Extension of open EM modeling platform towardselectrochemistry and energy materials

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***Abstract*—The paper reports recent developments of Open Innovation Environments in a focus of the European Union research projects. It presents a new extension of the open access computational electromagnetics platform to the modeling of coupled electrochemical phenomena occurring at electrolyte/electrode interfaces. The problems are solved using coupled Laplace / Poisson and drift-diffusion equations, which create a basic model of ion transport process in the electrolyte, as in e.g. in popular Li-ion batteries. The developed coupled FDTD solver is validated against analytical solutions for the electrostatics and independent FEM solutions for the electrochemistry. It is prepared to be openly used for the modeling of industrially representative test-fixtures for battery materials, such as those defined in the H2020 NanoBat project.**

Keywords—open modelling platform, open innovation environment, computational electromagnetics, computational chemistry, applied electromagnetics, coupled processes modelling, FD method, FDTD method.

I. INTRODUCTION

While computational electromagnetics (CEM) has become a well-established tool in electrical engineering, its expansion into other industries requires simultaneous solutions of the Maxwell equations with equations describing other physical processes. This became evident, for example, in the food industries of early 2000s, when the design of microwaveable food packages stimulated the extensions of CEM FDTD (finite-difference time-domain) codes with enthalpy-dependent material parameters, heat transfer [1], and load movement during the heating [2]. An intriguing range of applications for electromagnetics opens up these days in the area of energy materials, such as used in batteries or photovoltaics. Electromagnetic testing of such materials is gaining popularity [3][4] but requires that charge transport mechanisms be taken into account in order to properly interpret the testing results. For example, a physical model of the ion transport process in the electrolyte must be considered in Li-ion batteries, which are one of the most popular electrical energy storage devices in various applications [5]. Coupled electrochemical models are therefore necessary in battery research [6], which motivates our efforts to enhance our EM FDTD tools [7] with drift-diffusion models [8][9]

Our recent work has been performed in the framework of the European Horizon 2020 projects [3][4], where a significant attention is given to Open Innovation. Open Modeling Platforms are expected to deliver the results of research for the usage by a wide scientific community as well as for the teaching. Accordingly, we have set up an Open Platform of Tools and Examples [10][11], based on reduced-power versions of commercial CEM tools and supplemented with models and procedures dedicated to material testing applications. They are accessible via a license-free graphical user interface, which in turn is capable of invoking various other EM and multi-physical solvers under different licenses.

Herein, we report an extension of EM FDTD to charge transport with the equations derived in Section II. Benchmarking examples are discussed in Section II and conclusions are drawn in Section IV.

II. PHYSICAL MODEL

We consider a region filled with an electrolyte and polarized by fixed-potential electrodes. In this work, we focus on a 2D case and our benchmarking examples are for a parallel-plate setup, but extensions to 3D are straightforward. The following physical quantities are analyzed:

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

all in time and space.

A. Electrostatics

The first instance the electrostatic model, consisting of eqs. (1), (2) and (3), is used for obtaining the electrical potential (U) distribution in space. Using the definition of electric potential, the electric field (E) distribution in space is obtained:

$$\boldsymbol{E} = -\nabla U \tag{1}$$

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

$$\nabla \cdot \boldsymbol{D} = \rho \tag{2}$$

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:

$$\oint_S \boldsymbol{D} \cdot d\boldsymbol{S} = q \tag{3}$$

Finally, the electric potential is updated until the Poisson equation is satisfied:

$$\Delta U = -\frac{\rho}{\epsilon_r \epsilon_0} \tag{4}$$

B. Drift-Diffusion model

In the second instance of the model, the process of the flow of ions (positive and negative) is taken into account. The separate currents for positive ($\boldsymbol{j_p}$) and negative ($\boldsymbol{j_n}$) ions are calculated using drift-difussion equations. They combine the influence of the existing electric field on the charges with the difussion process due to nonuniform charge distribution [8][9]:

$$\boldsymbol{j_p} = q_p \mu \boldsymbol{E} - D_c \nabla q_p \tag{5}$$

$$\boldsymbol{j_n} = q_n \mu \boldsymbol{E} + D_c \nabla q_n \tag{6}$$

where D_c – diffusion coefficient, μ – charge mobility. The resulting currents cause a change in the position of ions in the modeled space in time and using the continuity equation we obtain the distribution of ions for each moment in time.

