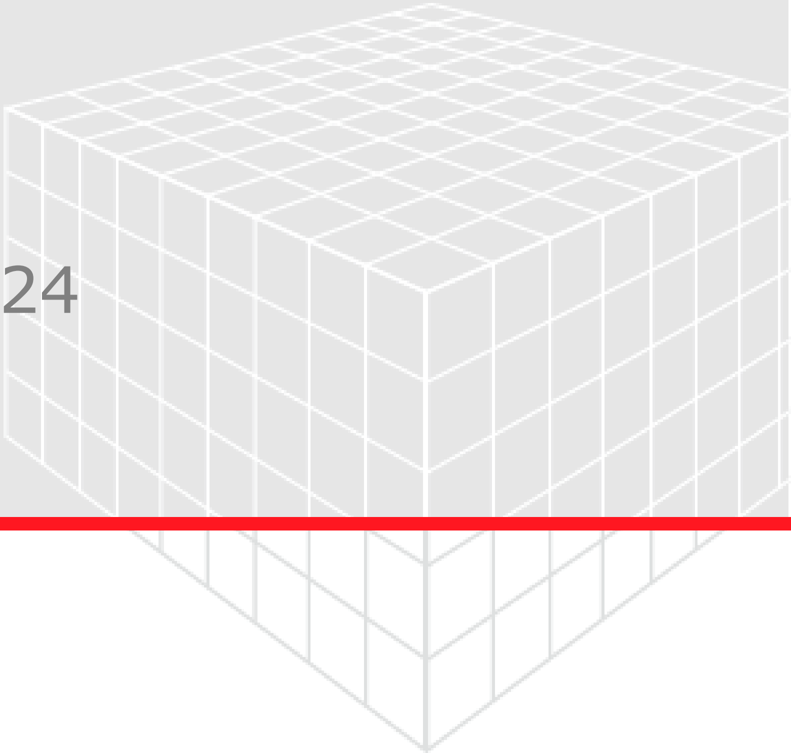
# BatteryDict



## User Guide

## GeoDict release 2024

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GeoDict

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# DIGITAL CHARGING & DISCHARGING OF LI-ION BATTERIES

BatteryDict simulates the performance of secondary lithium-ion batteries during charging and discharging on the micro and meso scale. With the Battery Designer, virtual cells can be created, based on 3D structures of electrode materials with a representative elementary volume (REV). The numerical calculation of the electrochemical processes governing ionic transport in the different material phases and across their interfaces are based on local charge and mass neutrality together with a Butler-Volmer reaction model.

A battery cell in BatteryDict consists of four different components: cathode, anode, separator, and the current collectors. The current collectors are represented as standardized layers, while the separator can be modeled as an effective material. The cathode and anode are individually modeled structures, consisting of multiple active materials, binder, and electrolyte. Up to four different active materials can be handled for each electrode. It is also possible to perform half cell simulations for single electrode structures, without designing the complete half cell first.

It is possible to run a fully resolved simulation on the created microstructure. This very accurate solution provides results that are fully resolved on the micro scale. Three solvers are provided for fully resolved simulations, the LIR solver, the BESTmicro solver (known as BEST:er-micro in GeoDict 2023) and, in GeoDict 2024 still available, the previous version of the BESTmicro solver. This is the version of the BESTmicro solver, that was available already in previous GeoDict versions. It is called BESTmicro (legacy) in GeoDict 2024 and will be removed in future GeoDict versions.

Since GeoDict 2023, BatteryDict additionally allows to run homogenized simulations with the BESTmeso solver that are much faster than the fully resolved simulation. A homogenized model that is created from the given battery structure is used in this case with effective parameters computed in GeoDict.

It is additionally possible to define charging profiles with different stopping criteria. This functionality is especially useful to simulate consecutive charging and discharging processes in the battery.

In GeoDict 2024, the relaxation of a battery cell after charging or discharging can be simulated as additional steps in the charging profiles.

Since GeoDict 2023, the functionality to compute mechanical deformations of a battery cell due to Lithium intercalation, is available as a command in BatteryDict (BatteryDict - Degradation). This add-on to BatteryDict allows to study mechanical stresses and strains due to deformations of the active materials in the battery cell from a previously run charging or discharging simulation.

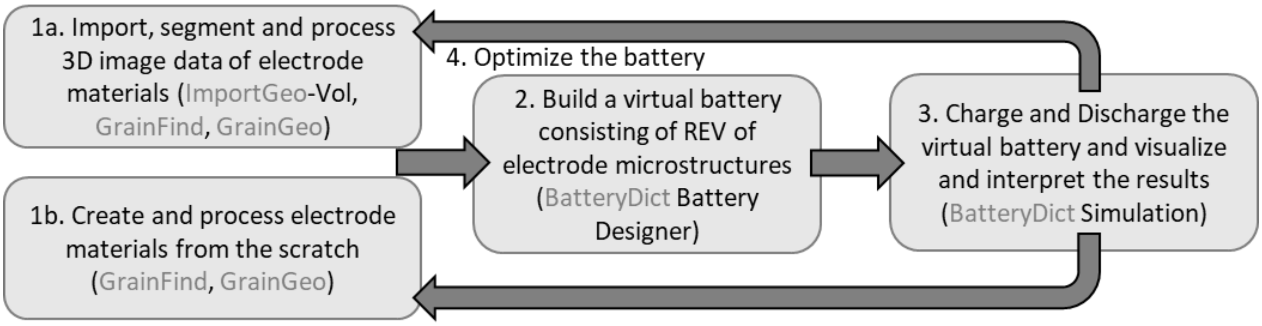
The input data for the electrode models can be either scanned data from µCT or FIB-SEM images of real cathode and anode materials, or realistic structures created in GeoDict. BatteryDict is capable of handling voxel-based structures, with a volume large enough (REV) to simulate the behavior of a real battery electrode. For each active material, the Open-Circuit Potential (OCV) curve can be specified and the characteristic values for ionic and electronic transport in the active materials, electrolyte and binder or binder and carbon black (represented as one CBD-phase), respectively, can be set. The separator and current collectors are represented as homogeneous materials with a specified thickness.

The models used for simulation and the parameters to be defined are explained in more detail in the section Theoretical Basis. In the section BatteryDict Computations, the use of the BatteryDict GUI and the different simulation options are outlined. The results of the simulations and their interpretation are discussed.

The characteristic application for BatteryDict is to simulate and optimize the charging performance of a battery cell, based on realistic electrode microstructures. To analyze or model electrode microstructures, also the use of other GeoDict modules is emphasized. Many properties of the microstructure are vital for the performance of a battery, like porosity, pore size distribution, surface area, tortuosity, thermal conductivity, thermal flux, electric conductivity, electric flux, thermal expansion, permeability, diffusivity, etc.. The GeoDict modules FlowDict, GrainGeo, GrainFind, PoroDict, DiffuDict and ConductoDict can be used to analyze these properties and to obtain detailed information about the microstructure of the electrodes.

With ImportGeo-Vol, 3D image data can be imported and segmented and be further processed with the modules mentioned above. GrainFind and GrainGeo are powerful tools to create Digital Twins based on image data or realistic microstructures from scratch.

Please refer to the other handbooks of the GeoDict User Guide for more information.


1a. Import, segment and process 3D image data of electrode materials (ImportGeo-Vol, GrainFind, GrainGeo)

1b. Create and process electrode materials from the scratch (GrainFind, GrainGeo)

2. Build a virtual battery consisting of REV of electrode microstructures (BatteryDict Battery Designer)

3. Charge and Discharge the virtual battery and visualize and interpret the results (BatteryDict Simulation)

4. Optimize the battery

# THEORETICAL BASIS

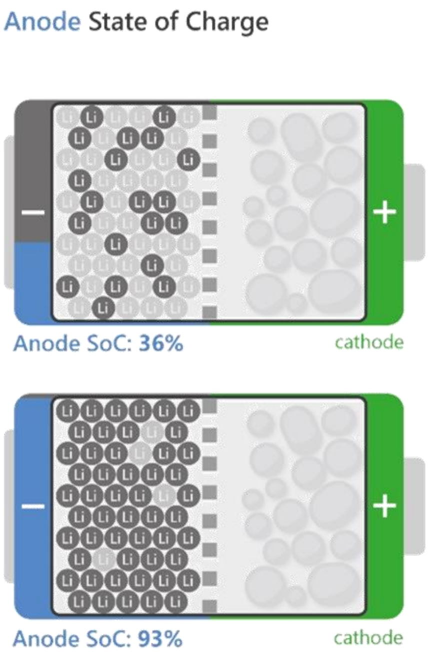
Upon charging a typical secondary Li-ion battery, the $Li^+$ ions initially stored in the active material of the cathode are transported to the anode side. During this process, the cathode active material is oxidized and $Li^+$ ions de-intercalate and diffuse through the electrolyte, towards the anode. This electrochemical process is induced by the applied charging potential, that drives the transport of free electrons through the cathode active material and through the binder with carbon black to the current collector. On the anode side, electrons flow from the current collector through the carbon black and active material. The active material of the anode is reduced by the $Li^+$ intercalation.

During discharging, $Li^+$ ions are transported in a corresponding process to the cathode side, while the electron flow powers the consumer device. The amount of lithium an electrode material can store per volume determines the volumetric energy density. The resulting cell potential is given by the difference between the electrochemical potential of the cathode and the electrochemical potential of the anode.

## STATE OF CHARGE (SOC)

Depending on context, we distinguish different definitions of state of charge:

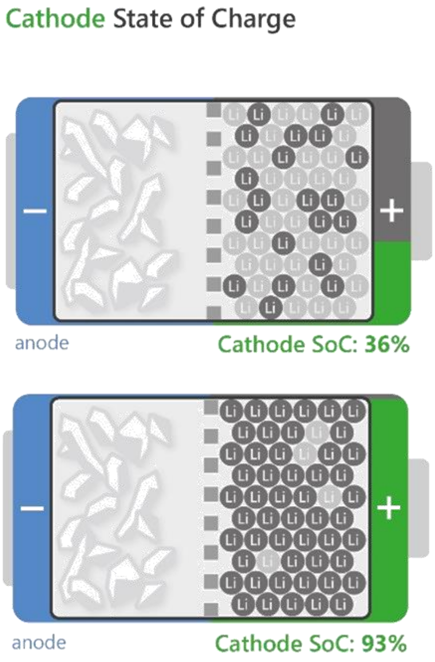
**Anode state of charge**: It measures the momentary Li-ion content of the anode relative to the maximal Li-ion content of the anode. The Li-ion content is the volume integral of the Li-ion concentration.



I.e. for the fully resolved model, for each active material voxel, the SOC is the voxel's Li-ion concentration divided by the voxel's maximum Li-ion concentration (see page 19). The anode SOC is the mean value of the voxel SOCs of all active-material voxels within the anode.

For the homogenized model, the anode SOC is the integral of the active material's SOC over all anode voxels.

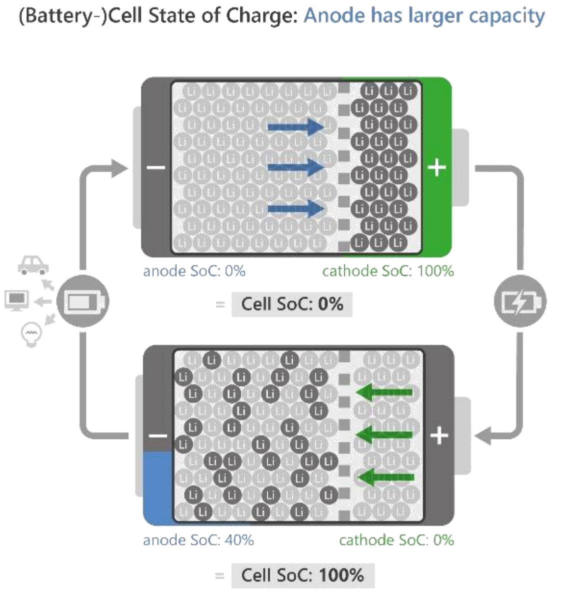
**Cathode state of charge**: It measures the Li-ion content of the cathode relative to the maximal Li-ion content of the cathode. The Li-ion content is the volume integral of the Li-ion concentration.

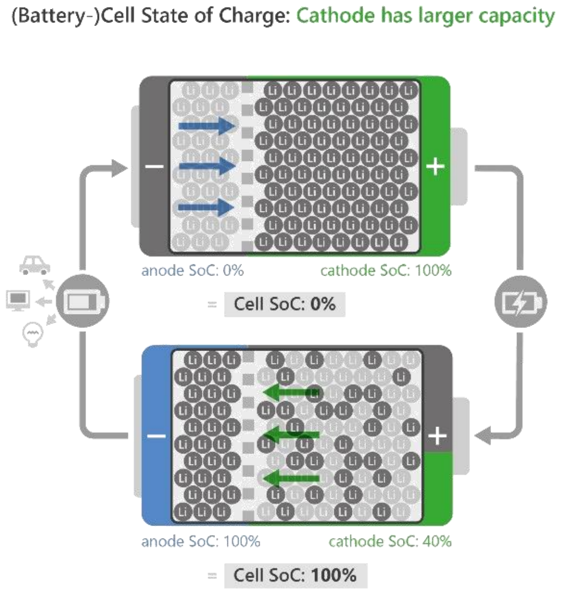


I.e. for the fully resolved model, for each active material voxel, the SOC is the voxel's Li-ion concentration divided by the voxel's maximum Li-ion concentration (see page 19). The cathode SOC is the mean value of the voxel SOCs of all active-material voxels in the cathode.

For the homogenized model, the cathode SOC is the integral of the active material's SOC over all cathode voxels.

**Cell state of charge**: It describes the overall state of charge of the battery cell. In BatteryDict, it is 0% if one of the following conditions is met: the anode is empty, or the cathode is full. It is 100% if one of the following conditions is met: the anode is full or the cathode is empty.





