Extension of Open EM Modelling Platform Towards Electrochemistry and Energy Materials

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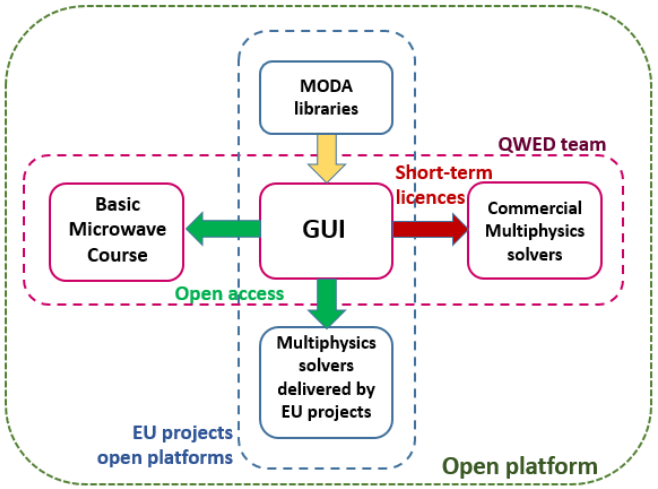
Outline

- ❑ Motivation & Objectives
- ❑ Physical model
- ❑ Governing equations
  - ❑ Electrostatics
  - ❑ Drift-Diffusion model
- ❑ Discretization
- ❑ Benchmarking and validation
- ❑ Conclusions

Motivation & Objectives

Open Modelling Platform – key objectives:

- providing research results for use by a wide research community and for teaching,
- delivering complete solutions for multi-scale multi-physics analysis of materials.



Modelling platform with exemplary commercial contribution of QWED tools

Recent developments:

- modelling of coupled electrochemical phenomena occurring at electrolyte/electrode interfaces

  → solving coupled Laplace / Poisson and drift-diffusion equations

  → basic model of ion transport process in the electrolyte, as in e. g. popular Li-ion batteries

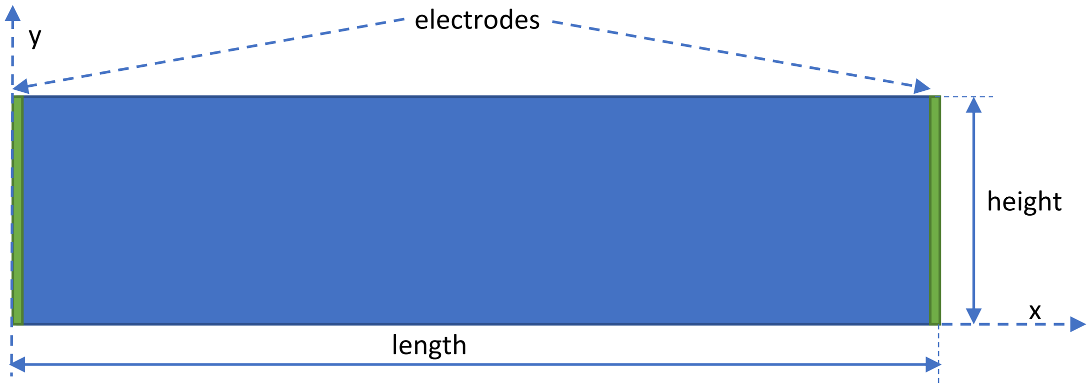
Prepared for open use for the modelling of industrially representative test-fixtures for battery materials - e. g. **H2020 NanoBat project**.

Physical model

➢ Model:

A region filled with an electrolyte and polarized by fixed-potential electrodes is considered.

The problem is: coupled; time-domain; 2D in space.



System geometry

➢ Physical quantities (all in time and space):

- electric potential distribution,
- E-, D- field distribution,
- charge distribution,
- drift and diffusion currents.