$$\oint_S \boldsymbol{j_p} \cdot d\boldsymbol{S} = -\frac{dq_p}{dt} \tag{7}$$

$$\oint_S \boldsymbol{j_n} \cdot d\boldsymbol{S} = \frac{dq_n}{dt} \tag{8}$$

C. Discretization

The FDTD approach after [12] is used to solve eqs. (1)-(8) in a coupled manner. Fig. 1 shows a fragment of the FDTD mesh. Different physical quantities are calculated at staggered positions, at the nodes marked in Fig. 1. This facilitates second order approximations in space and time to the differential operators as well as charge conservation over time, analogously as in the FDTD method for electromagnetics [12]. Using the notation of Fig. 1, the electric field components are obtained by the discretized eq. (1):

$$E_{x_{ij}} = -\frac{(U_{i+1,j} - U_{ij})}{\Delta x_{ij}} \tag{9}$$

$$\mathrm{E}_{y_{ij}} = -\frac{\left(U_{i,j+1} - U_{ij}\right)}{\Delta y_{ij}} \tag{10}$$

For convenience, fluxes of electric induction are also defined:

$$d_x = D_x * \Delta y_{avg} \Delta z_{avg} \tag{11}$$

$$d_y = D_y * \Delta x_{avg} \Delta z_{avg} \tag{12}$$

where $\Delta z_{avg} = 1$ is used with a view to future extension to 3D problems and:

$$\Delta x_{avg} = \frac{\Delta x_i + \Delta x_{i-1}}{2} \tag{13}$$

$$\Delta y_{avg} = \frac{\Delta y_j + \Delta y_{j-1}}{2} \tag{14}$$

The d_x and d_y values are used in the discretized form of the Gauss law to obtain a residual charge at each voltage node:

$$q_{g_{ij}} = d_{x_{ij}} - d_{x_{i-1,j}} + d_{y_{ij}} - d_{y_{i,j-1}} \tag{15}$$

In a space without charges, such as cross-sections of TEM transmission lines, any non-zero residual charge indicates that the physical solution for D- and E-fields, and hence for the potential U, has not been reached, and the potential distribution is updated by a relaxation procedure [7]. An analogous procedure is applied for the electrostatic problem with charges as in of *Subsection A*. Here, a relaxation technique is used to solve the Poisson equation (4):

$$U_{ij} = U_{ij} - r^* / \epsilon_0 (q_{g_{ij}} - q_{ij}) \tag{16}$$

where $r^*$is relaxation coefficient expressed as:

$$r^* = \frac{r}{\Delta z_{avg}} \tag{17}$$

and $(q_{g_{ij}} - q_{ij})$ is the difference between the residual charge obtained from Gauss law and total charge given as the initial condition.

For the case with moving charges, as in *Subsection B*, drift-diffusion equations are discretized to obtain currents:

$$j_{px_{ij}} = q_{px_{avg_{ij}}} \mu^* E_x - D_c{}^* \frac{q_{p_{i+1,j}} - q_{p_{ij}}}{\Delta x} \tag{18}$$

$$j_{nx_{ij}} = q_{nx_{avg_{ij}}} \mu^* E_x + D_c{}^* \frac{q_{n_{i+1,j}} - q_{n_{ij}}}{\Delta x} \tag{19}$$

where central averaging of the charges at the voltage nodes is used to approximate the charges at the current nodes:

$$q_{x_{avg_{ij}}} = \frac{q_{i+1,j} + q_{ij}}{2} \tag{20}$$

and μ^*, $D_c{}^*$ are normalized μ and D_c parameters:

$$\mu^* = \frac{\mu}{\Delta x_{avg} \Delta x} \tag{21}$$

$$D_c{}^* = \frac{D_c}{\Delta x_{avg}} \tag{22}$$

The discretized forms of continuity equations (7), (8) as presented below are now applied to update the distribution of positive and negative charges:

$$q_{p_{ij}}(t) = q_{p_{ij}}(t-1) - (j_{px_{i,j}} - j_{px_{i-1,j}})\Delta t - (j_{py_{i,j}} - j_{py_{i,j-1}})\Delta t \tag{23}$$

$$q_{n_{ij}}(t) = q_{n_{ij}}(t-1) + \left(j_{nx_{i,j}} - j_{nx_{i-1,j}}\right)\Delta t + (j_{ny_{i,j}} - j_{ny_{i,j-1}})\Delta t \tag{24}$$

