**MODA**

**MOdelling DAta providing a description**

**for the Half-Cell User Case**

**simulated in project NanoBat**

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| OVERVIEW of the SIMULATION | | | |
| 1 | **User Case** | *A coaxial tip, as extruded from a coax line, is placed above the sample-under-test (SUT) of a battery-relevant material (MUT - material-under-test). The tip is electrically excited through the coax, which itself is excited by a vector network analyser (VNA). Information about the MUT is obtained either from electric field distribution or from the signal reflected by MUT and measured by the VNA.*  *Our MUT will, typically, be a graphene (anode) deposited on copper or a SEI (solid electrolyte interface) formed on the graphene anode due to electrolyte decomposition during the battery formation/operation.* | |
| 2 | **Chain of Models** | **Model 1** | *Continuum Modelling of Materials: Electromagnetic Model (Maxwell Equations), reduced to Quasi-Electro-Statics at DC limit* |
| **Model 2** | *Continuum Modelling of Materials: Transport in Diluted Species (Nernst-Plank-Poisson or Nernst-Plank Equations)* |
| 3 | **Publication Peer-Reviewing the data** | *To be filled at the later stage of the project.*  *[Please give the publication which documents the data of this ONE simulation.*  *This article should ensure the quality of this data set (and not only the quality of the models).]* | |
| 4 | **Access conditions** | *Three groups of the WP3 will be involved in this task. JKU will apply COMSOL commercial FEM-based solvers. QWED will use their own FDTD commercial solver.*  *Part of the models and simulated results will be free.*  *The GUI and representative software versions dedicated to teaching and dissemination will be free (open access, but not open source).*  *Open Platform created in the NanoBat project (*<https://www.nanobat.eu/>*) will provide access to:*  *- the Models (CAD data files and results in Gwyddion format),*  *- Open GUI needed for examining and modifying the models as well as for visualising and analysing the computed results,*  *- dedicated FDTD solvers suitable for teaching and dissemination of major project results concerning the Models.*  *Commercial vendors should be contacted for full-power versions of FEM and FDTD solvers.* | |
| 5 | **Workflow and its rationale** | *The chosen user case is a typical experimental arrangement relevant for the study of nanoscale material and electrochemical effects in energy materials like Lithium-ion Battery (LIB).*  *Model 1: will be used to compute the electric field in the entire structure by solving Maxwell equations*. *The main numerical result of the simulation will be the E -field everywhere in the structure. The obtained E- and H-values will be integrated at the post-processing stage to obtain the S-parameter (S11) at the input.*  *Model 2: will couple the electric fields with the transport equation for electrochemical species and include equations for electrochemical reactions on the electrode surfaces.* | |