Governing equations

Electrostatics

Electrical potential (U) distribution in space:

$$\boldsymbol{E} = -\nabla U.$$

The electric charge density (ρ) in space is checked using the Gauss law:

$$\nabla \cdot \boldsymbol{D} = \rho,$$

which we shall consider in the integral form, providing charge stored in each FDTD cell and assigned to a node at which potential U is defined:

$$\oint_S \boldsymbol{D} \cdot d\boldsymbol{S} = q$$

Electric potential update using the Poisson equation:

$$\Delta U = -\frac{\rho}{\epsilon_r \, \epsilon_0}$$

Drift-Diffusion model

Taking into account the process of the flow of ions (positive and negative):

$$j_p = q_p \mu E - D_c \nabla q_p,$$
$$j_n = q_n \mu E + D_c \nabla q_n,$$

D_c – diffusion coefficient, μ – charge mobility, where:

$\mu = F \frac{D_c}{RT}$, F – Faraday constant

The resulting currents cause a change in the position of ions in the modeled space in time:

$$\oint_S j_p \cdot dS = -\frac{dq_p}{dt},$$

$$\oint_S j_n \cdot dS = \frac{dq_n}{dt}.$$

Discretization - Electrostatics

Discretized forms of equations used for electrostatics related phenomena:

Electric field

$$E_{x_{ij}} = -\frac{(U_{i+1,j} - U_{ij})}{\Delta x_{ij}}, \qquad E_{y_{ij}} = -\frac{(U_{i,j+1} - U_{ij})}{\Delta y_{ij}}$$

Electric displacement field

$$D_{x_{ij}} = E_{x_{ij}} * \epsilon_{ij}, \qquad D_{y_{ij}} = E_{y_{ij}} * \epsilon_{ij},$$

$$d_x = D_x * \Delta y_{avg} \Delta z_{avg}, \qquad d_y = D_y * \Delta x_{avg} \Delta z_{avg},$$

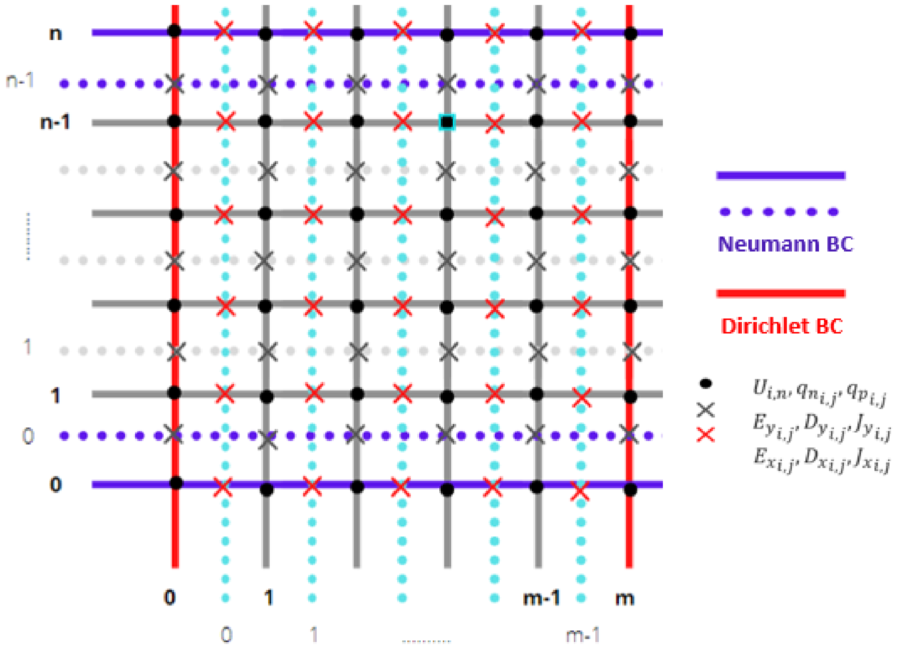
$$\Delta x_{avg} = \frac{\Delta x_i + \Delta x_{i-1}}{2}, \quad \Delta y_{avg} = \frac{\Delta y_j + \Delta y_{j-1}}{2}, \quad \Delta z_{avg} = 1.$$

Residual charge at each voltage node (from Gauss law)

$$q_{g_{ij}} = d_{x_{ij}} - d_{x_{i-1,j}} + d_{y_{ij}} - d_{y_{i,j-1}}.$$

Relaxation technique (solving **Poisson equation**)

$$U_{ij} = U_{ij} - r^* / \epsilon_0 (q_{g_{ij}} - q_{ij}).$$



Staggered mesh used for FDTD solution of Poisson coupled with Drift-Diffusion equations.