For a half cell simulation the lithium reservoir has always the same capacity as the other electrode. To get a numerically stable solution, the state of charge can be set in GeoDict between 5% and 95%, see page 9.

**Material state of charge:** In BatteryDict's fully resolved model on voxel scale, each voxel has a unique Material ID. In simulations with the homogenized model using the BESTmeso solver, a voxel can represent a porous electrode with electrolyte and solid volume fractions. Lithium ions intercalate or deintercalate from active materials during lithiation or delithiation, therefore the lithium composition $x$ of these materials changes during the (dis)charge process. Each material has a maximum lithium composition and a minimum lithium composition.

For anode materials, the minimum lithium composition usually is the status without intercalated lithium ions (e.g. for graphite). Analogously, the maximal lithium composition is the maximum amount of lithium ions that can reversibly be intercalated into the material.

For cathode materials, the maximum lithium composition is usually the stoichiometric lithium composition (e.g. $x$=1 for $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$). The minimum lithium composition is the lithium composition where the maximal amount of lithium ions is removed reversibly from the structure. Often the minimum lithium composition does not mean that all lithium was taken out of the material because the potential rises to values where the material would get intrinsically unstable while some lithium is still present in the material.

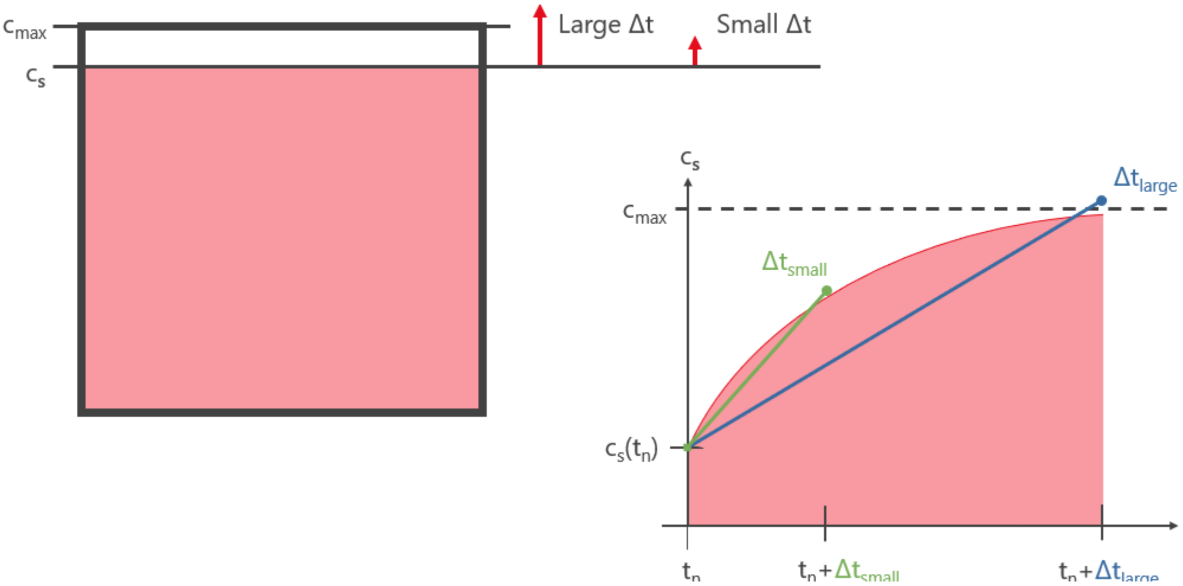
For both anode and cathode materials, BatteryDict works with lithium concentrations instead of lithium compositions on a voxel scale basis. BatteryDict estimates for each active material voxel (in the fully resolved simulation) or each porous electrolyte voxel (in the homogenized model) a certain "material state of charge" by comparing the current lithium concentration $c_s$ in the material to the maximum lithium concentration $c_{max}$ of the material. This material state of charge is defined as

$$SOC_{material} = \frac{c_s}{c_{max}} \cdot 100\%$$

where $c_s$ is the (removable) lithium concentration in the active material and $c_{max}$ is the maximum (removable) lithium concentration of the material. Due to this definition, the material SOC in an active material's voxel will always have a value between 0% (minimum lithium composition) and 100% (maximum lithium composition) and the removable lithium concentration assigned to the voxel is in the range between 0 and $c_{max}$. The active material voxels in fully-resolved model or the porous electrode voxels in homogenized model obtain always material SOC between 0% (i.e., $c_s \geq 0$) and 100% (i.e., $c_s \leq c_{max}$).

When time steps are set too large and a voxel's lithium concentration is close to the maximum lithium concentration, the lithium concentration might exceed the maximum lithium concentration in this time step and prevent convergence; analogously, voxels that are close to a lithium concentration of 0 might result in negative lithium concentrations with large time steps and prevent convergence.

In such circumstances, the solver will usually try to solve for smaller time steps to converge to a meaningful result.



Note that the material SOC will usually not coincide with the lithium composition *x* because the minimum (removable) lithium concentration for cathode materials might be $x>0$ and the maximum (removable) lithium composition for anode materials might be $x<1$.

## FULLY RESOLVED SIMULATION OF CHARGING AND DISCHARGING PROCESS

The main physical principles, describing the charging or discharging simulation in BatteryDict, are conservation of mass for lithium atoms and conservation of charge.

To describe the cell behavior, a fully resolved model is applied that describes on the micrometer scale the relevant transport process. As the length scale considered in BatteryDict is above the scale where positive and negative charges can be resolved, it is sufficient to consider the distribution of lithium concentrations and potentials. The basis of the battery cell model are the conservation equations for lithium ions and electrical charges, respectively:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{N} \tag{1}$$

$$0 = \nabla \cdot \mathbf{j} \tag{2}$$

Here, $c$ is the concentration of lithium ions, $N$ their flux and $j$ the electronic/ionic current density. In the different domains (active material or electrolyte) different constitutive relations apply for the fluxes $\boldsymbol{N}$ and $\boldsymbol{j}$.

### IN ACTIVE MATERIAL

In the active material lithium ions recombine with an electron and are therefore electrically neutral. Hence, they are independent of electrical potentials and undergo only diffusive motion driven by gradients in the lithium concentration. The ion flux is given by

$$\boldsymbol{N}_s = -D_s \nabla c_s \tag{3}$$

where $D_s$ is the diffusion constant of lithium in the solid material.

The diffusion of ions in the active material is therefore described by the equation

$$\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s) \tag{4}$$

In the active material domain, the electrical current is carried by electrons. Therefore, the electronic current density is simply given by Ohm's law

$$\boldsymbol{j}_s = -\kappa_s \nabla \varphi_s \tag{5}$$

Where $\kappa_s$ is the electronic conductivity and $\varphi_s$ the electrical potential. I.e.

$$0 = \nabla \cdot \boldsymbol{j}_s = -\nabla \cdot (\kappa_s \nabla \varphi_s) \quad . \tag{6}$$

### IN THE ELECTROLYTE

In the electrolyte, the flow of charged species (lithium and counter ions) are responsible for the electrical current. Under the assumption of electroneutrality it is sufficient to consider only the transport of lithium ions. Since they are charged, their motion is influenced by two driving forces, the differences in the ion concentration and in the potentials, such that the ionic current density is given by

$$\boldsymbol{j}_e = -\kappa_e \nabla \varphi_e + \kappa_e (1 - t_+) \frac{RT}{F} \nabla \log c_e \tag{7}$$

where $\kappa_e$ is the ionic conductivity and $t_+$ the transference number which (in the absence of concentration gradients) describes the fraction of current carried by the positive lithium ions. *R* is here the universal gas constant, *T* the temperature and *F* Faraday's constant.

To simplify the complexity, this equation assumes a constant activity of lithium ions such that the activity does not appear in the model. Additionally, we note, that the second term sometimes can be found in the literature with an additional factor of 2. This needs to be taken into account consistently in the determination of the transference number.

The charge conservation and electroneutrality equation in the electrolyte is therefore

$$0 = \nabla \cdot \boldsymbol{j}_e = -\nabla \cdot (\kappa_e \nabla \varphi_e) + \nabla \cdot \kappa_e \left( (1 - t_+) \frac{RT}{F} \nabla \log c_e \right). \tag{8}$$

Similar as the current density, also the ion flux depends on concentration and potential gradients. With the ionic diffusion constant $D_e$ the flux in the electrolyte can be formulated as

$$\boldsymbol{N}_e = -D_s \nabla c_e + \frac{t_+ \boldsymbol{j}_e}{F} \tag{9}$$

This leads to the diffusion an migration equation in the electrolyte

$$\frac{\partial c_e}{\partial t} = \nabla \cdot (D_e \nabla c_e) - \nabla \cdot \frac{t_+ \boldsymbol{j}_e}{F}. \tag{10}$$

Further explanation about the theoretical background for the ion transport in the electrolyte can be found in [1].

## IN THE CARBON BINDER DOMAIN (CBD-PHASE)

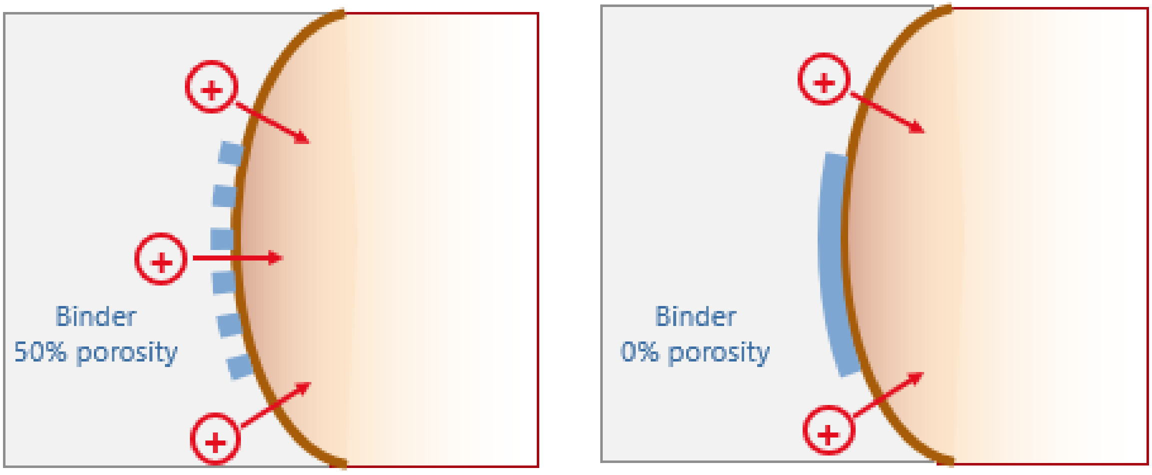
The Carbon Binder Domain (CBD Phase) is represented by respective voxels in the battery structure. The CBD phase can either be simulated as a non-porous material or as a porous material with non-resolved micropores (see page 52). In the GeoDict Material Database, the material of "PVDF Binder and Carbon Black" is shipped as an effective material representing the CBD properties.

For non-porous binder, the CBD phase is a pure electron conductor. So, only Ohm's law is solved (see equation (6) above for the active material). At interfaces to active materials, electrons can be transferred from CBD phase to active material and vice versa.

For porous binder, there is a solid fraction of the CBD phase and a pore fraction of the CBD phase. The solid fraction of the CBD phase conducts electrons and Ohm's law is solved considering the effective electronic conductivity of the porous binder. The pore phase of the CBD phase is filled with electrolyte and conducts lithium ions. For this fraction, the equations for the electrolyte as stated above (diffusion and migration equation (10) and charge conversation and electroneutrality equation (8)) are solved.

For the interface of non-porous binder and active material, a (de)intercalation of lithium ions is not possible. For the interface of porous binder and active material, a (de)intercalation of lithium ions to/from the pore fraction of the porous binder that is filled with electrolyte is possible. BatteryDict considers that the interfacial area of active material to porous binder is only partly available for lithium intercalation.

See the sketch below. The ion exchange is calculated with the Butler-Volmer equation. See equation (11) in the next section.



## INTERFACE BETWEEN ELECTROLYTE AND ACTIVE MATERIAL

On the interface between electrolyte and active material lithium ions move from the electrolyte into the active material on intercalation or vice versa on deintercalation. This flux of ions is continuous across the interface and its magnitude is given by the Butler-Volmer current density $i_{se}$ such that the interface conditions for the fluxes and current densities are given by

$$\hat{n} \cdot \boldsymbol{N}_e = \hat{n} \cdot \boldsymbol{N}_s = i_{se}/F$$

$$\hat{n} \cdot \boldsymbol{j}_e = \hat{n} \cdot \boldsymbol{j}_s = i_{se}$$

here, $\hat{n}$ is the interface normal pointing from solid into electrolyte. Hence, a positive $i_{se}$ corresponds to deintercalation while a negative sign indicates an intercalation reaction. The Butler-Volmer current density depends on concentrations and potentials on both sides of the interface and is given by

$$i_{se} = 2k_{BV}\sqrt{c_s c_e (c_{max} - c_s)} \sinh\left[(\varphi_s - \varphi_e - U_0(c_s))\frac{F}{2RT}\right]. \tag{11}$$

Here, $k_{BV}$ is the Butler-Volmer rate constant and $U_0$ the open-circuit potential of the active material versus lithium.

For Li-ion concentration $c_s = 0$ or $c_s = c_{max}$, the square root $\sqrt{c_s c_e (c_{max} - c_s)}$ in the Butler-Volmer interface current density gets 0, which can lead to numerical solver problems. As stated on page 5, the SOC is related to the Li-ion concentration in the active materials. Therefore, the range of the cell and electrode state of charge can be set between 5% and 95% only in the Charge Battery and the Charge Electrode dialog. A real battery in experimental conditions usually is set to operate in a certain voltage window (compare also the different stopping criteria, see page 15) to avoid permanent damage of the cell. The relevant voltage window usually is in a SOC range smaller than the range between 5% and 95% SOC and therefore can be fully covered in the simulation.

