

Open Platform tools to modelling electrochemical phenomena in solid electrolyte interphase

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Abstract— The paper reports recent developments of numerical methods in the framework of the EU H2020 NanoBat project. It presents an extension of the computational electromagnetics platform, previously extended to electrochemistry, to the modeling of coupled electrochemical phenomena occurring at the solid electrolyte interphase. Two new FDTD algorithms have been developed to solve coupled Poisson and drift-diffusion equations and electric double layer using FDTD method. All developments are prepared for use in modeling of industrially representative test fixtures for battery materials, under the open license of the H2020 NanoBat project.

Keywords—numerical methods, CEM, multiphysics modelling, computational chemistry, solid electrolyte interphase, Open Modelling Platform, OIE, batteries.

I. INTRODUCTION

Currently, the nanotechnology market is growing rapidly, despite the high cost of manufacturing nanoproducts, and testing them properly. However, investments in this area have made it possible to improve electricity storage systems, which directly reduces the environmental footprint of battery production. In particular, existing research on the interaction between the electrode and the electrolyte. To measure electrochemical behaviour of solid-electrolyte interphase (SEI), it is necessary to use hi-tech technology, especially electrochemical scanning tunnelling microscopy [1] (ECSTM). Before starting such research, it is worth checking what results are predicted by the specialized computer simulations. The dissemination of knowledge about the phenomena occurring in this area contributes to the development of such software. For this reason, a package of tools and examples was created under the NanoBat Open Platform license [2].

Our recent work [3] done in the European Horizon 2020 project has been enriched with two new applications. First of them simulates a nanometer space filled with an electrolyte and bounded by two electrodes. In such a system there is a physical phenomenon of the flow of ions. In simulation separate currents are taken into account for positive and negative ions. They combine the influence of the existing electric field on the charges with the diffusion process due to charge distribution. Electric potential at the two electrodes is defined by the user and it is constant during the simulation, thus satisfying the Dirichlet boundary condition. After the user enters the rest of the initial conditions, the calculations of the current, charges and electric potential distribution begin by

solving the conjugate drift-diffusion with Poisson [4] equations. The FTDT [4-8] method is used to solve the equations numerically. The user now is allowed to perform calculations by initiating his own distribution of electric charges. An enriched approach to this phenomenon has been implemented in the second application. The electrolyte, under the influence of the coulomb force exerted by the electrode, is adsorbed to form a monolayer of ions. The ions of the opposite sign are attracted to the created layer, which causes the movement of ions in electrolyte, consequently changing the local concentration of the electrolyte. This phenomenon is called electric double layer (EDL) [9].

The paper is organized as follows. In Section II we present the physical models used to solve the presented physical problems. Section III describes the results of selected examples in the field of electrochemistry developed in the NanoBat project. Section IV concludes with an outline of the on-going works of the NanoBat consortium and our invitation for collaboration addressed to other consortia.

II. PHYSICAL MODEL

Due to the charge conservation principle in an isolated system, the sum of the charges of all bodies does not change. It is worth noting that the problem of electrostatics itself assumes that the charges in the considered systems are at rest or move very slowly. This makes it possible to ignore the effect of this phenomenon on the system. Influence between such charges is described by Coulomb's law. Charges placed in space create a property called a field electrical power, which acts on every other endowed body within it by exerting an electrical force on it. In the presence of the action of conservative forces, which are electrostatic forces, it makes sense to introduce the concept of potential energy.

A. Poission-Drift-Diffusion – physical model and FDTD algorithm

Let us start with a bulk model of an electrolyte. Assuming that the charges move at a constant velocity over the considered time, changes in the kinetic energy may be neglected. The potential energy divided by the electric charge gives us the value of the electric potential. Changes of this electric potential along some space gives the value of the electric field. A semiconductor or electrolytes when connected to a voltage and current source can act as a path along which charges flow. If at the ends of such materials the potential

difference is sustained, then a non-zero electric field is created in it inside (non-stationary state). The amount of charge flowing through such material to unit of time is called the amperage. The electric field propagating in such a medium affects the electrons causing their thermal motion to overlap a certain average drift velocity [10]. The diffusion problem described by Fick's law [11], which allows for prediction of concentration change as a function of time. Diffusion coefficient and the electron mobility for a semiconductor or electrolyte are related by Einstein relation [12].