**User Case Parameters**

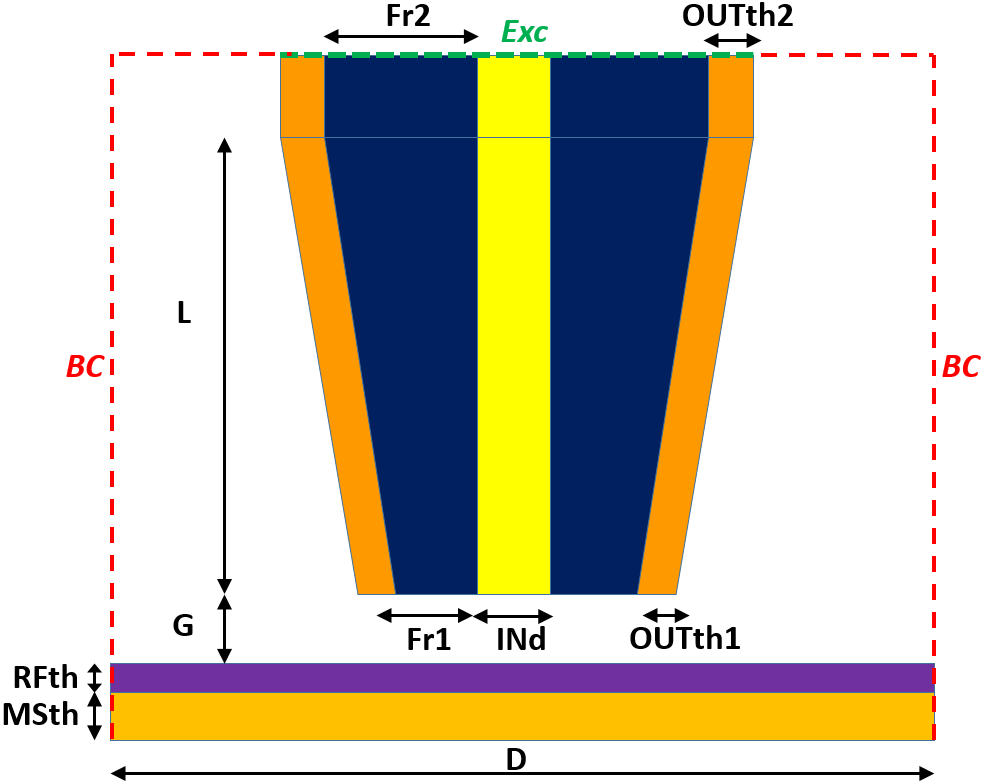
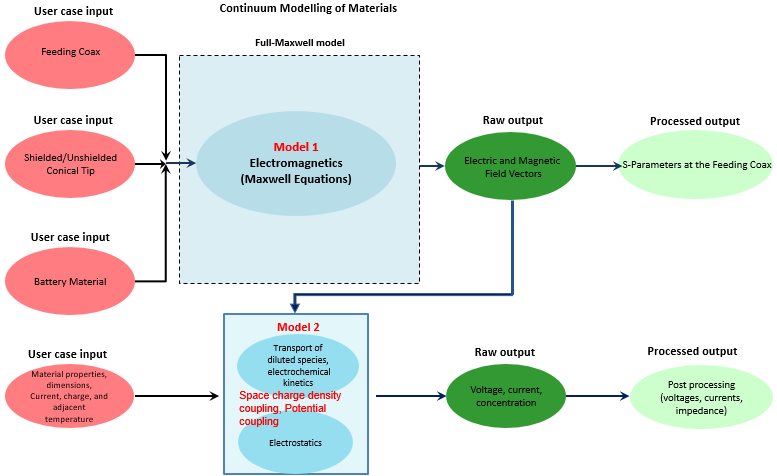


Fig. 1. Cross-section of the half-cell structure.

Table 1. Parameters of the half-cell User Case.