Discretization – Drift-Diffusion

Discretized forms (FDTD) of equations used for the case that takes into account the process of ions flow:

Drift-diffusion equations
(calculation of currents)

$$j_{px_{ij}} = q_{px_{avg_{ij}}} \mu^* E_x - D_c{}^* \frac{q_{p_{i+1,j}} - q_{p_{ij}}}{\Delta x}, \qquad j_{nx_{ij}} = q_{nx_{avg_{ij}}} \mu^* E_x + D_c{}^* \frac{q_{n_{i+1,j}} - q_{n_{ij}}}{\Delta x},$$

$$q_{x_{avg_{ij}}} = \frac{q_{i+1,j} + q_{ij}}{2}, \qquad \mu^* = \frac{\mu}{\Delta x_{avg} \Delta x}, \qquad D_c{}^* = \frac{D_c}{\Delta x_{avg}}.$$

Continuity equations
(charges distribution update)

$$q_{p_{ij}}(t) = q_{p_{ij}}(t-1) - (j_{px_{i,j}} - j_{px_{i-1,j}})\Delta t - (j_{py_{i,j}} - j_{py_{i,j-1}})\Delta t,$$

$$q_{n_{ij}}(t) = q_{n_{ij}}(t-1) + \left(j_{nx_{i,j}} - j_{nx_{i-1,j}}\right)\Delta t + (j_{ny_{i,j}} - j_{ny_{i,j-1}})\Delta t.$$

Total charge

$$q_{ij} = q_{p_{ij}} - q_{n_{ij}}.$$

Benchmarking and validation

Three different models of increasing complexity, for validation of developed FDTD codes, have been proposed.

Example 1

- Electrostatics in a region with no charges
- Solving Laplace equation → electrostatic potential distribution

Example 2

- Uniformly distributed static ions (initial condition)
- Solving Poisson equation → electrostatic potential distribution

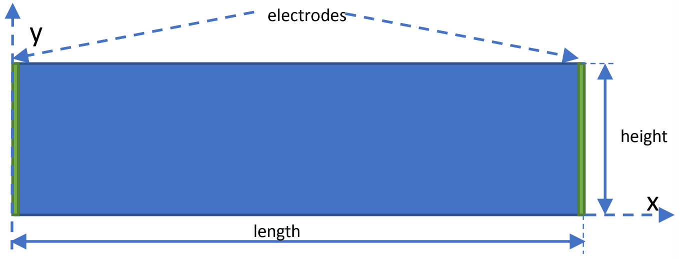
Example 3

- Uniformly distributed static ions with finite diffusivity and mobility (initial condition)
- Solving Poisson equation coupled with the drift-diffusion equations → electrostatic potential, currents and ions distribution

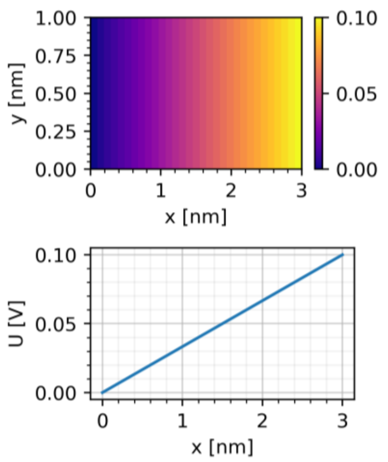
In all three cases, a region of **3 nm** length is terminated by **two planar electrodes**, **one grounded** and the **other at 0.1 V**. Such settings as well as the applied material parameters are representative of the so-called half-cell setup for the testing of battery materials.