Combining the above physics leads in a bulk electrolyte leads us to the so called Poisson-Drift-Diffusion (PDD) model. The analytical equations in 1D space and time, as well as their numerical FDTD formulation (further referred to as PDD-FDTD) are available on our Open Platform of the NanoBat project [13].

B. Electric Double Layer – models and new FDTD algorithm

Performance of batteries is strongly influenced by the formation of an interfacial layer between the electrode and electrolyte, called solid electrolyte interface (SEI). A complete description of the physical-chemical phenomena occurring at SEI is very complex and its rigorous modelling would require an enormous amount of computing power. For the sake of simplification, various approaches are used, known more generally as the electric double layer (EDL). The most commonly used physical EDL models[14-16] are shown in the figure 1 below.

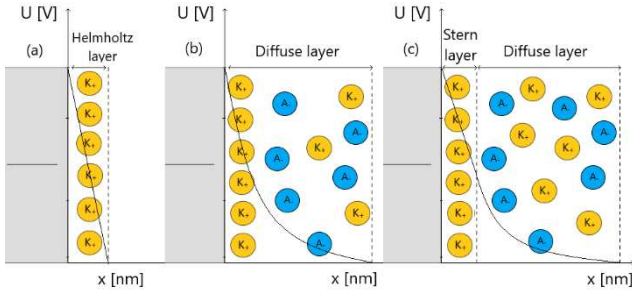


Fig. 1. Models characterizing the Electric Double Layer phenomenon

The Helmholtz (a) model assumes that in SEI an ionic layer is formed on the solid, which does not cause diffusion of the remaining ions in the electrolyte. The width of the formed layer of ions is equal to their diameter [17]. It is a small area compared to the width of the electric double layer. For this reason, its width can be omitted. It was also noticed that the ionic concentration of the electrolyte changes with the distance from the electrode satisfying the Maxwell-Boltzmann statistic [16]. These assumptions are included in the Gouy-Chapman (b) model. The above two models have been combined and enhanced with additional features of this phenomenon. The next model (c) takes into account the adsorption of ions on the electrode surface, which causes the counter-ions to attract. This region is called the Stern layer. Along with the distance, the diffusion layer extends, in which the Coulomb interactions are taken into account. The newly developed software is based on this particular model.

A half-cell system is considered in which the physical parameters of the electrolyte are known and the electric potential at the electrode is defined. It should be assumed that the Stern layer immediately appears next to the electrode,

which is flat, uniformly charged and the ions adsorbed to it do not repel each other. In the diffusion part, the ions are treated as points and satisfy the Maxwell-Boltzmann equations. There is a continuous distribution of the dielectric constant ϵ_r and temperature T along the entire system. Values such as electron mobility μ and diffusion coefficients D_c are discretized in relation to a given space. The electric potential U changes according to the molar concentration n_0 change due to the movement of the ions. This directly affects to the charge density ρ . This relationship is related by the conjugate Poisson and Boltzmann equation;

$$\frac{d^2U}{dx^2} = \frac{\rho}{\epsilon_0\epsilon_r} = \frac{ze(n_+-n_-)}{\epsilon_0\epsilon_r} = \frac{2ze n_0}{\epsilon_0\epsilon_r} \sinh\left(\frac{zeU}{k_B T}\right), \quad (1)$$

where z is valence, $n_{+/-}$ positive/negative molar concentration, ϵ_0 absolute permittivity, e is elementary charge and k_B is Boltzmann constant.

