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Outline

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- Physical model
- Governing equations
  - Electrostatics
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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.

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.

- Physical quantities (all in time and space):
  - electric potential distribution,
  - E-, D- field distribution,
  - charge distribution,
  - drift and diffusion currents.
Electrostatics

Electrical potential (U) distribution in space:
\[ E = - \nabla U. \]

The electric charge density (\( \rho \)) in space is checked using the Gauss law:
\[ \nabla \cdot D = \rho, \]

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:
\[ \oint_S D \cdot dS = q \]

Electric potential update using the Poisson equation:
\[ \Delta U = - \frac{\rho}{\varepsilon_r \varepsilon_0} \]

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, \( \mu \) – 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:

<table>
<thead>
<tr>
<th>Equation Type</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric field</td>
<td>[ E_{x_{ij}} = -\frac{(U_{i+1,j} - U_{ij})}{\Delta x_{ij}} ], [ E_{y_{ij}} = -\frac{(U_{i,j+1} - U_{ij})}{\Delta y_{ij}} ]</td>
</tr>
</tbody>
</table>
| Electric displacement field | \[ D_{x_{ij}} = E_{x_{ij}} \epsilon_{ij}, \quad D_{y_{ij}} = E_{y_{ij}} \epsilon_{ij}, \]
| | \[ d_x = D_x \Delta y_{avg} \Delta z_{avg}, \quad d_y = D_y \Delta x_{avg} \Delta z_{avg}, \]
| | \[ \Delta x_{avg} = \frac{\Delta x_i + \Delta x_{i-1}}{2}, \quad \Delta y_{avg} = \frac{\Delta y_j + \Delta y_{j-1}}{2}, \quad \Delta z_{avg} = 1. \]
| 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) | \[ U_{ij} = U_{ij} - r^* / \varepsilon_0 (q_{g_{ij}} - q_{ij}). \] |

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)

\[
\begin{align*}
  j_{px_{ij}} &= q_{px_{avg}} \mu^* E_x - D_c \frac{q_{p_{i+1,j}} - q_{p_{ij}}}{\Delta x}, \\
  j_{nx_{ij}} &= q_{nx_{avg}} \mu^* E_x + D_c \frac{q_{n_{i+1,j}} - q_{n_{ij}}}{\Delta x},
\end{align*}
\]

\[
q_{x_{avg}} = \frac{q_{(i+1,j)} + q_{ij}}{2}, \quad \mu^* = \frac{\mu}{\Delta x_{avg} \Delta x'}, \quad D_c^* = \frac{D_c}{\Delta x_{avg}}.
\]

**Continuity equations**  
(charges distribution update)

\[
\begin{align*}
  q_{p_{ij}}(t) &= q_{p_{ij}}(t - 1) - (j_{px_{ij}} - j_{px_{i-1,j}}) \Delta t - (j_{py_{ij}} - j_{py_{i-1,j}}) \Delta t, \\
  q_{n_{ij}}(t) &= q_{n_{ij}}(t - 1) + (j_{nx_{ij}} - j_{nx_{i-1,j}}) \Delta t + (j_{ny_{ij}} - j_{ny_{i-1,j}}) \Delta t.
\end{align*}
\]

**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 $\rightarrow$ electrostatic potential distribution

Example 2
- Uniformly distributed static ions (initial condition)
- Solving Poisson equation $\rightarrow$ 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 $\rightarrow$ 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

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

Validation against analytical solution

Analytical solution is:

$$U = -\frac{\rho}{2\varepsilon} x^2 + \frac{U_0}{L} x + \frac{\rho}{2\varepsilon} L x$$

For $\rho = 0$:

$$U = \frac{U_0}{L} x$$
**Benchmarking and validation – Example 2**

**Poisson equation**

![System geometry diagram](image)

Analytical solution is:

\[ U = \frac{-\rho}{2 \epsilon} x^2 + \frac{U_0}{L} x + \frac{\rho}{2 \epsilon} L x \]

Electric potential (U) distribution in 3 nm space limited by electrodes of 0.1 V potential difference, filled with electrolyte of \( \varepsilon_r = 2.82 \).

- **c** - molar concentration

Validation against analytical solutions

- **c** = 1 mol/m³
- **c** = 10 mol/m³
- **c** = 15 mol/m³

August 1-5, 2021, Virtual Conference
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 $\varepsilon_r = 2.82$, with initial uniform concentration of positive and negative ions of 1 mol/m$^3$ and $D_c=10^{-9}$ m$^2$/s.
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.

**Conclusions**
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NanoBat No 861962.

(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!