Benchmarking and validation – Example 1

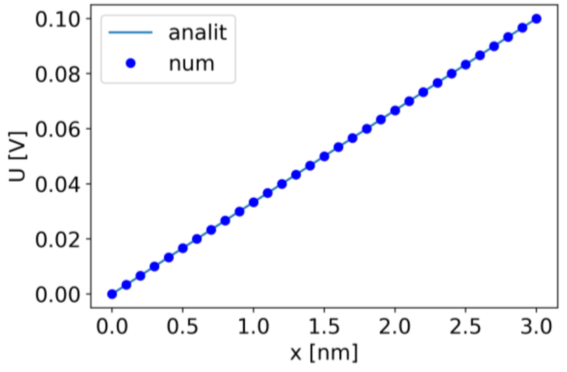
Laplace equation



System geometry



Validation against analytical solution



Analytical solution is:

$$U = \frac{-\rho}{2\,\epsilon}x^2 + \frac{U_0}{L}x + \frac{\rho}{2\,\epsilon}Lx$$

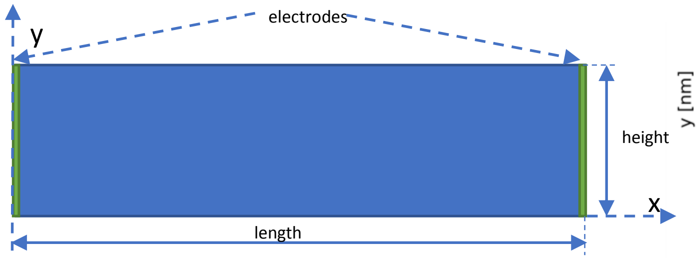
For $\rho = 0$:

$$U = \frac{U_0}{L}x$$

Electric potential (U) distribution in **3 nm** space filled with non-ionized electrolyte of **ε_r = 2.82**, limited by electrodes of **0.1 V** potential difference

Benchmarking and validation – Example 2

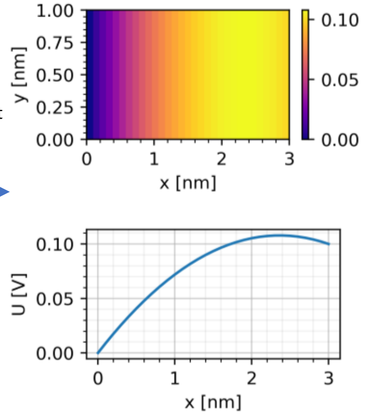
Poisson equation



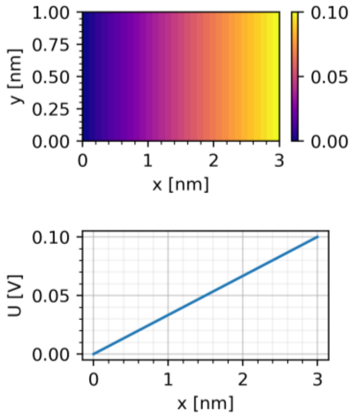
System geometry

Analytical solution is:

$$U = \frac{-\rho}{2\,\epsilon}x^2 + \frac{U_0}{L}x + \frac{\rho}{2\,\epsilon}Lx$$