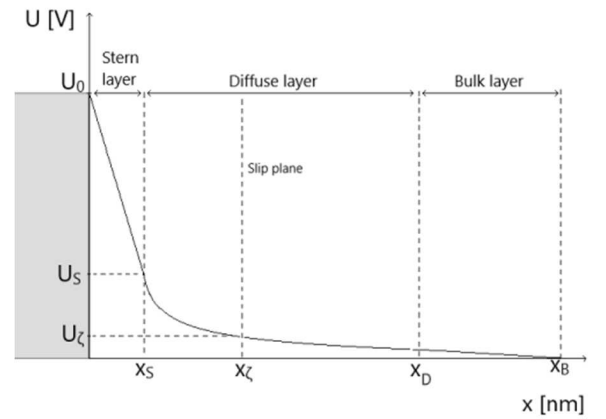


Fig. 2. Electric potential distribution in electric double layer EDL (Stern model)

The solution to this problem can be divided into three areas with different boundary conditions (Fig. 2). Knowing what ions fill the electrolyte allows one to determine the width x_S of the Stern layer and what is the distribution of electric charges in it. This makes it possible to calculate the boundary potential;

$$U_S = \frac{2k_B T}{ze} \sinh\left(\frac{\rho}{\sqrt{n_0 N_A \epsilon_0 \epsilon_r k_B T}}\right), \quad (2)$$

where N_A is Avogadro constant.

The effect of the formed adsorbate layer on the rest of the electrolyte decreases with the distance from the solid. The Coulomb potential becomes so small that it can be ignored. This place becomes a natural border for the system under consideration. It is known as the Debye length[9];

$$x_D = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{n_0 N_A e^2 z^2}}. \quad (3)$$

With the end of the diffusion layer begins the bulk layer in which the ions remain neutral to the solid placed in the electrolyte and thus assuming that the electric potential in this area is zero.

Experiments often performed on SEI are electrophoresis or electroosmosis because of the zeta potential [18]. This potential is located in the slip plane, which divides the ions in the electrolyte into those that are attracted to the Stern layer

and those that become inert to it. With this potential the stability of the SEI can be determined. FDTD calculations for the diffusion layer allows to determine the approximate location of the Slip plane by analyzing the electric charge distribution and hence the zeta potential.

III. OPEN PLATFORM SIMULATION RESULTS

We consider a 1D electrochemical system analogous to [4]. The same constants and electrode/electrolyte parameters are used. The potential difference of the electrode with respect to the ground potential is equal to 0.1 V. There is a constant temperature T of 293 K and an relative permittivity ϵ_r of 2.82 F/m along the entire system. The movement of ions is described by a diffusion coefficient $D_c=10^{-9}$ m²/s. The mesh of 100 FDTD cells is set up and the time step is 0.1 ns. The simulation ends when the convergence condition for the equilibrium state of the system is satisfied.

A. FDTD simulations of bulk electrolyte

In order to verify the correctness of the newly created EDL-FDTD software, we compare it to the previously reported FDTD and FEM implementations for bulk electrolyte [4]. In the example of [4], the initial condition was a uniform molar concentration of 1 mol/m³, of both positive and negative ions. The simulation starts with relaxation steps of the electric potential distribution, until its convergence is reached. In the first FDTD iteration, a linear distribution of potential is obtained, as there is zero net charge at each FDTD cell. This gives rise to non-zero electric field in the region, which causes the charges to move. The distribution of positive and negative currents are calculated and consequently the charge in each FDTD cell is updated. As the simulation runs, charge distribution. As shown in Fig. 3, the new EDL-FDTD results coincide with PDD-FDTD and PDD-FEM of [4].