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| ***Parameter*** | ***Meaning*** | ***Value/values range*** | ***Comment*** |
| ***INd*** | Diameter of inner conductor | 100nm - 5μm |  |
| ***OUTth1*** | Thickness of outer conductor at tip bottom | 100nm - 1μm |  |
| ***OUTth2*** | Thickness of outer conductor at tip top | 100nm - |  |
| ***Fr1*** | Radius of the tip dielectric filling at the tip bottom | 1μm-10 μm |  |
| ***Fr2*** | Radius of the tip dielectric filling at the tip top | 100μm-500 μm |  |
| ***L*** | Length of the tip | 10 – 10000 μm |  |
| ***G*** | Gap between the tip and material sample | 1nm-100nm |  |
| ***RFth*** | Thickness of the resistive film | 5 – 50 nm | Porosity |
| ***MSth*** | Thickness of the metallic substrate | 1 mm | To be modelled as a boundary |
| ***D*** | Diameter of computational scenario | >Fr2+OUTth2+0.5INd | Subject to boundary conditions, typically mm – cm. |
| ***BC*** | Outer boundary condition | PEC (E tangential=0) or  PMC (H tangential=0)  or  ABC (absorbing / free space) | For quasistatic scenario fields this choice should be of minor importance, as fields are concentrated in the vicinity of the tip |
| ***medIN*** | Medium of the inner conductor | PEC |  |
| ***medOUT*** | Medium of the outer conductor | PEC |  |
| Metal with finite conductivity:  σ= 9.4 106 S/m | Platinum |
| None |  |
| ***medF*** | Medium of the tip dielectric filling | Glass:  εr= 4.6 , tanδ= 0.002 | Borosilicate glass |
| ***medRF*** | Medium of the resistive film | Dielectric:  εr= 2-10,  σ= 10-4 - 104 S/m |  |
| ***medMS*** | Medium of the metallic substrate | PEC |  |
| ***medE*** | Medium of the electrolyte | Dielectric constants: εr; tanδ.  **diethyl carbonate (DEC)**  εr = 2.82 [*Wohlfarth, C. Permittivity (Dielectric Constants) of Liquids. In*  *CRC Handbook of Chemistry and Physics (Internet Version 2015)*]  **dimethyl carbonate (DMC)**  εr= 3.08 [W. M., Ed.; CRC Press/Taylor and Francis: Boca Raton, FL,  2015; pp 6-187−6-208.]  **ethyl methyl carbonate (EMC)**  εr = 2.9 [*McEwen, A. B. et. al; Electrochem. Soc. 1997,*  *144 (4)]*  **dimethoxyethane (DME)**  εr = 7.2 [*Ue, M, et. al.,*  *J.Electrochem. Soc. 1995, 142 (8), 2577−2581*]  Note: Dielectric constant values are obtained at room temperature 25°C. | To be obtained from literature, if possible, some parameters compared to experiments. (Dielectric constant varies with temperature and concentration) |
| ***Problem type*** |  | BOR | One central hole (axisymmetric) |
| ***Excitation*** |  | TEM mode incident from a coaxial line, from which the tip is extruded  or  lumped voltage source between the inner and outer conductor at the upper end of the tip | These are standard port definitions in EM software |
| ***Freq*** | Frequency of analysis | DC to 10 GHz |  |
| ***Requested output*** |  | S11(f)  or  electric field distribution at selected frequencies |  |

**Workflow**



**MODEL 1**

*Time domain (FDTD) and frequency domain (FEM) Electromagnetic Analysis*

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| **1** | **Aspect of the User Case/System to be Simulated** | |
| 1.1 | **Aspect of the User Case to be simulated** | *Compute the E- field (and H- field for full-wave Maxwell) of the entire structure for a given excitation at the input port (the beginning of the extruded coaxial tip).* |
| 1.2 | **Material** | *See figure and table for materials of the test fixture and environment*  *The MUT is a battery anode sample (e.g. graphite coated on copper) covered with electrolyte material used for Li-ion batteries (e.g. LiPF6), with/without SEI.* |
| 1.3 | **Geometry** | *See figure and table* |
| 1.4 | **Time Lapse** | *The chosen frequency range is DC to 10GHz. Depending on the goal of simulation several to 100 periods of the source signal at its lowest frequency are to be simulated.* |
| 1.5 | **Manufacturing process or**  **in-service conditions** | *Material-under-test deposited on metallic background; coaxial tip extruded using the technologies of METAS.*  *unshielded tips made by JKU Linz.*  *Keysight VNA connected through a coax line to the top port of the coaxial tip*  *The electrical boundary conditions are PEC below the sample, free space around.* |
| 1.6 | **Publication on this data** | *Several papers are foreseen at the later stage of the project.* |