Furthermore, during the intercalation of Li-ions from the electrolyte into the active material, these Li-ions attain one electron per ion and become neutral in charge. During the de-intercalation of Li from the active material into the electrolyte, every Li atom loses one electron and becomes a positively charged Li-ion.

Hence, in the solid material, the charge transport is performed solely by electrons, whereas in the electrolyte, the charge transport is performed solely by ions.

## INTERFACE BETWEEN ELECTROLYTE AND LITHIUM RESERVOIR

For the simulation of a single electrode, the other electrode is modelled as a never-ending lithium reservoir, not limiting the battery performance. Therefore, there exist no $c_s$ and $c_{max}$ and the Butler-Volmer interface condition (equation (11)) simplifies to

$$i_{se} = 2k_{BV,Li}\sqrt{c_e}\sinh\left[(\varphi_s - \varphi_e - U_0)\frac{F}{2RT}\right].$$

The build-in default value for the Bulter-Volmer rate constant of a lithium reservoir is $k_{BV,Li} = 20\frac{A}{(m\cdot mol)^{0.5}}$, based on an assumed exchange current density between the lithium reservoir and the electrolyte of 64 mA/cm² at an electrolyte concentration of 1000 mol/m³ [11].

Note, that due to the different equation for Butler-Volmer interface condition for the interface between electrolyte and lithium reservoir, the unit of Bulter-Volmer rate constant for a lithium reservoir, $k_{BV,Li}$, is $A/(m\cdot mol)^{1/2}$ in contrast to the unit of $k_{BV}$ for active materials that is $A\cdot m^{5/2}\,/mol^{3/2}$.

## INTERFACE BETWEEN TWO ACTIVE MATERIALS

At interfaces between active material grains, exchange of Li ions is possible only if both grains are modelled with the same material ID in GeoDict. In case of different material IDs, no exchange of Li ions is possible between the grains. Especially, if different grains of the same active material are assigned to separate Material IDs in the GeoDict structure, no ion exchange happens between the IDs.

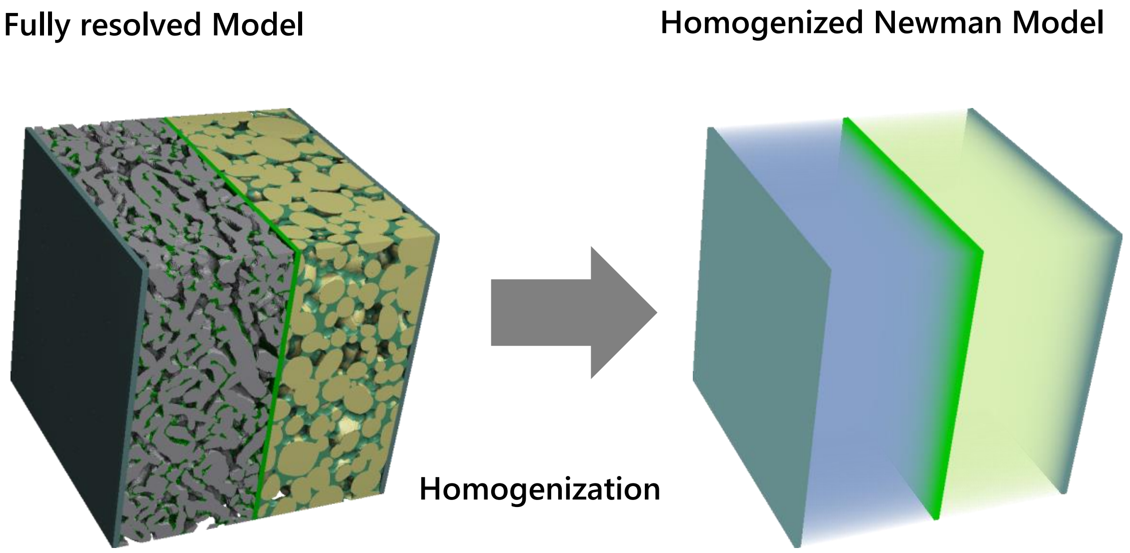
## INTERFACE BETWEEN ACTIVE MATERIALS AND SEPARATOR

In case the separator is modelled as non-porous material (see page 51), it is considered as filled with electrolyte throughout the simulation and the interface is modelled in the same way as the interface between electrolyte and active materials (see page 9) or the interface between electrolyte and lithium reservoir (see above).

Also, in the case of a porous separator with effective properties (see page 51), it is always assumed that the direct interface between separator and active material is completely filled with some electrolyte. The whole interface is therefore described by the equations for interaction between electrolyte and active material (see page 9). The same is valid for the interface between separator and a lithium reservoir.

## HOMOGENIZED SIMULATION OF CHARGING AND DISCHARGING PROCESS

Fully resolved charging and discharging simulations are based on the voxel geometry and thus fully resolve the micro-structure of the battery. But basically, the charge transport in a battery is one-dimensional. Therefore, BatteryDict also provides a pseudo-2D Newman model simulation with the BESTmeso solver. Although it does not fully resolve the structures within the battery cell, it can provide an approximation for the charging-curve and takes much shorter computation time.



In this model, BatteryDict first calculates input parameters for the homogenized simulation, such as ionic diffusivity and electrical conductivities, see page 13. These effective parameters depend both on the geometry of the structure and on the material properties of the fully resolved model. With these parameters, the homogenized simulation is able to consider the different characteristics of anode and cathode.

In the next step, the battery structure is then recomposed of representative effective voxels. These voxels are arranged in 1D in the x-direction. Each voxel in the 1D model is now not completely filled with active material, electrolyte or binder, but consists of a mixture of the different materials. The voxel therefore has both active material and electrolyte properties. Ionic and electronic current are computed in this 1D model in charging direction (currently x-direction) and are linked by a Butler-Volmer exchange current.

Each of the 1D voxels contains a sphere-shaped representative active particle for every active material. The effective radius of these spheres is calculated analyzing the fully resolved microstructure and gives a second degree of freedom. This has no spatial dimension and is thus called "pseudo-dimension". Therefore, the method is called pseudo-2D. With the representative active material particles, it is possible to simulate diffusion of Lithium inside the active material, even if only 1D representative effective voxels are used for the simulation. This is necessary to be able to compute the overpotentials during the charging or discharging simulation. These overpotentials depend on the Lithium concentration at the active materials surface.

The effective parameters are calculated separately for anode and cathode and assigned to the anode and cathode voxels respectively. The concentrations and potentials computed during the charging or discharging simulation however can be different for each voxel.

## HOMOGENIZED MODEL EQUATIONS

In the homogenized model, each voxel consists of a mixture of active material and electrolyte. Therefore, the system of partial differential equations solved by the BESTmeso solver does not consist of separate equations for active material, the electrolyte and the interface between them as in the fully resolved model.

The equations of the fully resolved model for diffusion and migration as well as for charge conservation and electroneutrality of the electrolyte (equations (10) and (8)) and Ohm's law for the active materials (equation (6)) are therefore supplemented by additional source terms. These source terms account for the Butler-Volmer current from electrolyte to active material and vice versa through the (no longer resolved) interface between these materials. The 1D movement of Lithium ions and electrons is described by the following three equations:

$$\frac{\partial(\varepsilon_e c_e)}{\partial_t} = \nabla\cdot\left(D_{eff,e}\nabla c_e\right) - \nabla\cdot\frac{t_+ j_e}{F} + \nabla\cdot\frac{j_e}{F} \tag{12}$$

$$\nabla j_e = -\nabla\cdot\left(\kappa_{eff,e}\nabla\varphi_e\right) + \nabla\left[\kappa_{eff,e}(1-t_+)\frac{RT}{F}\nabla\log c_e\right] = \sum_{p\epsilon P} a_p i_{BV,p} \tag{13}$$

$$\nabla j_s = -\nabla\cdot\kappa_{eff,s}\nabla\varphi_s = -\sum_{p\epsilon P} a_p i_{BV,p} \tag{14}$$

The equation of diffusion in the active materials transforms to a radial diffusion on the representative active particle scale:

$$\text{For all } p \in P\text{:}\ \frac{\partial c_{s,p}}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{N}_{s,p} = 0 \tag{15}$$

$$\text{and } \boldsymbol{N}_{s,p}\cdot\boldsymbol{n}|_{r=R_p} = F^{-1} i_{BV,p} \tag{16}$$

$$\text{with the flux } \boldsymbol{N}_{s,p} = -D_{s,p}\nabla c_{s,p}. \tag{17}$$

Finally, the Butler-Volmer interface condition depends now on the overpotential at the boundary of the spherical particles.

$$i_{BV,p} = 2\cdot k_{BV}\sqrt{c_{s,p}\cdot c_e\cdot\left(c_{s,p,max} - c_{s,p}\right)}\cdot\sinh\left(\left(\varphi_s - \varphi_e - U_{0,p}\left(c_{s,p}\right)\right)\cdot\frac{F}{2RT}\right) \tag{18}$$

In the fully resolved model, the interface is located between active material and electrolyte voxels. In contrast to this, the interface in the homogenized model is within the 1D voxels and not resolved in the structure.

Parameters, appearing in the equations above are:

| **Electrolyte** | |
|---|---|
| $\varepsilon_e$ | Volume fraction of electrolyte in the electrode |
| $D_{eff,e}$ | Effective ionic diffusivity of electrolyte |
| $t_+$ | Transference number |
| $\kappa_{eff,e}$ | Effective ionic conductivity |
| **Active Materials and Binder** | |
| $\kappa_{eff,s}$ | Effective electric conductivity of active materials and binder |
| **Active Materials** | |

| | |
|---|---|
| $P$ | Number of active materials |
| $D_{s,p}$ | Ionic diffusivity of active material *p* |
| $R_p$ | Effective radius of spherical particle of active material *p* |
| $a_p$ | Specific surface area between electrolyte and active material *p* |
| **Representative active material particle** | |
| $c_e$ | Lithium concentration in electrolyte |
| $c_{s,p}$ | Lithium concentration in active material *p* |
| $c_{s,p,max}$ | Maximum Lithium concentration in active material *p* |
| $\varphi_e$ | Electric potential in electrolyte |
| $\varphi_{s,p}$ | Electric potential in active material *p* |
| **Constants** | |
| $F$ | Faraday number |
| $R$ | Gas constant |
| $T$ | Absolute temperature |

## COMPUTATION OF EFFECTIVE PROPERTIES FROM THE MICRO MODEL

The computation of effective properties in the homogenized model precedes charging or discharging simulations, which are run with **BESTmeso** solver. For a full battery simulation, effective parameters for each electrode are calculated separately.

The computed effective properties can be found in the **Result Map** of charging or discharging simulation under **FoundMesoParameters** and are displayed in the Results Report, see page 69. In the case of an electrode simulation, calculated effective parameters are always listed in **Cathode** tab.

The following effective properties are computed:

For **electrolyte**:

- $D_{eff,e}$ - effective ionic diffusivity
- $\kappa_{eff,e}$ - effective ionic conductivity

Both properties are computed for the x-direction of the electrode, using algorithms of ConductoDict with EJ solver, assuming symmetric boundary conditions of the structure and taking into account the (non-zero) electrolyte diffusivity and conductivity respectively. The diffusivity or conductivity constants for all active materials are set to zero. In case of porous binder, effective ionic diffusivity and conductivity are used, for non-porous binder both constants are also set to zero.

For **active materials and binder**:

- $\kappa_{eff,s}$ - effective electronic conductivity

The parameter is computed using the same setting as for electrolyte (ConductoDict algorithms with EJ solver, computation in X-direction of the electrode, symmetric boundary conditions). In this case, the conductivity of electrolyte is set to zero, while for all active materials and binder their electronic conductivity is considered.

For **active materials**:

- $R_p$ - effective radius of representative spherical particle of active material *p*
- $a_p$ - specific surface area between electrolyte and active material *p*

The computation of effective radius is similar to the algorithm Estimate Grain Diameters in the GrainFind module. The effective radius for each active material is found as the average radius of all particles of this active material. All particles are considered as spheres in this estimation.

The specific surface area is calculated as voxelized area between electrolyte and connected voxels for each active material. The voxel connectivity is checked according to the algorithm, which is explained in **Analyze Battery** (see page 40) for the structure with symmetric tangential boundary conditions.

For **separator**:

In case of porous separator, the effective values for ionic conductivity and ionic diffusivity and the porosity are used in the same way as for fully resolved simulations (see page 51).

## BOUNDARY CONDITIONS AT THE CURRENT COLLECTORS

A battery can be operated in two modes, either by prescribing the current or the voltage.

In the first case, the cell potential is a simulation result and in the second case, it is a time-dependent current that is computed. In a current-controlled simulation, the current can be specified in three different ways: Prescribing the electronic current directly (in A), the current density (in A/m²), or the C-rate. Using the C-rate is useful since it allows an intuitive understanding of the load that is applied on the cell without the need to know the cell capacity. Note that the same C-rate might correspond to different currents for different geometries with different capacity! Similarly, the same current density might correspond to a different current if the cross section of the cell changes. So be aware of this relation when comparing different simulation cases.

Battery charging and discharging with constant potential can be simulated since GeoDict 2022. In case of constant potential, the time-dependent current, charge rate, etc. are not constant anymore and can be analyzed for the charging simulation in the GeoDict Result Viewer.

Additionally, since GeoDict 2022, it is possible to define a charging profile. This allows to simulate the charging or discharging with different boundary conditions at the current collectors one after the other.

In GeoDict 2024, relaxation of the battery or electrode after charging and discharging can be simulated as separate step in the charging profile, see page 57.