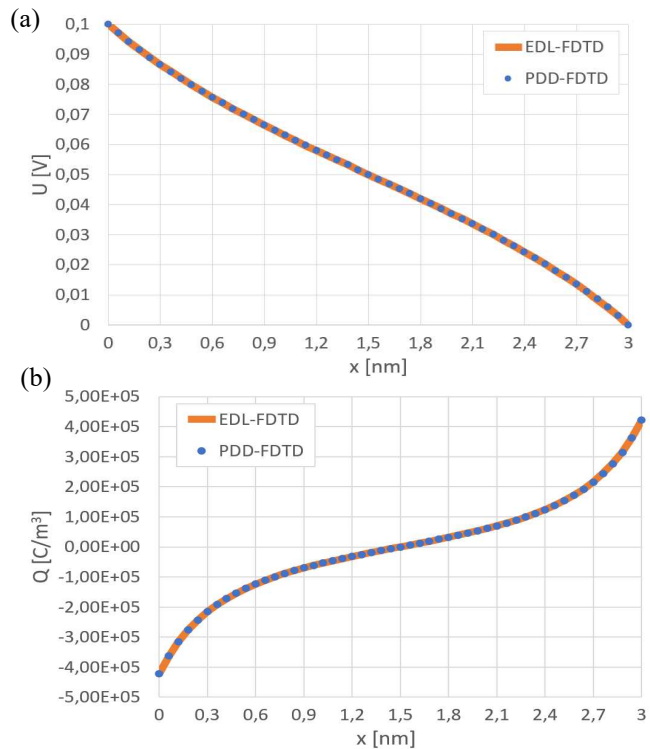


Fig. 3. Comparison of electric potential (a) and total charge (b) distribution for a bulk electrolyte example, neglecting the interfacial effects and assuming uniform initial charge distribution, as obtained by new EDL-FDTD and reference PDD-FDTD (and PDD-FEM) in [4].

Our new EDL-FDTD, except for the option of including a Stern model of the interface, has an additional functionality relevant to purely bulk models. Namely, it allows importing the initial distribution of charges from text files and starting the FDTD simulations from other than spatially uniform charge distributions. All steady-state simulation results (i.e., the distributions of potential and negative and positive charges) can also be saved to text files. This will allow multiphysics modelling of more complicated real-life scenarios by future coupling of our EDL-FDTD to external solvers for other physical-chemical effects.

To demonstrate the functionality of starting from a non-trivial initial condition, pre-calculated by an external solver, we run the previous example with reversed polarisation and save the negative and positive charge distributions (of Fig. 3) to text files. We then start a new simulation of the same scenario, but with the initial distribution of charges imported from the text files. Note that the initial distribution of potential is not precalculated and imposed – as in the example of Fig. 3, we start by polarising the bulk electrolyte with 0.1V voltage.

The first FDTD iteration starts with solving the Poisson equation in a charged region, with the imported initial charge distributions. Since these distributions are nonuniform and amount to non-zero net charges in FDTD cells, the obtained electric potential distribution is non-linear. In fact, it then remains unchanged with time and so do the initially imported charges, as both distribution correspond to the physical equilibrium (steady-state). In other words, as physically expected, the final patterns of potential and charges calculated with initial uniform charge distribution (as in Fig. 3) coincide with those obtained the with initial charge distributions pre-calculated as the steady-state patterns of the same scenario coincide (Fig. 4). In both cases, the total charge in the considered 3 nanometer space did not change so that the principle of conservation of electric charge was maintained.

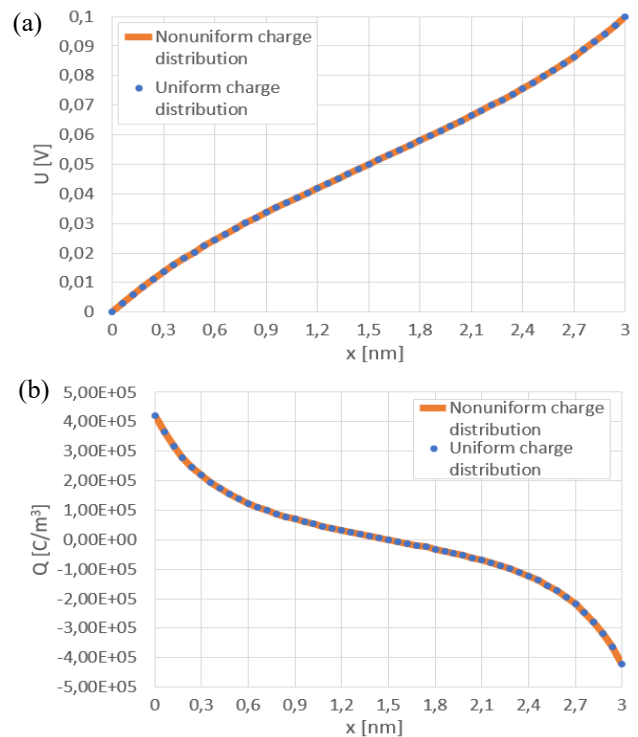


Fig. 4. Comparison of electric potential (a) and total charge (b) distribution for a bulk electrolyte example with nonuniform and uniform initial charge distribution obtained by new EDL-FDTD.