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| **2** | **Generic Physics Of The Model Equation** | | |
| 2.0 | **Model type and name** | *Continuum Modelling of Materials: Electromagnetics* | |
| 2.1 | **Model entity** | *Finite volumes (elements or cells)* | |
| 2.2 | **Model** **Physics/ Chemistry equation**  **PE** | **Equation** | *Maxwell equations (full-wave or in quasi-electro-static approximation)* |
| **Physical  quantities** | *Spatial coordinates (3 scalars), time (scalar), E-field, H-field (vectors), magnetic permeability, electric permittivity, electric conductivity (scalars or diagonal tensors).* |
| 2.3 | **Materials relations** | **Relation** | *, ,* |
| **Physical quantities/**  **descriptors for each MR** | *The values are obtained by own measurements or taken from the available literature.* |
| 2.4 | **Simulated input** | *Simulated input is either a voltage applied or a guided wave launched at the top of the coaxial tip. The amplitude and the frequency of the wave is to be chosen by the user. For time-domain simulations a pulse covering the assumed spectrum can also be chosen as excitation.* | |

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| **3** | **Solver and Computational translation of the specifications** | | |
| **3.1** | **Numerical Solver** | *FDTD, FEM.* | |
| **3.2** | **Software tool** | *Comsol, QuickWave,* | |
| **3.3** | **Time step** | *Needed only for the TD solver of QWED, will be taken according to the stability condition.* | |
| **3.4** | **Computational Representation** | **Physics Equation, Material Relations, Material** | *no special computer representation - physical quantities directly modelled (scaled for convenience)* |
| **3.5** | **Computational boundary conditions** | *The computational domain should be surrounded by a cylindrical boundary condition (PEC, PMC or ABC); bottom boundary in PEC; top is excitation region* | |
| **3.6** | **additional Solver Parameters** | * *FEM and FDTD: size of the computational box (D of figure) - chosen so as not to influence the simualted reuslt* * *FDTD: Stability limit for the given mesh; time lapse to achieve converged computed result* * *FEM: Convergence criteria.* | |

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| **4** | **POST PROCESSING** | |
| **4.1** | **The processed output** | *The E-field (and H-field for full Maxwell) vectors in each element of the mesh are directly obtained. E-field is integrated to approximate local voltages. For full Maxwell, the fields at the input (upper port) are converted to S-parameters.* |
| **4.2** | **Methodologies** | *FDTD (Discrete Fourier Transformation and S-parameters extraction) and FEM (frequency domain vector solution approach yielding directly the needed frequency characteristics)* |
| **4.3** | **Margin Of Error** | *to be discussed in future publications* |

**MODEL 2**

*Frequency domain (FEM) Electromagnetic Analysis* *coupled with transport equation for electrochemical species*

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| **1** | **Aspect of the User Case/System to be Simulated** | |
| 1.1 | **Aspect of the User Case to be simulated** | *Chemical reactions computed as functions of concentrations of reactant species, while accounting for surface concentrations of active sites and surface adsorbed species. Transport of electrochemical species by diffusion/migration due to an electric field for a given excitation at the input port (the beginning of the extruded coaxial tip)*  *The electric fields are coupled with the transport equation at lower frequencies for electrochemical species, equations for electrochemical reactions on the electrode surfaces are considered.* |
| 1.2 | **Material** | *See figure and table for materials of the test fixture and environment.*  *The MUT is a conductive sample (e.g. battery anode sample: graphite coated on copper) covered with electrolyte material used for Li-ion batteries (e.g. LiPF6)* |
| 1.3 | **Geometry** | *See figure and table above* |
| 1.4 | **Time Lapse** | *Considering a characteristic frequency range from DC to 1 MHz and depending on the aim of simulation several periods of the source signal at its lowest frequency are to be simulated. For example, time lapse can be from a few seconds up to 1 hour.* |
| 1.5 | **Manufacturing process or**  **in-service conditions** | *Material-under-test deposited on metallic background; coaxial tip extruded using the technologies of METAS /RUB/ JKU.*  *Keysight VNA connected through a coax line to the top port of the coaxial tip.*  *In service boundary conditions: The electrical boundary conditions are PEC below the sample, free space around.*  *Ambient temperature* |
| 1.6 | **Publication on this data** | *Targeted publication/s during the project e.g. Physical Chemistry Chemical Physics:* PCCP 2017, 19, 3884-3893 |