## STOPPING CRITERIA FOR CHARGING SIMULATIONS

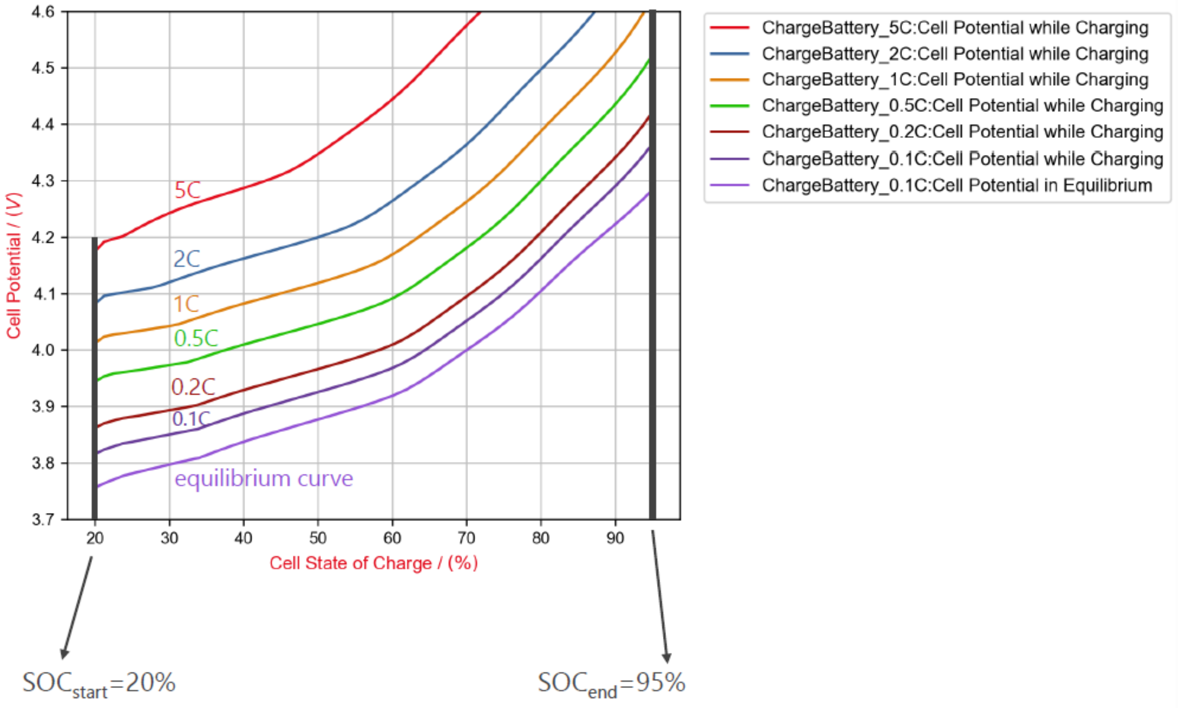
Since GeoDict 2022, different stopping criteria for a charging simulation can be defined. Choosing a final state-of-charge for the whole battery or for both electrodes, is the stopping criterion that was available already in previous BatteryDict releases.

If a charging profile is defined, additionally a reached cell potential, charge rate, current density, or current can be defined as stopping criterion. Setting the stopping criterion in the GeoDict GUI is explained on page 55 and 57.

In the following, as an example, the difference between the stopping criteria final state-of-charge and final cell potential is shown for simulations with constant charge rate.

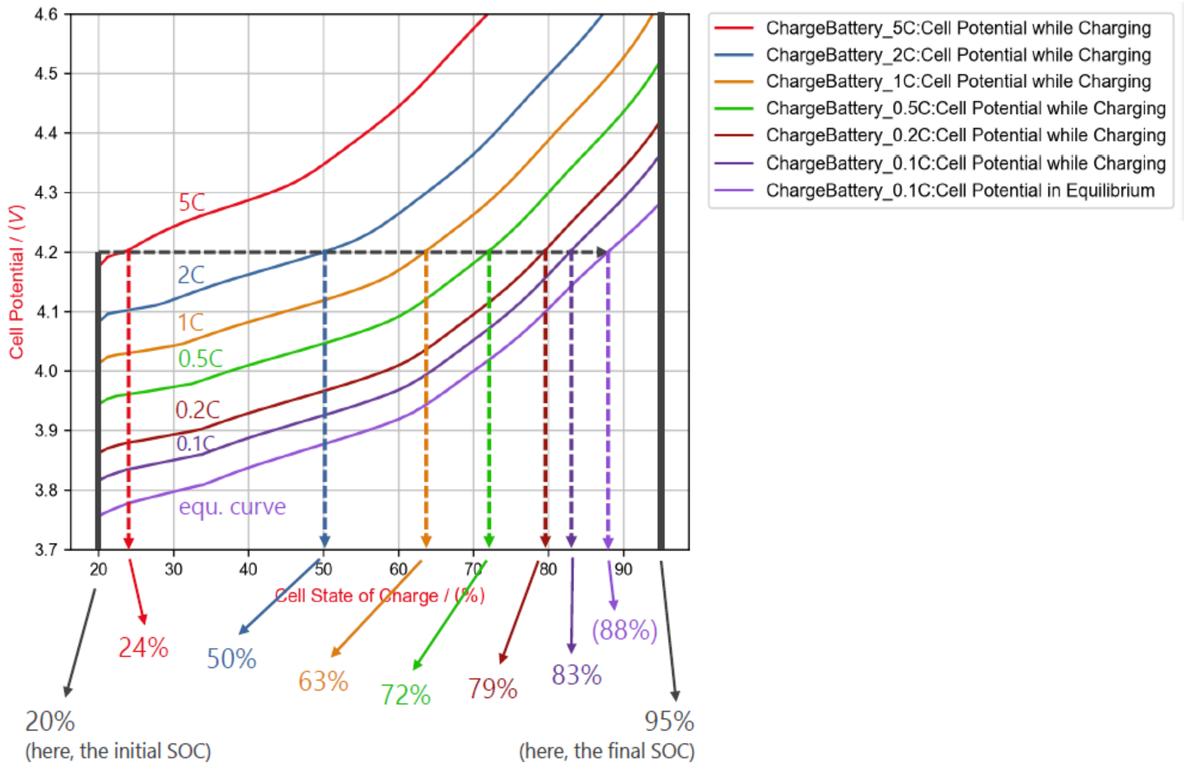
For simulations with constant charge rate, the time evolution of the cell potential depends on the charge rate selected. The higher the charge rate, the larger the deviation of the cell potential curve from the equilibrium charge curve, since the overpotentials get larger for higher charge rates (see below on page 16).

In the following figure, a charging simulation from state-of-charge 20% till 95% is shown for different charge rates using an example structure.



For the stopping criterion *final state-of-charge*, the computation always runs until the final state-of-charge is reached, here 95%. Depending on the charge rate, the cell potential reached for this final state-of-charge, is very different. Especially for high charge rates, it might not be possible to reach this stopping criterion at all, or the voltages reached may be unphysically high.

On the other hand, if a final potential – here 4.2 V - is defined as stopping criterion, the state-of-charge reached at the end of the simulation will vary depending on the charge rate, while the cell potential remains the same. In the following figure, the reached state-of-charge at the end of the simulation is indicated for simulations with different charge rates. As a result of the varying state-of-charge at the end of the simulation, the capacitance of the battery differs depending on the charge rates.



## OVERPOTENTIALS IN BATTERY CHARGING SIMULATIONS

Since GeoDict 2022, overpotentials of the (dis-)charging process, can be visualized for a finished simulation in the Result Viewer (see page 74).

Overpotentials are the reason why the real charging curve deviates from the equilibrium potential curve in the charging process. The equilibrium potential curve is the cell potential in equilibrium for each state-of-charge.

To charge the battery with an increased charge rate, an additional potential, i.e. additional energy, is necessary due to the inner resistivities of the battery cell. In the same way, while discharging, these resistivities are responsible for the potential difference compared to the equilibrium potential. Less energy can be taken out of the battery which produces heat instead, compared to the equilibrium situation. These differences are characterized by the overpotentials. The larger the charge rate, the higher the overpotentials get.

In GeoDict, three sources of overpotential are considered:

- **Kinetic overpotentials** define the additional potential necessary for bringing the lithium ions from the electrolyte into the active materials of cathode or anode. They are computed from the Butler-Volmer expression.

- **Diffusive overpotentials** result from the distribution of lithium ions in the active materials of an electrode that is not uniform during charging or discharging. E.g., during charging, lithium ions enter the anode active materials at the surface of the grains and diffuse into the grains. The slower this diffusion in the active materials, the higher the difference in the distribution of lithium and the higher the additional potential necessary for keeping a desired charge rate. If the simulation is started from an equilibrium situation, these concentration differences in the active materials increase during the simulation. The diffusive overpotentials can be time-dependent and might get higher the longer the charging process is running.

Diffusive overpotentials can even get negative in certain situations. The reason is that to compute the overpotential, the local surface concentration is compared to the concentration over the whole electrode. Two effects are therefore relevant for the diffusive overpotential, diffusion in one grain and the possible inhomogeneity in the loading of particles in the electrode.

A diffusive overpotential can also build up in the electrolyte due to concentration gradients that can form during charging in the electrolyte. Please note that overpotential due to concentration gradients in the separator is accounted to the diffusive overpotential of the electrolyte.

- **Resistive overpotentials** define the additional potential necessary to overcome bulk electrical resistivities in the charging process. These resistivities depend on the electrical bulk conductivities of the different battery materials. For electrodes, it relates from the electronic conductivities of the binder and active materials in this electrode, as well as the corresponding current collector. For the electrolyte, it relates to the ionic conductivity of the electrolyte and separator.

In the Result Viewer of the *.gdr result file, these three kinds of overpotentials are shown separately. Like this, it is possible to analyze for a simulation which process in the battery causes the largest amount of additional potential during charging and is responsible for the largest potential loss during discharging.

## BATTERYDICT: DEGRADATION SIMULATIONS

Since GeoDict 2023, the simulation of one-way battery volumetric changes due to lithium intercalation of active materials is included in the module BatteryDict as an add-on called BatteryDict -Degradation.

After a finished charging or discharging simulation of a battery or a half cell, the mechanical expansion or contraction of the cell as well as the stresses and strains resulting from this deformation can be computed. To this purpose ElastoDict's FeelMath solver is called internally from BatteryDict-Degradation (see the ElastoDict handbook for details of the solver).

The expansion, $\Delta l$, of an active material in each coordinate direction depends on the changes in lithium concentration during charging simulation,

$$\Delta l = (C_{end} - C_{start}) \cdot \alpha \cdot l,$$

with $\alpha$ the concentration expansion coefficient, $C_{start}$ and $C_{end}$ the lithium concentration at the start and end of the (charging) simulation and $l$ the length of the material in the coordinate direction under consideration. It is computed equivalently to the thermal expansion of a material due to temperature change.

Note that the concentration expansion coefficient used in BatteryDict -Degradation is a coefficient for the linear expansion in each coordinate direction. In literature, often an expansion coefficient for volumetric changes due to lithium intercalation, $\alpha_{vol}$ , can be found. To get the coefficient required here, use $\alpha = \sqrt[3]{\alpha_{vol}}$.

## SIMULATION PARAMETERS FOR CHARGING SIMULATIONS

The parameters occurring in the equations of charging simulations are explained in the following:

- **Maximum Lithium Concentration ($c_{max}$)**: Maximum lithium concentration that can be stored to or taken out of the active material. This is not the maximum lithium concentration of the active material itself, but the difference between the minimum and maximum reachable lithium concentration. Usually, the minimum reachable lithium concentration of common active materials used in cathodes is not zero. The reason is that often the last lithium ions cannot be removed or could only be removed with a cell potential that is so high that it could damage the battery. $c_{max}$ can be calculated from the maximum experimentally accessible specific capacity of a material $C_{\text{spec,max}}$ when determining the open circuit voltage potential (see below), the material density $\rho$, and Faraday's constant $F$:

  $$c_{max} = \frac{C_{spec,max} \cdot \rho}{F}$$

  Its unit is $\frac{mol}{m^3}$, i.e. the concentration is provided as amount of accessible lithium ions per volume.

- **Electronic Conductivity**: Measures a material's ability to conduct electrons.

- **Ionic Conductivity**: Measures the electrolyte's ability to conduct ions (such as Li ions). GeoDict can consider the concentration dependence of ionic conductivity constants for electrolyte, see page 50.

- **Ionic Diffusion Constant**: Measures a material's ability to equilibrate differences in concentration. The ionic diffusion constant in active materials is often measured via Galvanostatic Intermittent Titration Technique (GITT), where the reaction of a half cell to a current pulse and the subsequent relaxation is recorded [4]. It can also be measured by Electrochemical Impedance Measurements (EIS) [5]. The ionic diffusion constant of an active material can depend on the material SOC, see page 5. GeoDict can consider the concentration dependence of ionic diffusion constants for electrolyte, see page 50.

- **Butler-Volmer Rate Constant**: This is not a material parameter of one material alone but depends on the active material as well as on the electrolyte. It is necessary to define the interface condition between voxels of active material and those of electrolyte. It characterizes "how easy" ions can be exchanged between active material and electrolyte. Experimentally, it can be determined via the exchange current density.