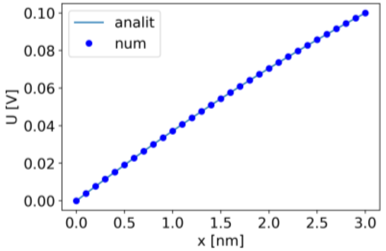


a) **Only positve ions, c*=10 mol/m3**

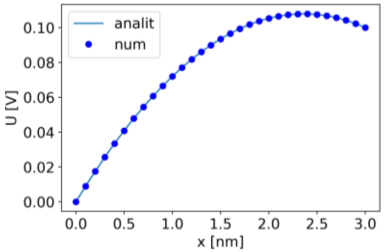


b) **Positve and negative ions, c*=10 mol/m3**

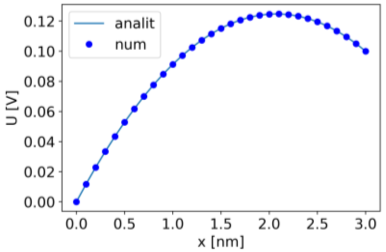
Validation against analytical solutions



c) **c*=1 mol/m3**



d) **c=10 mol/m3**

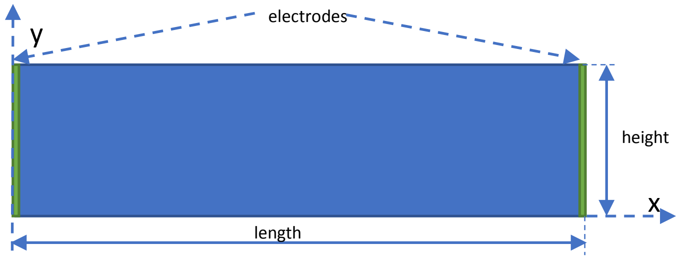


e) **c=15 mol/m3**

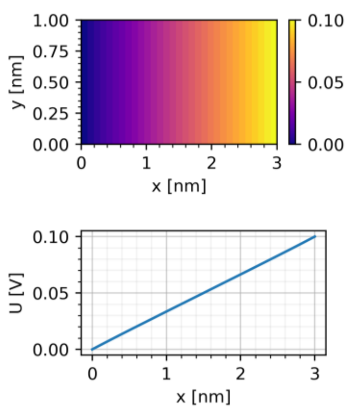
Electric potential (U) distribution in **3 nm** space limited by electrodes of **0.1 V** potential difference, filled with electrolyte of **εr = 2.82.**
c* - molar concentration

Benchmarking and validation – Example 3

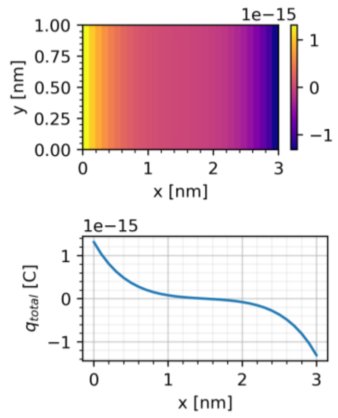
Poisson equation coupled with the drift-diffusion equations



System geometry

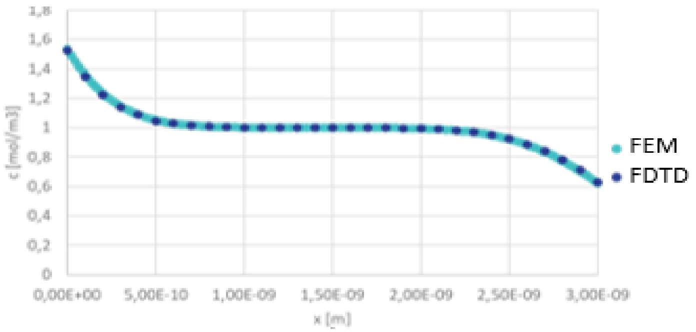


a)



b)

Validation against independent FEM solutions for the electrochemistry.



c)

Electric potential (a), **total charge (b)** and **positive charge (c)** distribution in space limited by electrodes of **0.1 V** potential difference, filled with electrolyte of **εr = 2.82**, with initial uniform concentration of positive and negative ions of **1 mol/m3** and **Dc=10-9 m2/s**.

Conclusions

- The new extension of the open access simulation software platform being developed within the European Horizon 2020 Framework projects was presented.
- The platform is dedicated to the **modelling of physical processes in materials and material test-fixtures**.
- **The coupling to drift-diffusion equations for ions has been developed, which allows for the modelling of electrochemistry phenomena in batteries and battery-testing equipment**, of interest to the automotive industry and beyond.
- The FDTD discretization of governing equations has been conducted
- The FDTD coupled solver was developed
- Three benchmarking examples were proposed and validated against analytical and alternative numerical solutions.
- **Excellent agreement for the above has been demonstrated**.
- The presented coupled solver will be disseminated in two ways: as a module of the Open Modelling Platform and within commercial QuickWave software by QWED
- Our FDTD software continues to be developed to further expand the capabilities for the modelling of multiphysics phenomena.

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(website: www.nanobat.eu)

For more details of our NanoBat research and Open Platform developments, please also refer to: https://www.qwed.eu/nanobat.html

Thank you for your attention!