned} 0 = G_i\left(\mathbf{C},\boldsymbol{\Phi}\right) &+ \sum_{j\in\mathcal{N}_i} \frac{\partial G_i}{\partial C_j}\left(\mathbf{C}^{(k)},\boldsymbol{\Phi}^{(k)}\right)\left(C_j^{(k)} - C_j^{(k+1)}\right) \\ &+ \sum_{j\in\mathcal{N}_i} \frac{\partial G_i}{\partial \Phi_j}\left(\mathbf{C}^{(k)},\boldsymbol{\Phi}^{(k)}\right)\left(\Phi_j^{(k+1)} - \Phi_j^{(k)}\right). \end{aligned} \tag{22}$$

Computing the derivatives is straightforward. Assume, without loss of generality that e_k is the only interface neighbor to the electrolyte cell e_i. Then:

$$\begin{aligned} \frac{\partial F_i}{\partial C_j} = \frac{|e_i|}{dt}\delta_{ij} + \sum_{s\in\mathcal{N}_i}|f_{is}|&\left[\alpha^{(k)}_{\frac{i+s}{2}}\frac{\delta_{sj}-\delta_{ij}}{2} + \frac{\partial\alpha_{\frac{i+s}{2}}}{\partial C_j}\frac{C_s^{(k)}-C_i^{(k)}}{d\left(x_i,x_j\right)} + \frac{\partial\beta_{\frac{i+s}{2}}}{\partial C_j}\frac{\Phi_s^{(k)}-\Phi_i^{(k)}}{d\left(x_i,x_j\right)}\right] \\ &+|f_{ij}|\left(\frac{\partial\mathcal{N}}{\partial C_e}(C_i,C_k,\Phi_i,\Phi_k)\delta_{ij} + \frac{\partial\mathcal{N}}{\partial C_s}(C_i,C_k,\Phi_i,\Phi_k)\delta_{kj}\right), \end{aligned} \tag{23}$$

$$\begin{aligned} \frac{\partial F_i}{\partial \Phi_j} = \sum_{s\in\mathcal{N}_i}|f_{is}|&\left[\beta^{(k)}_{\frac{i+s}{2}}\frac{\delta_{sj}-\delta_{ij}}{2} + \frac{\partial\beta_{\frac{i+s}{2}}}{\partial \Phi_j}\frac{\Phi_s^{(k)}-\Phi_i^{(k)}}{d\left(x_i,x_j\right)} + \frac{\partial\alpha_{\frac{i+s}{2}}}{\partial \Phi_j}\frac{C_s^{(k)}-C_i^{(k)}}{d\left(x_i,x_j\right)}\right] \\ &+|f_{ij}|\left(\frac{\partial\mathcal{N}}{\partial \Phi_e}(C_i,C_k,\Phi_i,\Phi_k)\delta_{ij} + \frac{\partial\mathcal{N}}{\partial \Phi_s}(C_i,C_k,\Phi_i,\Phi_k)\delta_{kj}\right), \end{aligned} \tag{24}$$

where δ_{pq} is the Kroneker delta symbol. The expressions for the partial derivatives of $\mathbf{G}$ are similar:

$$\begin{aligned} \frac{\partial G_i}{\partial C_j} = \sum_{s\in\mathcal{N}_i}|f_{is}|&\left[\lambda^{(k)}_{\frac{i+s}{2}}\frac{\delta_{sj}-\delta_{ij}}{2} + \frac{\partial\lambda_{\frac{i+s}{2}}}{\partial C_j}\frac{C_s^{(k)}-C_i^{(k)}}{d\left(x_i,x_j\right)} + \frac{\partial\kappa_{\frac{i+s}{2}}}{\partial C_j}\frac{\Phi_s^{(k)}-\Phi_i^{(k)}}{d\left(x_i,x_j\right)}\right] \\ &+|f_{ij}|\left(\frac{\partial\mathcal{J}}{\partial C_e}(C_i,C_k,\Phi_i,\Phi_k)\delta_{ij} + \frac{\partial\mathcal{J}}{\partial C_s}(C_i,C_k,\Phi_i,\Phi_k)\delta_{kj}\right), \end{aligned} \tag{25}$$