  First, the derivation of Butler-Volmer Interface Current Density, $i_{se}$, as calculated in BatteryDict is shown. The Butler-Volmer equation found in literature is (see [5])

  $$i_{se} = I_D/S = j_0\left(\exp\left[\frac{\alpha zF}{RT}\eta_D\right] - \exp\left[-\frac{(1-\alpha)zF}{RT}\eta_D\right]\right), \tag{12}$$

with the current $I_D$, the contact area $S$ between electrode's active material(s) and electrolyte, the exchange current density $j_0$, the charge transfer coefficient $\alpha$, the charge number $z$ (which is $z=1$ for a lithium-ion battery), and the overpotential $\eta_D$. Considering $\alpha=½$, the Butler-Volmer equation simplifies to

$$i_{se} = 2j_0 \sinh\left[\frac{F}{2RT}\eta_D\right]. \tag{13}$$

For insertion electrodes, literature provides a relation of the exchange current density to the lithium concentration in the electrolyte and the lithium concentration in the solid with considering the charge transfer coefficient $\alpha$=0.5 [5]

$$j_0 = k_0 F\sqrt{c_s c_e (c_{max} - c_s)} = k_{BV}\sqrt{c_s c_e (c_{max} - c_s)} \qquad (14)$$

where the Butler-Volmer rate constant is defined as $k_{BV} = k_0 \cdot F$ with a particle transfer rate $k_0$ and Faraday's constant $F$. When this relation is inserted into equation (13) above and the overpotential is equal to $\eta_D = (\varphi_s - \varphi_e - U_0)$, the equation describing the Butler-Volmer Interface Current Density $i_{se}$ in BatteryDict is obtained,

$$i_{se} = 2k_{BV}\sqrt{c_s c_e (c_{max} - c_s)}\,\sinh\left[(\varphi_s - \varphi_e - U_0)\frac{F}{2RT}\right]. \qquad (15)$$

To obtain a value of $k_{BV}$ from the measured exchange current densities at different material SOCs (see page 5) of the electrode material, the experimental data for $j_0$(SOC) are fit to a modified equation (14) using $c_s = c_{max} \cdot \frac{SOC}{100\%}$:

$$j_0(SOC) = k_{BV}\sqrt{c_e c_{max}^2 \left(\frac{SOC}{100\%} - \left(\frac{SOC}{100\%}\right)^2\right)}$$

Note that it might be necessary to convert literature data for $j_0$ from a function of lithium composition to a function of SOC as described in (16). The next figure shows the experimental data $j_0$ as a function of SOC for NMC333 and a reference electrolyte (EC/DMC/EMC 1:1:1, salt $LiPF_6$, concentration 1 mol/L) as reported in [6] and [7].

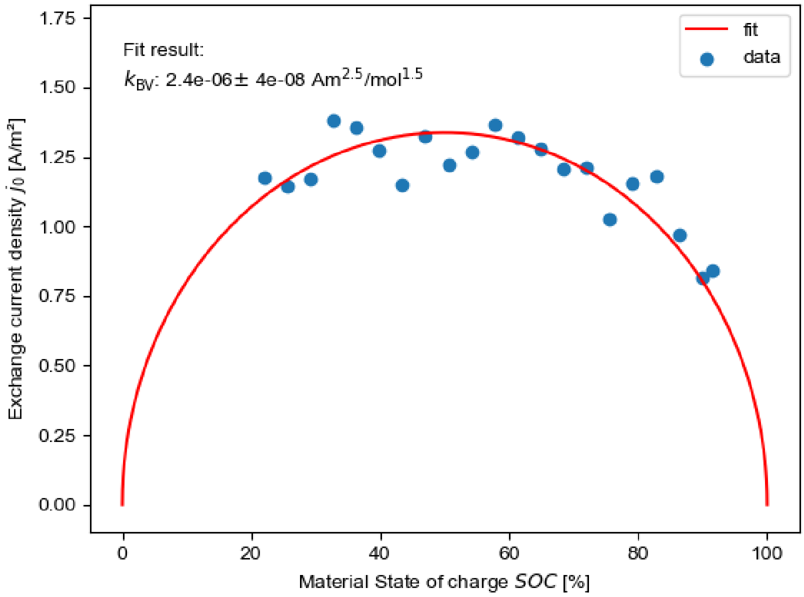


Figure 1: Measured data for $j_0$ of NMC333 at 15°C from the Supplementary Information of [7] as a function of electrode SOC and fit to the data using the above equation. The fit results in $k_{BV}$ = 2.4e-6 $Am^{2.5}/mol^{1.5}$.

- **Open-Circuit Potential (OCV) Function**: The open-circuit potential is directly related to the chemical potential of lithium within the active material.

Experimentally, it is determined by measuring the potential difference between the respective electrode and a lithium counter electrode in equilibrium, i.e. without load applied to the electrode. To this end, either relaxation steps are introduced before measurement at a distinct SOC or a “quasi-OCV” function is measured at very low charging rates, e.g. of C/100 [6]. The open circuit potential is generally path-dependent, i.e., it can vary between the charging or discharging process. This phenomenon is known as OCV hysteresis and is observed when the chemical potential of the electrode varies between lithium intercalation and lithium deintercalation [8]. Additionally, it depends on the charging state of the electrode and is therefore a function of the state of charge (SOC) of the material

$$SOC = \frac{c_s}{c_{max}} \cdot 100\%,$$

see page 5.

In literature, the OCV function is often provided as a function of the specific capacity $C_{\mathrm{spec}}$, e.g. in mAh g$^{-1}$ against the potential vs Li/Li$^{+}$ [9]. The maximum experimentally accessible specific capacity of a material is denoted as $C_{\mathrm{spec,max}}$ and the OCV curve ends at this specific capacity. Figure 2 shows an example from literature for various cathode materials. In this case, the x-axis of the OCV function must be transformed from the specific capacity $C_{\mathrm{spec}}$ to the material SOC by the equation:

$$SOC\left(C_{spec}\right) = \frac{C_{spec}}{C_{spec,max}} \cdot 100\%$$

GeoDict interpolates the OCV curve between the points provided for the OCV function of the material. For the interpolation it is necessary that the OCV function is monotonous, i.e., the OCV must increase with decreasing material SOC.

Sometimes, data in literature are also provided as a function of lithium composition. For instance, for cathode materials the lithium composition $x$ ranges from the maximal lithium composition ($x_{max}$=1 for stoichiometric NMC333 ($Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$)) to the minimally reachable lithium composition $x_{min}$. This minimally reachable lithium composition can be calculated via the maximum experimentally accessible specific capacity $C_{spec,max}$ and the theoretical capacity $C_{spec,theo}$ which is calculated with the equation:

$$C_{spec,theo} = \frac{n_{Li}}{M} F$$

where $n_{Li}$ is the number of lithium atoms per unit cell in the maximally lithiated material, $M$ is the molar mass, and $F$ Faraday’s constant. For cathode materials, the minimum lithium composition is found by comparing $C_{spec,max}$ to $C_{spec,theo}$, for instance for NMC333:

$$x_{min} = 1 - \frac{C_{spec,max}}{C_{spec,theo}} \approx 0.27$$

The material SOC as a function of lithium composition $x$ is then given via linear transformation. E.g. for a cathode material such as NMC333:

$$SOC(x) = \frac{100}{1 - x_{min}}(x - x_{min}) \tag{16}$$

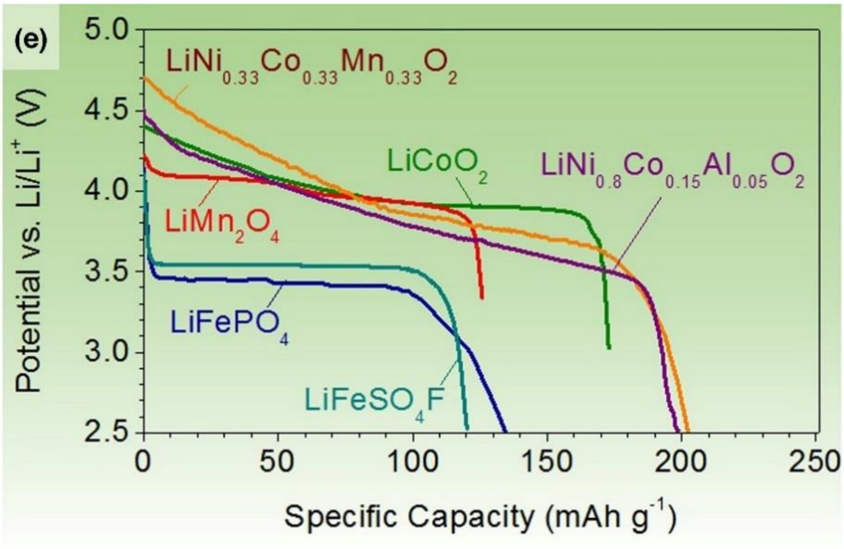


Figure 2: Typical discharge OCV potentials for intercalation cathode materials. Taken from [9].

- **Equilibrium Lithium Concentration**: Concentration of lithium ions in the electrolyte solution. This is the lithium concentration of the electrolyte if it is in thermodynamic equilibrium. As soon as the battery starts charging or discharging, local concentration gradients will build up in the electrolyte.
- **Transference Number**: In the absence of concentration gradients, the transference number measures the fraction of ionic current carried by lithium ions. GeoDict can consider the concentration dependence of transference number for the electrolyte, see page 50.
- **Concentration Expansion Coefficient**: The concentration expansion coefficient is needed to calculate the material expansion upon lithium intercalation using BatteryDict-Degradation. The expansion coefficient is calculated with the equation

$$\alpha = \frac{(1+\Delta V)^{\frac{1}{3}} - 1}{c_{max}}$$

where ΔV is the maximal volume change due to lithium intercalation and $c_{max}$ is the maximum (removable) lithium concentration, [10].

## ADDING CUSTOM ELECTROCHEMICAL MATERIALS: NECESSARY EXPERIMENTAL DATA

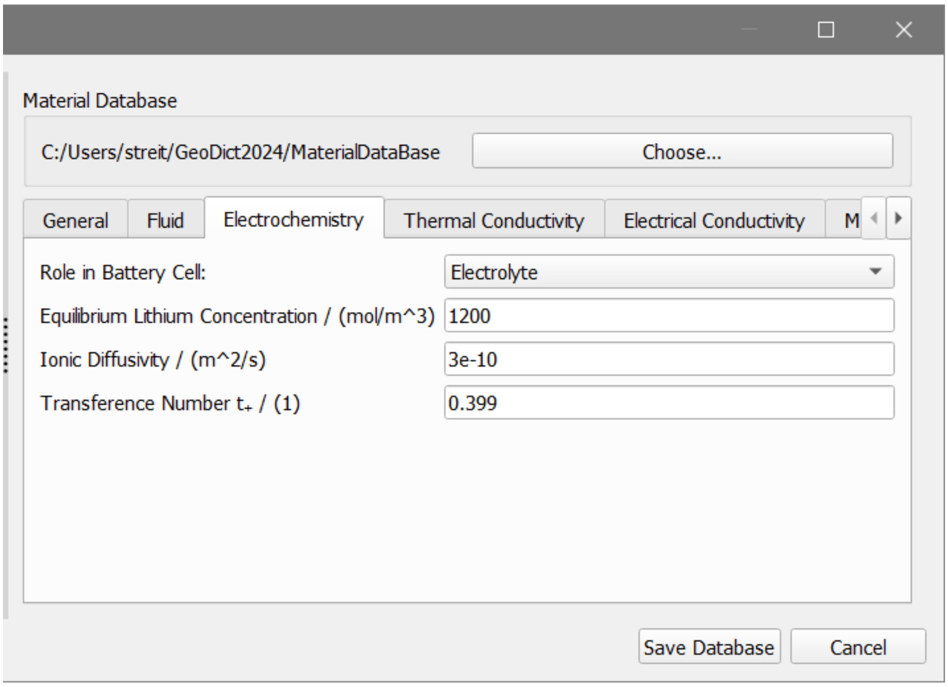
GeoDict provides standard materials in the GeoDict Material Database for electrolyte, active materials, and binder and carbon black. For more information on the Material Database, see the Material Database handbook.

The following material parameters are required to add new materials for electrochemical simulations to the GeoDict Material Database:

### Electrolyte

- Mandatory parameters:
  - Equilibrium lithium concentration
  - Ionic conductivity
  - Ionic diffusion constant
  - Transference number

- For all active materials that should be used together with the new electrolyte, the Butler-Volmer rate constant needs to be defined, see below.



Material Database

C:/Users/streit/GeoDict2024/MaterialDataBase

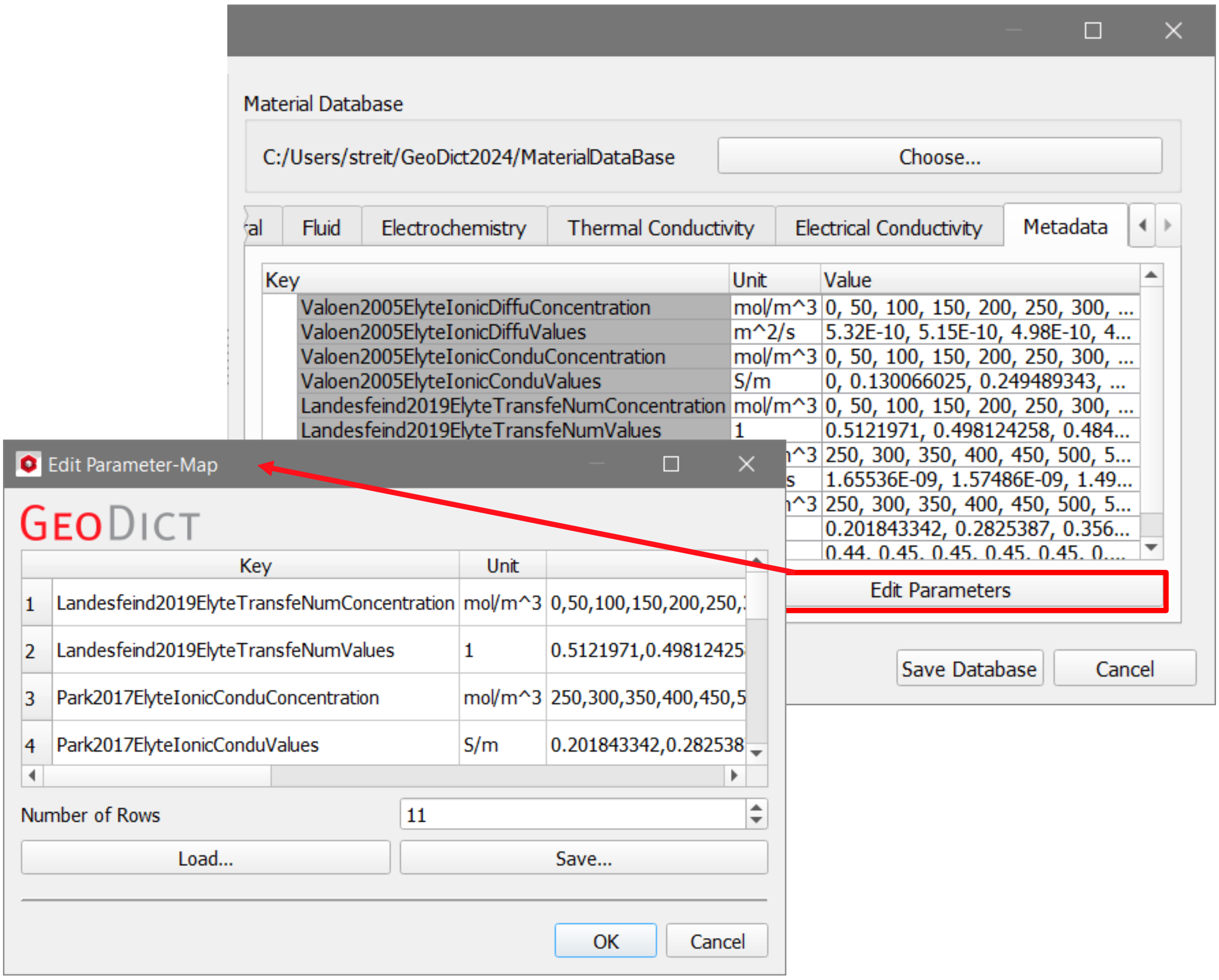
Role in Battery Cell: Electrolyte

Equilibrium Lithium Concentration / (mol/m^3) 1200

Ionic Diffusivity / (m^2/s) 3e-10

Transference Number $t_+$ / (1) 0.399

- Optional parameters: Concentration dependent values for ionic conductivity, ionic diffusion constant, and transference number in electrolyte. Concentration dependent values can be added under the **Metadata** tab, by clicking **Edit Parameters** and entering the values.



