**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 orlumped 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)orelectric 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** | $\vec{D}=ε\vec{E}$*,* $\vec{B}=μ\vec{H}$*,* $\vec{J}=σ\vec{E}$ |
| **Physical quantities/****descriptors for each MR** | *The values* $\left(μ,ε,σ\right)$ *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*$E=-∇V$$∇∙\left(ε\_{0}ε\_{r}E\right)=ρ\_{v}$$D=ε\_{0}ε\_{r}E$*Surface charge density*$n∙\left(D\_{1}-D\_{2}\right)=ρ\_{s}$*Transport properties*$∇∙J\_{i}=R\_{i}$$J\_{i}=-D\_{i}∇c\_{i}-z\_{i}u\_{m,i}Fc\_{i}∇V$$u\_{m,i}=\frac{D\_{i}}{RT}$*Space charge density coupling*$∇∙D=ρ\_{v}$$ρ\_{v}=F\sum\_{i}^{}z\_{i}c\_{i}$*Electrode surface reaction**Reaction coefficients*$R\_{i}=\frac{V\_{i}i\_{Ioc}}{nF} \sum\_{ox}^{}\left|v\_{ox}\right|Ox+ne^{-} \leftrightarrow \sum\_{red}^{}v\_{red}Red, v\_{red}>0$$\frac{∂c}{∂t}+∇∙\left(-D\_{s}∇c+cu\right)=0$*where* $D\_{s}$ *denotes the diffusivity of the reacting species,* $c$ *is its concentration, and* $u$ *is the velocity.)**Boundary conditions:**Zero charge boundary*$n∙D=0$*Terminal voltage boundary*$V=V\_{0}$*Ground boundary*$V=0$*No Flux boundary*$-n∙J\_{i}=0$*Initial concentration values*$c=(x.x) mol/m^{3}$$ci=(x.x) mol/m^{3}$*Symbols definitions:*Electric field density: $E$(V/m)Current density: $J\_{i}$(A/m2)Electric charge density**:** $ρ$ (C/m3)Electric displacement: ***D*** (C/m2)Electric potential: ***V*** (V)Solvent velocity field: ***u*** (m/s)Ionic mobility: $u\_{m,i}$ (mol.s/kg)Production/consumption rate expression: $R\_{i}$ (mol/m3.s)Concentration of species *i* : $c\_{i}$ (mol/m3)Permittivity: 𝜀 (F/m)Relative permittivity: 𝜀*r*Gas constant: *R* (J/(mol.K))Temperature: *T* (K)Diffusion coefficients: $D\_{i}$ (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* $\left(μ,ε,σ\right)$ *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.* |