$$\begin{aligned} \frac{\partial G_i}{\partial \Phi_j} = \sum_{s\in\mathcal{N}_i}|f_{is}|&\left[\kappa^{(k)}_{\frac{i+s}{2}}\frac{\delta_{sj}-\delta_{ij}}{2} + \frac{\partial\kappa_{\frac{i+s}{2}}}{\partial \Phi_j}\frac{\Phi_s^{(k)}-\Phi_i^{(k)}}{d\left(x_i,x_j\right)} + \frac{\partial\lambda_{\frac{i+s}{2}}}{\partial \Phi_j}\frac{C_s^{(k)}-C_i^{(k)}}{d\left(x_i,x_j\right)}\right] \\ &+|f_{ij}|\left(\frac{\partial\mathcal{J}}{\partial \Phi_e}(C_i,C_k,\Phi_i,\Phi_k)\delta_{ij} + \frac{\partial\mathcal{J}}{\partial \Phi_s}(C_i,C_k,\Phi_i,\Phi_k)\delta_{kj}\right). \end{aligned} \tag{26}$$

The two field variables in our problems, c and ϕ, represent different physical quantities, which have very different scales. As a result, the stopping criteria for the Newton iteration has to be adjusted accordingly. A relative criterion was used individually for each component, that is, the iteration is terminated if:

$$\frac{\left\|\mathbf{F}\left(\mathbf{C}^{(k)},\mathbf{\Phi}^{(k)}\right)\right\|}{\left\|\mathbf{F}\left(\mathbf{C}^{(0)},\mathbf{\Phi}^{(0)}\right)\right\|} \leq TOL \text{ and } \frac{\left\|\mathbf{G}\left(\mathbf{C}^{(k)},\mathbf{\Phi}^{(k)}\right)\right\|}{\left\|\mathbf{G}\left(\mathbf{C}^{(1)},\mathbf{\Phi}^{(1)}\right)\right\|} \leq TOL \tag{27}$$

where TOL is a prescribed tolerance. Observe that the residual for the electrostatic equation (16) is scaled with the value at the first Newton iteration. The reason is the following. Given a converged time step t_n, the values for $\mathbf{c}(t_n)$ and $\boldsymbol{\phi}(t_n)$ are used as initial guess for the Newton iteration for the time step t_{n+1}. However, the only difference in the residual will be contribution to $\mathbf{F}$ of the discretization of the time derivative in (15). Thus, the initial residual for $\mathbf{G}$ will be zero, rendering it useless for scaling purposes.

4 Numerical Examples

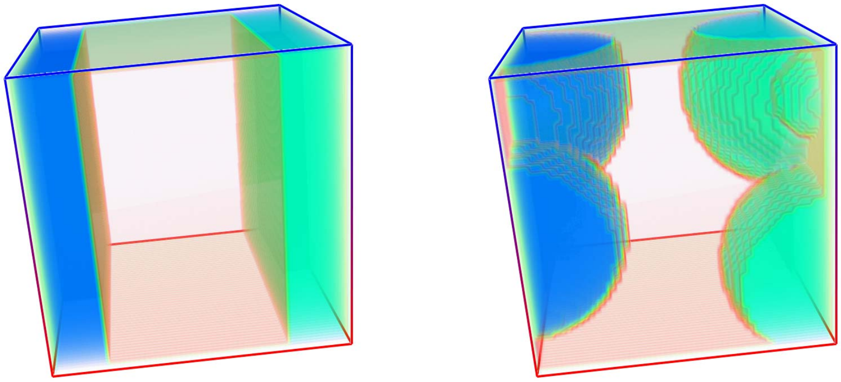
Two numerical examples were designed to test the model and finite volume discretization. Both examples are on a micron length-scale, where the active particles and the electrolyte occupy distinctive domains. The geometry is given in Figure 1. In both cases, Ω is a cube with a $50\mu m$ side. The first example was designed to test the simplest planar cathode-electrolyte-anode configuration. The second example is representative of the actual porous microstructure of the active particles. Both examples were discretized on a 50^3 regular voxel grid.

Table 1. Material specific parameters and initial conditions.