Material Database

C:/Users/streit/GeoDict2024/MaterialDataBase

| Key | Unit | Value |
|---|---|---|
| Valoen2005ElyteIonicDiffuConcentration | mol/m^3 | 0, 50, 100, 150, 200, 250, 300, ... |
| Valoen2005ElyteIonicDiffuValues | m^2/s | 5.32E-10, 5.15E-10, 4.98E-10, 4... |
| Valoen2005ElyteIonicConduConcentration | mol/m^3 | 0, 50, 100, 150, 200, 250, 300, ... |
| Valoen2005ElyteIonicConduValues | S/m | 0, 0.130066025, 0.249489343, ... |
| Landesfeind2019ElyteTransfeNumConcentration | mol/m^3 | 0, 50, 100, 150, 200, 250, 300, ... |
| Landesfeind2019ElyteTransfeNumValues | 1 | 0.5121971, 0.498124258, 0.484... |
|  | ^3 | 250, 300, 350, 400, 450, 500, 5... |
|  | s | 1.65536E-09, 1.57486E-09, 1.49... |
|  | ^3 | 250, 300, 350, 400, 450, 500, 5... |
|  |  | 0.201843342, 0.2825387, 0.356... |
|  |  | 0.44, 0.45, 0.45, 0.45, 0.45, 0.... |

Edit Parameter-Map

|  | Key | Unit |  |
|---|---|---|---|
| 1 | Landesfeind2019ElyteTransfeNumConcentration | mol/m^3 | 0,50,100,150,200,250, |
| 2 | Landesfeind2019ElyteTransfeNumValues | 1 | 0.5121971,0.49812425 |
| 3 | Park2017ElyteIonicConduConcentration | mol/m^3 | 250,300,350,400,450,5 |
| 4 | Park2017ElyteIonicConduValues | S/m | 0.201843342,0.282538 |

Number of Rows 11

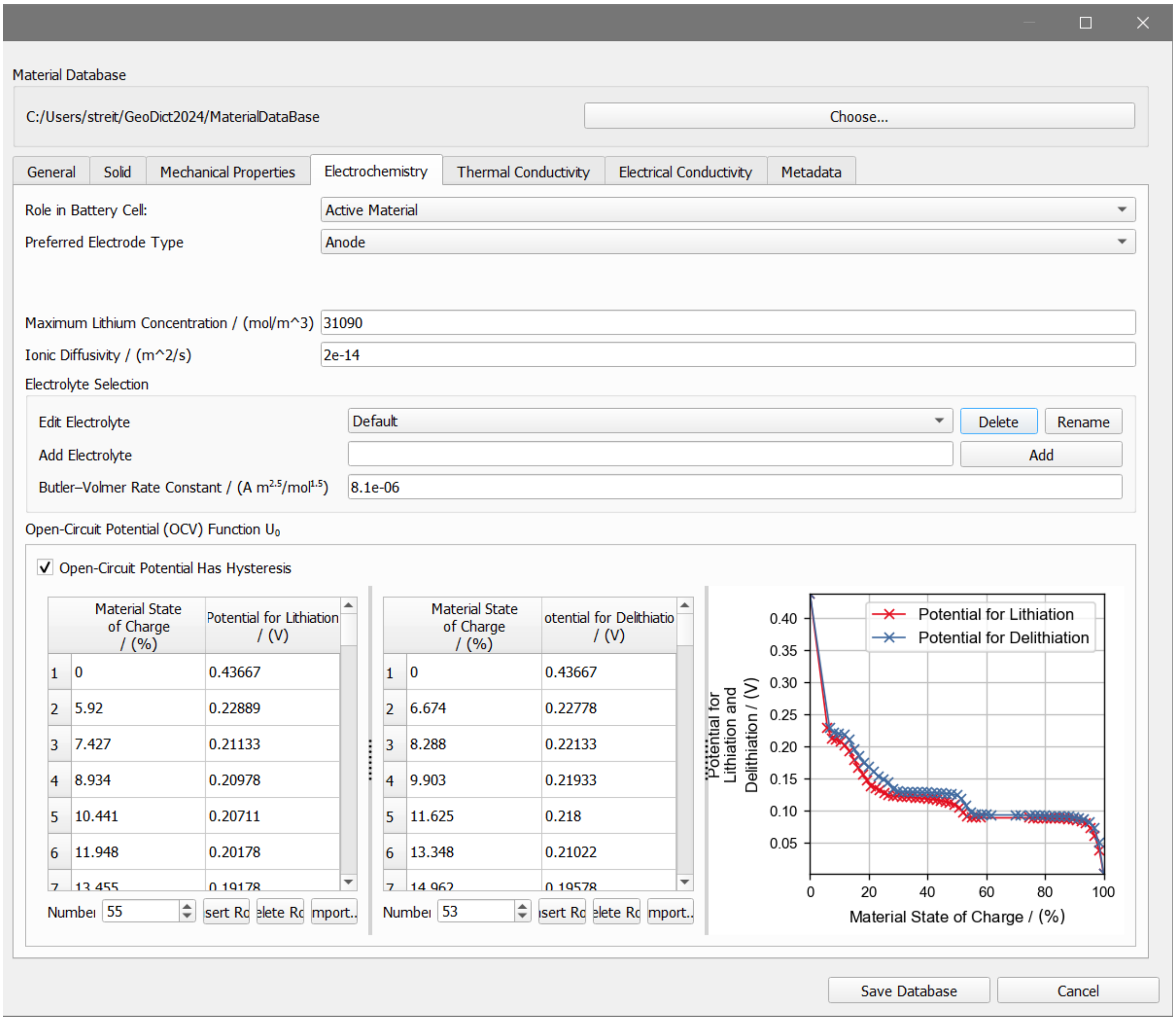
Click **OK** to return to the **Metadata** tab of the Material Database.

Finally, click **Save Database**, to save the new values in your GeoDict Material Database folder.

Copy the values from the Metadata tab for the charging simulations to the **Charge Battery** or **Charge Electrode** dialog, see page 50.

## Active material:

- Mandatory parameters:
  - Maximum lithium concentration
  - Open-circuit potential (OCV) function curve
  - Density
  - Ionic diffusion constant
  - Electrical conductivity
  - Butler-Volmer rate constant. This value depends not only on the active material, but also on the electrolyte. It can be therefore defined for different electrolyte materials.



C:/Users/streit/GeoDict2024/MaterialDataBase

Role in Battery Cell: Active Material

Preferred Electrode Type: Anode

Maximum Lithium Concentration / (mol/m^3): 31090

Ionic Diffusivity / (m^2/s): 2e-14

Electrolyte Selection

Edit Electrolyte: Default

Add Electrolyte:

Butler–Volmer Rate Constant / (A $m^{2.5}/mol^{1.5}$): 8.1e-06

Open-Circuit Potential (OCV) Function $U_0$

☑ Open-Circuit Potential Has Hysteresis

| | Material State of Charge / (%) | Potential for Lithiation / (V) |
|---|---|---|
| 1 | 0 | 0.43667 |
| 2 | 5.92 | 0.22889 |
| 3 | 7.427 | 0.21133 |
| 4 | 8.934 | 0.20978 |
| 5 | 10.441 | 0.20711 |
| 6 | 11.948 | 0.20178 |
| 7 | 13.455 | 0.19178 |

Numbei 55 | sert Rc | elete Rc | mport..

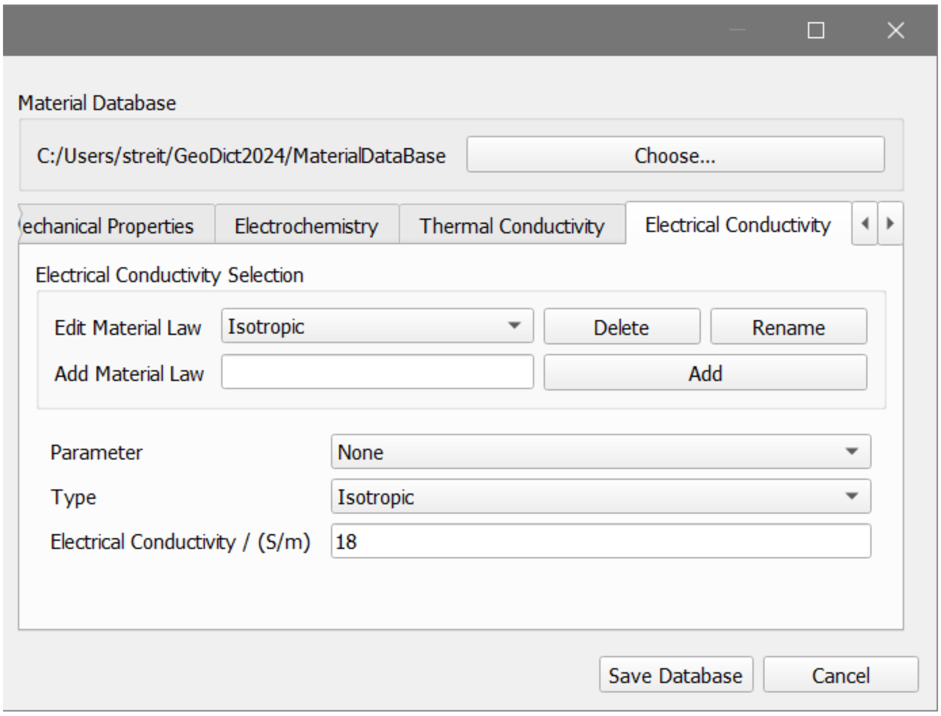
| | Material State of Charge / (%) | otential for Delithiatio / (V) |
|---|---|---|
| 1 | 0 | 0.43667 |
| 2 | 6.674 | 0.22778 |
| 3 | 8.288 | 0.22133 |
| 4 | 9.903 | 0.21933 |
| 5 | 11.625 | 0.218 |
| 6 | 13.348 | 0.21022 |
| 7 | 14.962 | 0.19578 |

Numbei 53 | sert Rc | elete Rc | mport..

- Optional parameters (see below):

  - Lithium concentration expansion coefficient:
    Used for volume expansion during lithiation with BatteryDict-Degradation, measured e.g. by electrochemical dilatometry.
  - Mechanical parameters for computation of mechanical deformations with BatteryDict-Degradation.
  - Concentration dependent diffusivity and electrical conductivity (possible via Expert Setting only, please contact support@math2market.de for details).

### CBD phase (Binder+Carbon Black):



Material Database
C:/Users/streit/GeoDict2024/MaterialDataBase

Electrical Conductivity Selection
Edit Material Law: Isotropic
Add Material Law:

Parameter: None
Type: Isotropic
Electrical Conductivity / (S/m): 18

- Mandatory parameters:
  - Effective electrical conductivity

Note that to determine temperature effects, the material parameters must also be determined at different temperatures.

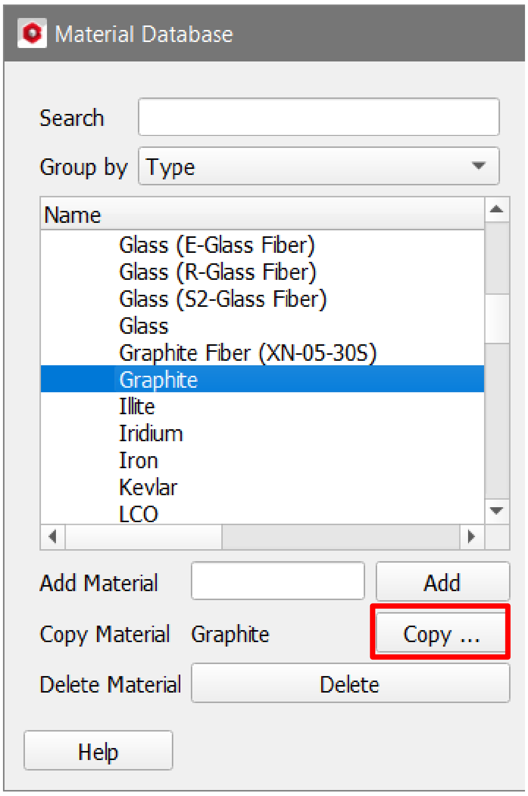
For all materials, save the changes in the Material Database by clicking **Save Database**. The new material can now be used like any of the standard materials delivered with GeoDict.

## ADDING MATERIAL INFORMATION FOR DEGRADATION SIMULATION

To be able to use an active material in a degradation simulation with BatteryDict-Degradation, apart from the mandatory material parameters for a charging simulation (see above), the concentration expansion coefficient and the mechanical parameters need to be defined.