Finally, the total charge q_{ij} needed for eq. (16) is obtained as the difference between the positive and negative charges at each node:

$$q = q_p - q_n \tag{25}$$

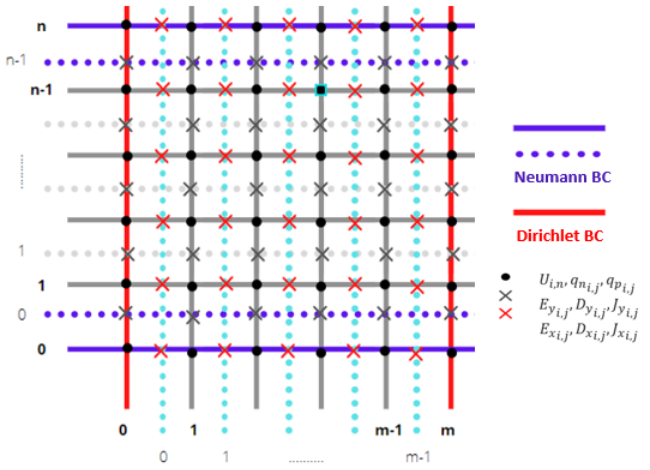

Fig. 1. Staggered mesh used for FDTD solution of Poisson coupled with Drift-Diffusion equations.

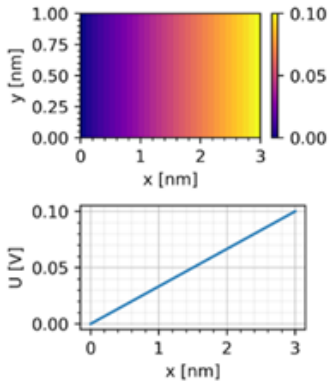

Fig. 2. Electric potential (U) distribution in 3 nm space filled with non-ionized electrolyte of $\varepsilon_r = 2.82$, limited by electrodes of 0.1 V potential difference.

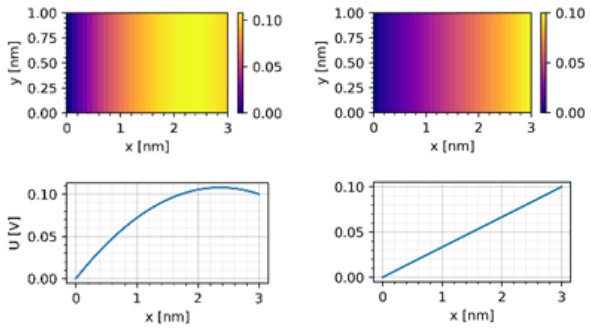

Fig. 3. Electric potential (U) distribution in 3 nm space limited by electrodes of 0.1 V potential difference, filled with electrolyte of $\varepsilon_r = 2.82$ and static charges of molar concentration equal 10 mol/m^3: (left) only positive ions and (right) positive and negative ions.

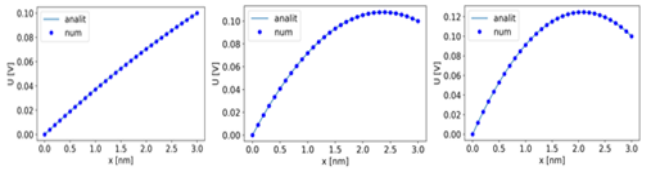

Fig. 4. Electric potential (U) distribution in 3 nm space limited by electrodes of 0.1 V potential difference, filled with electrolyte of $\varepsilon_r = 2.82$ and static positive charges of molar concentration: (a) 1 mol/m^3, (b) 10 mol/m^3, and (c) 15 mol/m^3.