Material type	D_e	κ	c^0	c_{max}	U_0
	$\left[\frac{cm^2}{s}\right]$	$\left[\frac{A}{V\cdot cm}\right]$			
Electrolyte	7.5×10^{-7}	0.002	0.001		
Cathode	1.0×10^{-9}	0.038	0.020574	0.02286	0.001
Anode	3.9×10^{-10}	1.0	0.002639	0.02639	0

The material constants and model parameters of (2) were taken as follows: $F = 96486\left[\frac{A\cdot s}{mol}\right]$, $R = 8.314\left[\frac{A\cdot V\cdot s}{K\cdot mol}\right]$ and $t_+(c) = 0.2$. The Li^+ diffusion coefficient D_e, ionic conductivity κ, the initial Li^+ concentrations c^0, the maximum Li^+ concentration in the electrodes c_{max} and the open circuit potential for the electrodes U_0, all material dependent parameters, are given in Table 1. All simulations were performed in isothermal conditions with $T = 300\,[K]$.

The first series of numerical runs were performed with the above data. Since all material parameters were constant, the equations in each subdomain were linear, thus the nonlinearity was entirely due to the interface condition (7)-(11). The time step was $50s$ and a total of 20 timesteps were performed. It took slightly



(a) Example 1 (b) Example 2

Fig. 1. Electrode geometry for each numerical example. The void space is occupied by the electrolyte.

more than $1000s$ before the battery the ionic concentration in parts of the domain became close to zero. A snapshot of the concentration and electric potential, for each of the two examples, are given in Figures 2 and 3, respectively. Throughout the computational runs, the Newton iteration converged in 3 iterations at each time step, for both examples.

A second set of numerical experiments was performed, this time with nonlinear parameters for the electrolyte. In the absence of solid experimental data, a transference number $t_+ = 0.2 + 0.8c^2$ and $D_e = 1.27 \times 10^{-7}(1 + \phi^2)$ were used for the electrolyte, the remaining parameters being the same. This runs were done for the sake of testing the fully nonlinear system of equations. Again, the Newton iteration converged in 3 iterations at each time step, for both examples.

5 Conclusions

The main goal of this paper was to discretize and solve the system of coupled equations, which describes the diffusion of Li ions in a battery. A cell centered finite volume method was used to discretize the problem on a regular voxelized grid. The nonlinearity was treated with a full Newton method, both for the material parameters and the interface condition. It was found that the standard Newton method can handle both nonlinearities in nearly optimal number of iterations.

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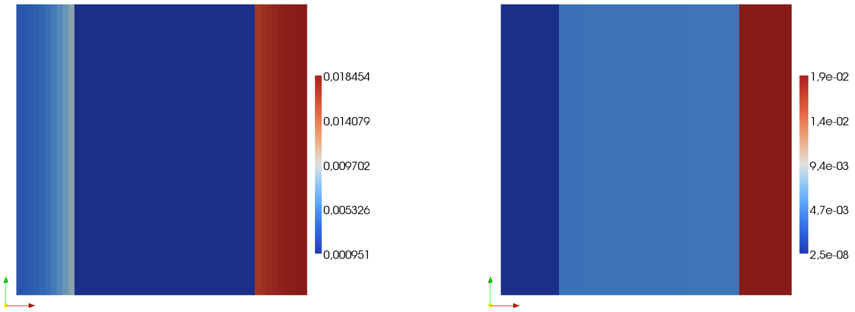
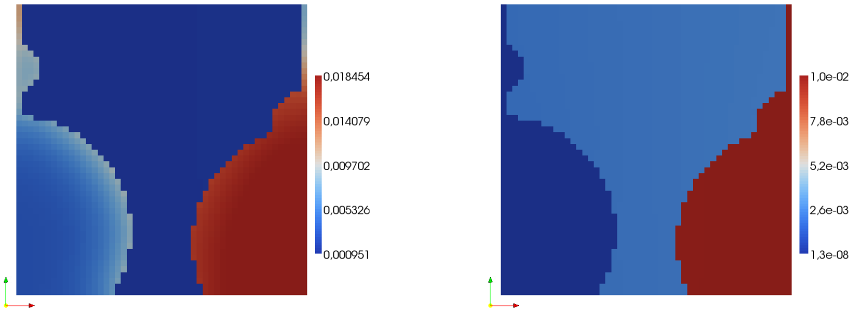


(a) Concentration

(b) Potential

Fig. 2. Concentration (a) and potential (b) at time $t = 500s$ for the first example 1, $x - y$ cross-section.



(a) Concentration

(b) Potential

Fig. 3. Concentration (a) and potential (b) at time $t = 500s$ for the first example 1, $x - y$ crossection.

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