The GeoDict Material Database currently provides the materials Graphite, NMC333, NMC532, NMC622, and Silicone with these parameters.

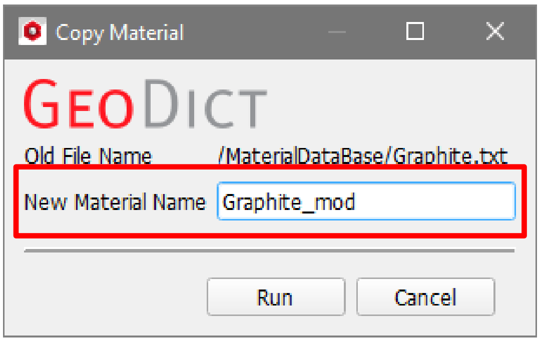
To define the parameters for another material, in the GeoDict Material Database, select the material, e.g. Graphite in the example shown here. To avoid changing the material parameters delivered with GeoDict, first create a Copy of the material. Save it with a new name in the Material Database.



Group by: Type

Name: Glass (E-Glass Fiber), Glass (R-Glass Fiber), Glass (S2-Glass Fiber), Glass, Graphite Fiber (XN-05-30S), Graphite, Illite, Iridium, Iron, Kevlar, LCO

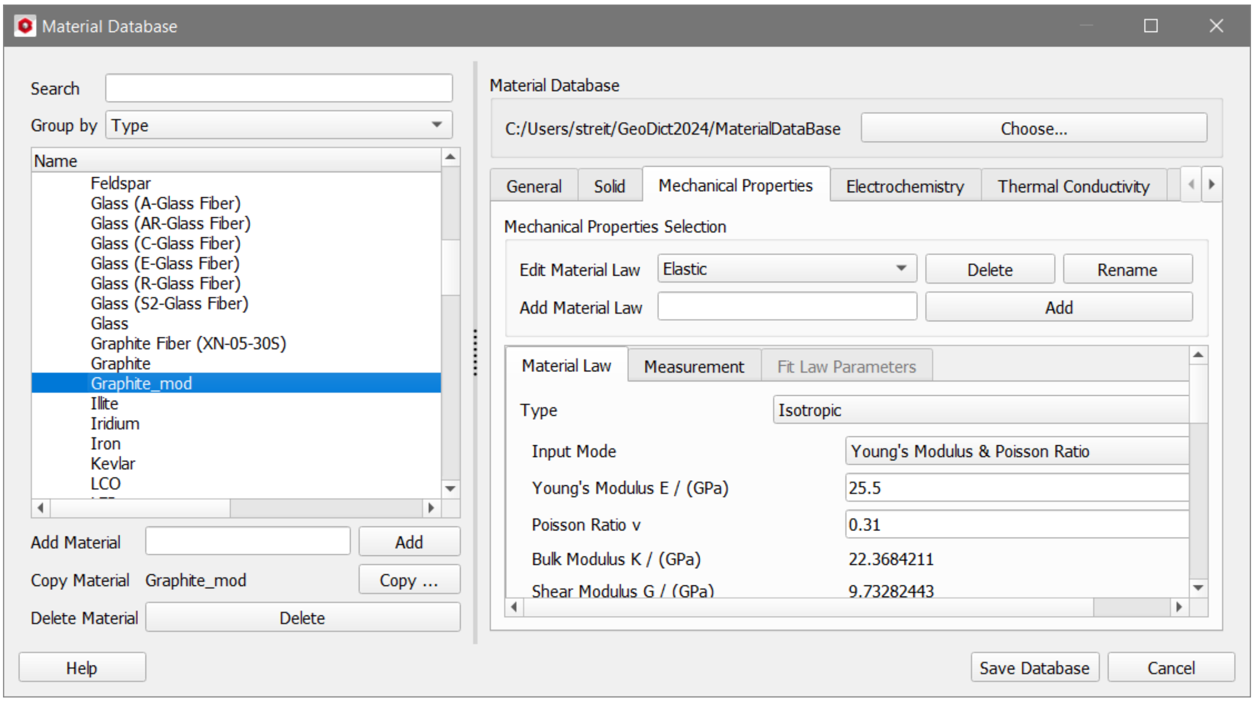
Copy Material: Graphite



Old File Name: /MaterialDataBase/Graphite.txt

New Material Name: Graphite_mod

On the **Mechanical Properties** tab, add the name of a new Material Law and call it e.g., **Lithium Intercalation**.



Group by: Type

Name: Feldspar, Glass (A-Glass Fiber), Glass (AR-Glass Fiber), Glass (C-Glass Fiber), Glass (E-Glass Fiber), Glass (R-Glass Fiber), Glass (S2-Glass Fiber), Glass, Graphite Fiber (XN-05-30S), Graphite, Graphite_mod, Illite, Iridium, Iron, Kevlar, LCO

Copy Material: Graphite_mod

Material Database: C:/Users/streit/GeoDict2024/MaterialDataBase

Edit Material Law: Elastic

Type: Isotropic

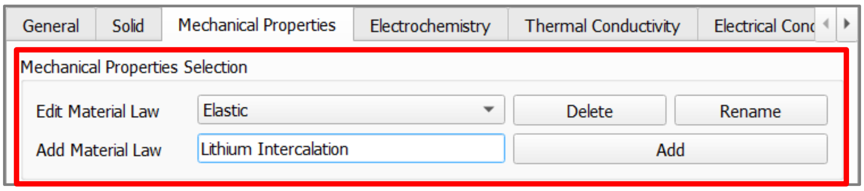
Input Mode: Young's Modulus & Poisson Ratio

Young's Modulus E / (GPa): 25.5

Poisson Ratio v: 0.31

Bulk Modulus K / (GPa): 22.3684211

Shear Modulus G / (GPa): 9.73282443

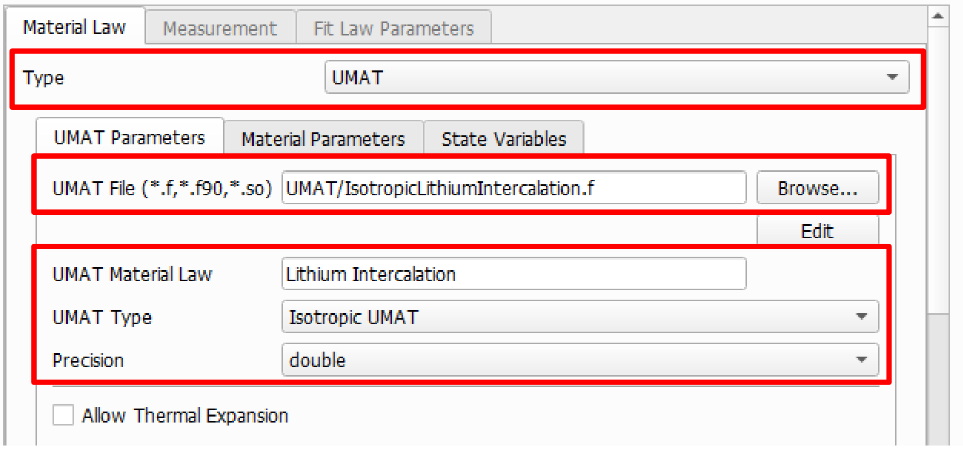


Edit Material Law: Elastic

Add Material Law: Lithium Intercalation

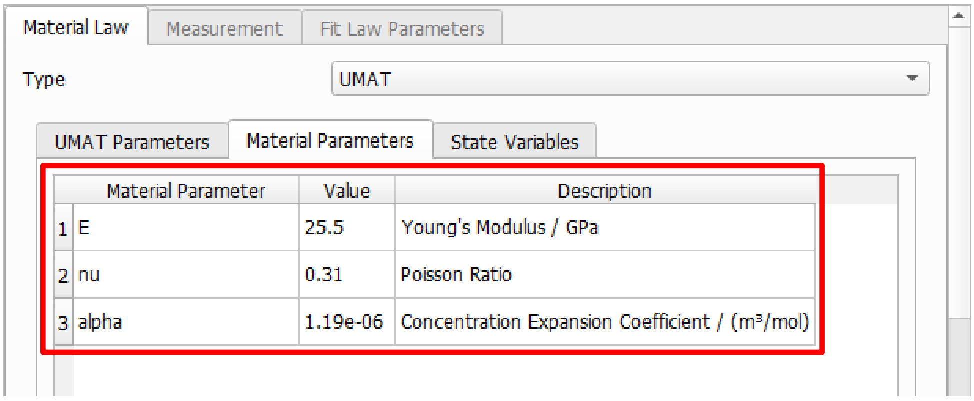
On the **Material Law** tab below, choose the Type **UMAT**. Two UMAT files for concentration dependent expansion are provided in the UMAT folder of your GeoDict installation. For isotropic expansion, select the file IsotropicLithiumIntercalation.f, for transversal isotropic expansion the file LithiumIntercalation.f.

On the subtab **UMAT Parameters**, browse to the file you want to use. Set the appropriate **UMAT Type** and choose the **Precision** desired for the computation. We recommend using double precision.



Type: UMAT
UMAT File (*.f,*.f90,*.so): UMAT/IsotropicLithiumIntercalation.f
UMAT Material Law: Lithium Intercalation
UMAT Type: Isotropic UMAT
Precision: double

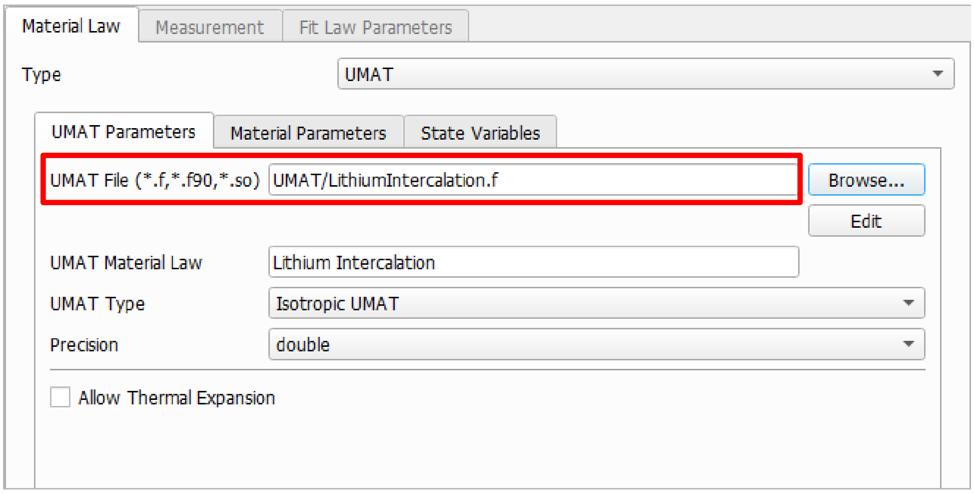
On the subtab **Material Parameters**, define now **Young's Modulus**, **Poisson Ratio** and **Concentration Dependent Expansion Coefficient** for the isotropic case.



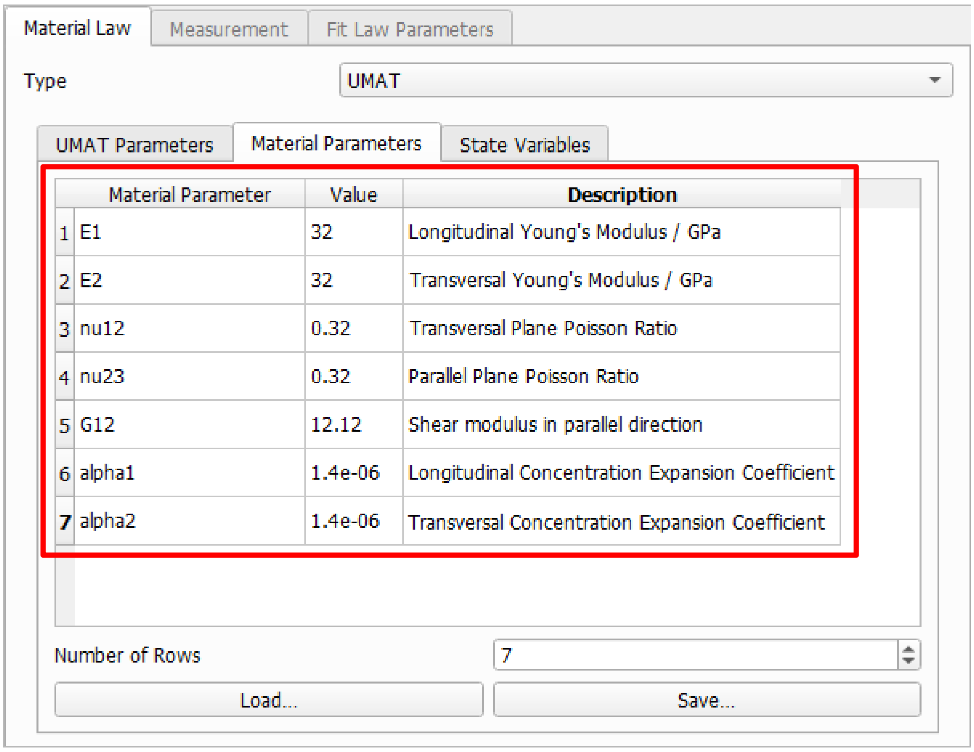
Type: UMAT

| | Material Parameter | Value | Description |
|---|---|---|---|
| 1 | E | 25.5 | Young's Modulus / GPa |
| 2 | nu | 0.31 | Poisson Ratio |
| 3 | alpha | 1.19e-06 | Concentration Expansion Coefficient / ($m^3$/mol) |

For the transverse isotropic case, with the UMAT LithiumIntercalation.f, define the **Young's modulus** and the **Concentration Expansion Coefficient** in longitudinal and transversal direction, the transversal plane and parallel plane **Poisson Ratio** and the **Shear modulus**.