B. FDTD simulations including the interfacial layer

We now extend the simulation of the bulk electrolyte model to the model including interfacial effects. At the boundary of the system, there is an electrode/metal with a given potential of 0.1 V. The surrounding electrolyte is much larger than this electrode, so that its depth can be neglected. To implement the EDL model, it is necessary to define new initial conditions. An additional parameter of the electrolyte is the radius of its ions equal to 152 picometers and their valence equal to 1. Based on these values, the Stern potential U_S and the Debye length x_D are obtained analytically with (2) and (3). With these boundary conditions, the FDTD algorithm is run. Concurrently solved equations for Stern and diffusion layers until currents cease in the system. The result obtained from the simulation is the electric potential distribution, which is shown in the following Fig. 5.

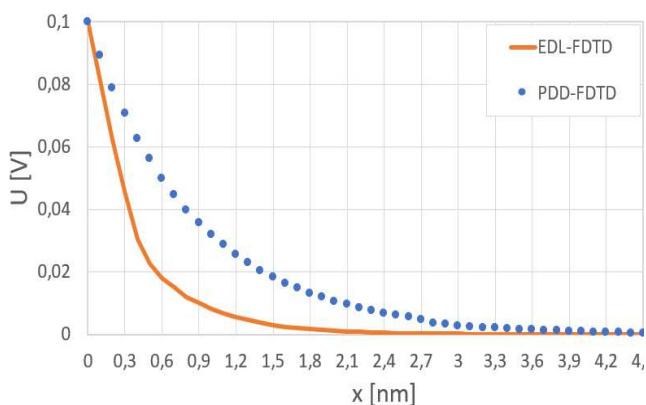


Fig. 5 Comparison of electric potential distribution for a bulk electrolyte example, including the interfacial effects obtained by new EDL-FDTD and reference PDD-FDTD (and PDD-FEM).

In the Stern layer, the interpolated electric potential is linear and decreases strongly. Just near the adsorbed ions at the boundary of the Stern layer, the potential U_S is equal to 42.7 mV. From this point onwards the electric potential decreases until it reaches a value close to zero at a x_D point equal 2.58 nm.

IV. CONCLUSIONS

The paper has presented recent extensions of FDTD algorithms for coupled electrical-chemical battery models, as developed within the EU H2020 NanoBat project. The algorithms form part of the Open Innovation Environment (OIE) dedicated to the modelling of physical processes in materials and material test fixtures. The new EDL-FDTD software includes two functionalities added to the previously reported FDTD algorithm [4] for the Poisson-Drift-Diffusion model. The first functionality allows solving the coupled PDD equations starting from non-trivial nonuniform initial charge distributions, imported from text files and allowing one to couple the new EDL-FDTD solver to other multiphysics solvers. The second functionality extends the physical model to the interfacial effects, relevant to the SEI formation.

Besides foreseen applications in the characterisation of industrial battery materials, our work promotes the physical insights. The results obtained show the behavior of the used patterns in specific situations. The distributions of electric charges in the given space allow one to interpret the coulombic interactions. Negative charges are attracted to the electrode with greater electrical potential and positive charges

are repelled. Depending on the value of the potential difference, this phenomenon becomes stronger. Consequently, once the system is equilibrated, there are no charges at the center of the system. Charges build up near the electrodes. With a greater potential difference, the maximum charges at the edges of the system increase. Accordingly, the width of the peak decreases. By starting the algorithm with a regular distribution of electric charges, it becomes irregular as a result of the applied potential difference. This distribution can be saved and loaded as a initial condition. After solving such a system the same electric potential distribution is obtained.

The newly created software generates results comparable to already existing solutions. The applications are available in open access, which will facilitate teaching in academia and dissemination in industry, in line with European open research policy.

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