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| **2** | **Generic Physics Of The Model Equation** | | |
| 2.0 | **Model type and name** | *Continuum Modelling of Materials: Electrostatics, Transport of diluted species, electrochemistry* | |
| 2.1 | **Model entity** | *Finite volumes (elements or cells)* | |
| 2.2 | **Model** **Physics/ Chemistry equation**  **PE** | **Equation** | *Charge conservation dynamic*  *Nernst-Plank-Poisson Equation (diffusion, concentration)*  *Nernst-Einstein relation (mobility)*  *Gauss law, Faraday’s law* |
| **Physical  quantities** | *Spatial coordinates (3 scalars), displacement (scalar), time (scalar), E-field, electric permittivity, electric conductivity (scalars or diagonal tensors), diffusion (scalar), concentration (scalar)* |
| 2.3 | **Materials relations** | **Relation** | *Charge conservation*        *Surface charge density*    *Transport properties*        *Space charge density coupling*      *Electrode surface reaction*  *Reaction coefficients*      *where denotes the diffusivity of the reacting species, is its concentration, and is the velocity.)*  *Boundary conditions:*  *Zero charge boundary*    *Terminal voltage boundary*    *Ground boundary*    *No Flux boundary*    *Initial concentration values*      *Symbols definitions:*  Electric field density: (V/m)  Current density: (A/m2)  Electric charge density**:**  (C/m3)  Electric displacement: ***D*** (C/m2)  Electric potential: ***V*** (V)  Solvent velocity field: ***u*** (m/s)  Ionic mobility: (mol.s/kg)  Production/consumption rate expression: (mol/m3.s)  Concentration of species *i* : (mol/m3)  Permittivity: 𝜀 (F/m)  Relative permittivity: 𝜀*r*  Gas constant: *R* (J/(mol.K))  Temperature: *T* (K)  Diffusion coefficients: (m2/s)  Faraday’s constant: *F* (A.s/mol)  Capacitance: *C* (F)  Normal vector to surface: *n*  Charge number: *z* (unitless)  **Note**: bold symbols are vectors. |
| **Physical quantities/**  **descriptors for each MR** | *The values are obtained by own measurements or obtained from available literature.*  *Concentration*  *Displacement*  *Temperature*  *Charge* |
| 2.4 | **Simulated input** | *Simulated input is either a voltage applied, or a guided wave launched at the top of the coaxial tip. The amplitude and the frequency of the wave is to be chosen by the user. For time-domain simulations a pulse covering the assumed spectrum can also be chosen as excitation.* | |

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| **3** | **Solver and Computational translation of the specifications** | | |
| **3.1** | **Numerical Solver** | *Finite Element Method (FEM).* | |
| **3.2** | **Software tool** | *Comsol* | |
| **3.3** | **Frequency step** | *DC up to GHz. Logarithmic stepping applied.* | |
| **3.4** | **Computational Representation** | **Physics Equation, Material Relations, Material** | *no special computer representation - physical quantities directly modelled (scaled for convenience)* |
| **3.5** | **Computational boundary conditions** | *The computational domain should be surrounded by a cylindrical boundary condition (PEC, PMC or ABC); bottom boundary in PEC; top is excitation region.*  *Terminal voltage, ground and initial concentrations.* | |
| **3.6** | **additional Solver Parameters** | * *FEM: size of the computational box (D of figure) - chosen so as not to influence the simualted result* * *FEM: Convergence criteria.* | |

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| **4** | **POST PROCESSING** | |
| **4.1** | **The processed output** | *Terminal current is used to calculate the tip sample impedance.* |
| **4.2** | **Methodologies** | *FEM (frequency domain vector solution approach yielding directly the needed frequency characteristics)* |
| **4.3** | **Margin Of Error** | *to be discussed in future publications. Depending on truncation error, system size and thresholding for convergence.* |