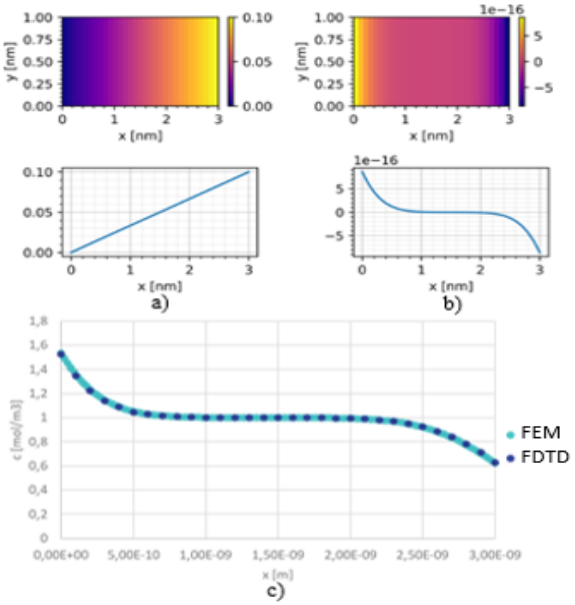

Fig. 5. Electric potential (a), total charge (b), and positive charge (c) distribution in space limited by electrodes of 0.1 V potential difference, filled with electrolyte of $\varepsilon_r = 2.82$, with initial uniform concentration of positive and negative ions of 1 mol/m^3 and D_c=10^{-9} m^2/s.

III. Examples

The FDTD equations presented in Section II have been implemented in Python, a commonly used scripting language for prototyping electromagnetic problems [13]. Three different models of increasing complexity have been analyzed with the developed FDTD codes. 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 [14].

The first problem concerns electrostatics in a region without charges. This corresponds to the computation of the Laplace equation and finding the electrostatic potential distribution. The solution shown in Fig. 2 clearly matches that expected for the canonical case of a parallel-plate capacitor.

In the second problem, ions are uniformly distributed as the initial condition. The ions are assumed to be static, which has the physical sense of zero diffusivity and mobility. Due to the charges, instead of the Laplace equation, the Poisson equation is now computed to find the electrostatic potential distribution. If densities of negative and positive charges are equal, as in the right column of Fig. 3, the net charge is zero and the solution is the same as for the Laplace equation in Fig. (2). Any net charge will, however, cause a deformation of the linear $U(x)$ solution by a parabolic component, as shown in the left part of Fig. 3 where only positive charges are considered in the modeled space. In Fig. 4, three cases of different charge densities are considered. The first considered molar density of 1 mol/m^3 is too small to cause a visible distortion of the linear potential distribution. For the increasing molar densities of positive charges, the parabolic component of the potential distribution becomes increasingly significant and a local maximum of the potential shifts towards the grounded (lower potential) electrode.

In the third problem, the Poisson equation is coupled with the drift-diffusion equations. The initial condition is imposed by uniformly distributed positive and negative ions, but now

the ions have finite diffusivity and mobility. The evolution of the distribution of charges is found by the time-stepping of eqs. (23), (24); at each time step, a new potential distribution is obtained by relaxation (9)-(16) leading to new current distributions given by (18)(19). The eventual steady-state patterns of potential and charges are shown in Fig. (5). In this case, an analytical solution is not easily available, so for comparison, a FEM solution is obtained using commercial COMSOL software [15]. A perfect agreement between the FDTD and FEM solutions is demonstrated in Fig. 5c.

IV. Conclusions

The paper has presented a new extension of the open access simulation software platform being developed within the European Horizon 2020 Framework projects. The platform is dedicated to the modelling of physical processes in materials and material test-fixtures and in its previous versions [10] has been restricted to the electromagnetic phenomena. Herein, 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 article has described the equations on the basis of which the FDTD coupled solver was created as well as three benchmarking examples. Excellent agreement has been demonstrated with the analytical solution for the Poisson equation and with the FEM solution by commercial software for the coupled Poisson-Drift-Diffusion equations. Our FDTD software continues to be developed to further expand the capabilities for the modelling of multiphysics phenomena. The forthcoming versions will be provided in open access [16] facilitate the teaching in academia and dissemination in industry, in accordance with the European open research policies.

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