Type: UMAT
UMAT File (*.f,*.f90,*.so): UMAT/LithiumIntercalation.f
UMAT Material Law: Lithium Intercalation
UMAT Type: Isotropic UMAT
Precision: double

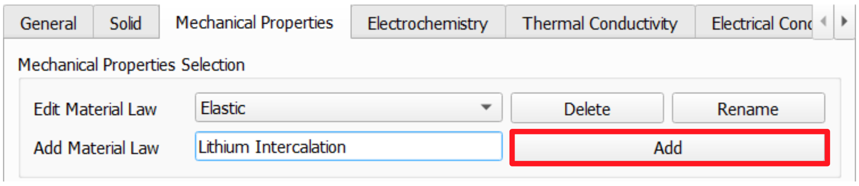


Type: UMAT

| | Material Parameter | Value | Description |
|---|---|---|---|
| 1 | E1 | 32 | Longitudinal Young's Modulus / GPa |
| 2 | E2 | 32 | Transversal Young's Modulus / GPa |
| 3 | nu12 | 0.32 | Transversal Plane Poisson Ratio |
| 4 | nu23 | 0.32 | Parallel Plane Poisson Ratio |
| 5 | G12 | 12.12 | Shear modulus in parallel direction |
| 6 | alpha1 | 1.4e-06 | Longitudinal Concentration Expansion Coefficient |
| 7 | alpha2 | 1.4e-06 | Transversal Concentration Expansion Coefficient |

Number of Rows: 7

Finally, if all parameters are set, click **Add** to add this material law, and save the database.



Edit Material Law: Elastic

Add Material Law: Lithium Intercalation

For other materials of the battery cell (electrolyte, in case of solid electrolyte, binder and carbon black, current collectors and separator), mechanical parameters need to be defined as well to be able to use them in a degradation simulation, see page 91.

## SOLVER CONVERGENCE

The solver in BatteryDict strives to perform a physically accurate simulation for any given set of material parameters (like conductivities), material structure parameters (morphological), and simulation parameters (like the applied current). This is done by calculating the time evolution of the battery simulation step-by-step.

First, the solver works to establish the initial state or equilibrium state for every simulation in BatteryDict. Then, the solver undertakes performing time steps. In every time step, the solver first attempts a time step with the “maximum time step” given by the user. If this time step does not result in a physically meaningful state of the battery cell, the solver reduces the time step and tries again. This time-step reduction is repeated until the solver finds a physically meaningful state. If it cannot find one, the solver produces a warning message indicating that “Time step has not converged”.

In some cases, the cell-potential might rise well above any reasonable end-of-charging voltage, like for example if a large charge rate is applied. The solver might reach 10 V or even 100 V, but at some point, it will stop. In these kinds of situations, *the cell-potential diverges*, but the solver produces a meaningful and helpful result.

However, there are other situations in which the cell-potential does not diverge, but the solver stops regardless of that and as mentioned above, *the solver has not converged*.

In BatteryDict, the possible reasons why the solver does not converge are revealed in warnings, shown before the solver starts and written into the report (see page 69). The warnings help figuring out why the solver stopped and include:

1. not having enough RAM,
2. having very large particles with very low ionic diffusion at a very fast charge rate,
3. having chosen untested material parameters.

Regarding the second point above: If grains of the active material are large or the diffusion is slow, the lithium takes a long time to get from the active surface to the core of the active material grain or from the core of the grain to the surface. In this case it can happen that the lithium concentration at the surface of the active material gets larger than the maximum lithium concentration defined for the material or even smaller than zero. This can happen also, if the active surface is small, the charge rate is high, or if there are at least two active materials and one of them is nearly filled or nearly empty.

For the third reason of problems with the convergence of the solver, different tests have been carried out during the development of BatteryDict to identify material parameters that should lead to converging simulations.

## OVERLAPPING OCV CURVES FOR SEVERAL ACTIVE MATERIALS

If several active materials are used in an electrode, an additional check controls that the value ranges of the open-circuit potential (OCV) curves of all materials overlap. Otherwise, there is no well-defined equilibrium state of the battery cell, which is the starting point for the simulation.

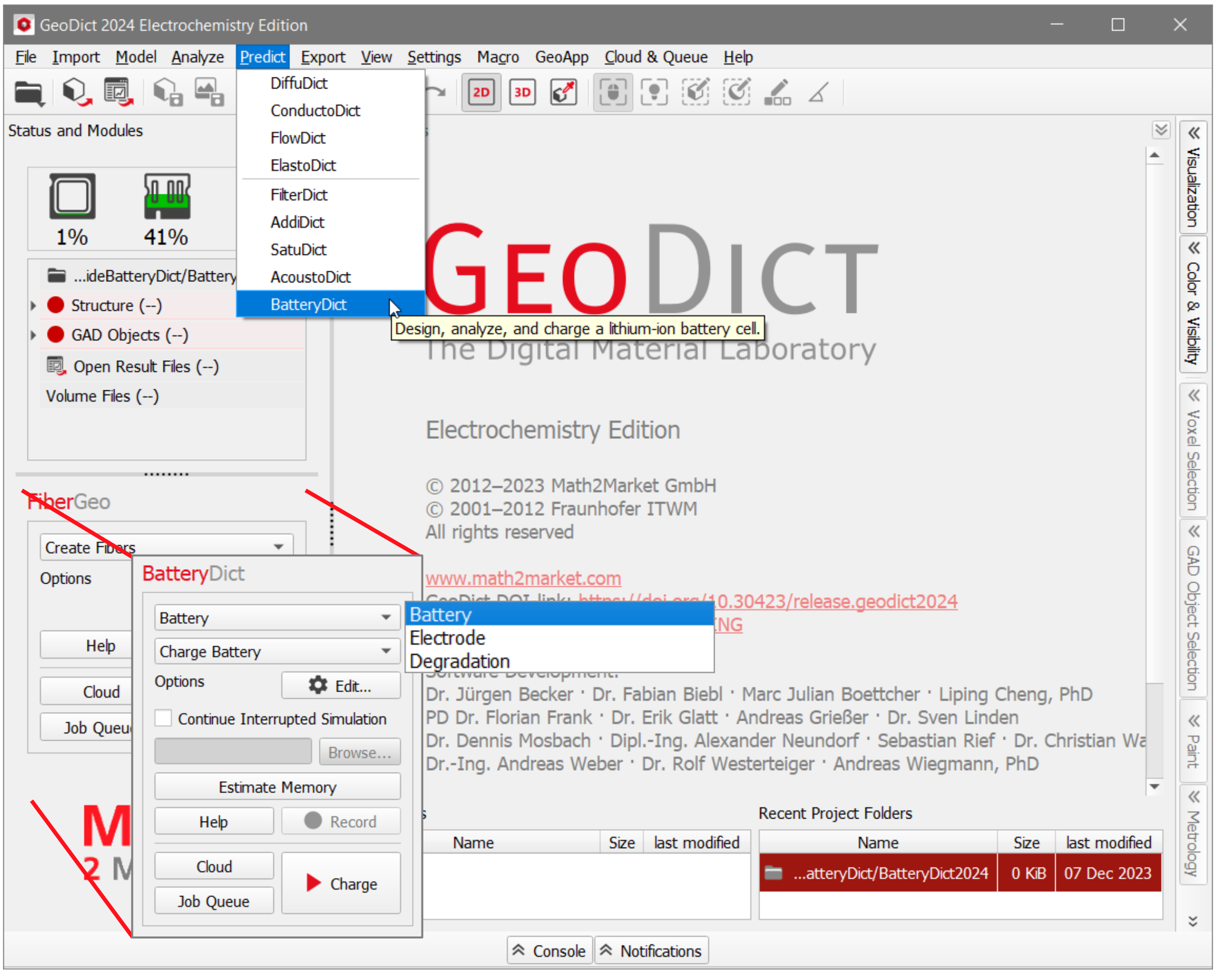
OCVs are the driving force in a battery that make lithium ions flow from materials with low OCV to materials with high OCV. If a battery is used in an electrical device and the two electrodes are conductively connected, ions flow from the negative electrode (low OCV) to the positive electrode (high OCV). The charging process requires an additional external driving force (the charging device) to cause ions to flow in the opposite direction.

If one of the electrodes is composed of several active materials, the OCV-curves of the active materials differ (at least a bit). Since the active materials in an electrode are conductively connected, there will be a driving force that will move ions from particles with low OCV to particles with high OCV. This process continues until all active materials within the electrode have the same OCV value and the electrode is in equilibrium.

In BatteryDict, the Cell-SOC or the electrode-SOC determine the initial amount of charge (i.e. lithium ions) stored in the electrode. Before starting the simulation, the solver will try to distribute this initial amount of charge between the different active materials of an electrode. This is done in such a way that the electrode is in equilibrium, i.e., that the OCVs are equal. This can only be achieved if the OCV curves of the active materials share common values.

# BATTERYDICT COMPUTATIONS

Start BatteryDict by selecting **Predict** → **BatteryDict** in the menu bar.



In the **BatteryDict** section, the pull-down menu includes the possibility to choose first between **Battery**, **Electrode**, or **Degradation** simulation.

If **Battery** is chosen, the second pull-down menu allows to select between **Design Battery**, **Analyze Battery**, or to simulate the charging of a battery with **Charge Battery**.

If a simulation is selected, click **Charge** (or **Design**, **Analzye**, or **Run**) to start the computation. Select **Cloud** to run it in the GeoDict cloud or **Job Queue** to run the command on machines connected to your local network. See the High Performance Computing handbook for more details.

For **Charge Battery** it is also possible to continue a previously interrupted simulation, see page 80.

## BATTERY - DESIGN BATTERY

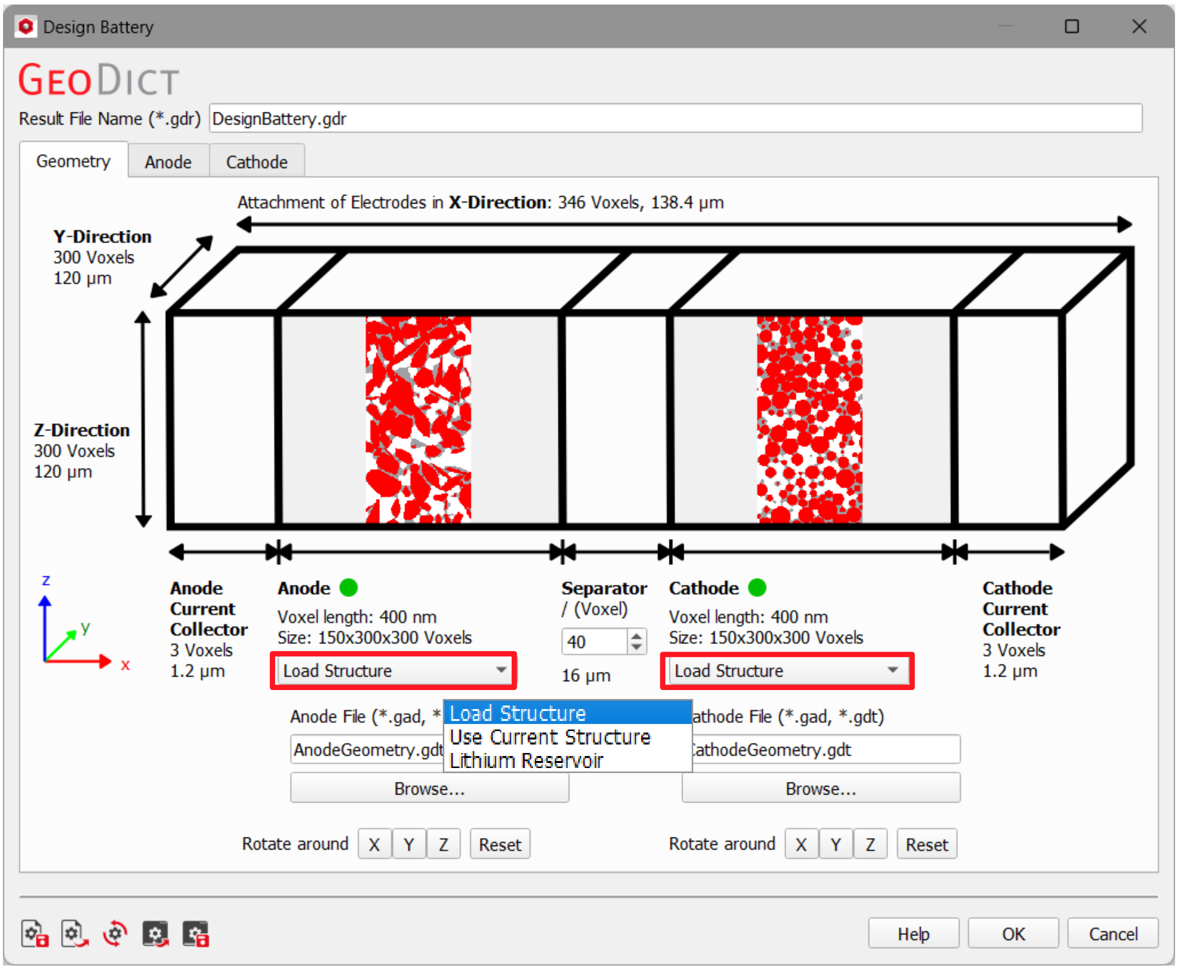
To design a battery, choose **Design Battery** from the second pull-down menu and click **Edit...** to choose the options.

The **Design Battery** dialog opens, containing three tabs where to define the morphology of the battery (**Geometry** tab) and the constituent materials for **Anode** and **Cathode**.

### GEOMETRY

For both electrodes, either the current structure loaded in the GeoDict Visualization Area can be used, a previously saved structure can be loaded, or the electrode can be modelled as a lithium reservoir.

On page 81, we show how to simulate the charging of a half cell starting from the microstructure of a single electrode with the **Electrode – Charge Electrode** command. Note, that since GeoDict 2022, it is not necessary anymore to create the geometry of the whole half cell first.



Result File Name (*.gdr) DesignBattery.gdr

Attachment of Electrodes in **X-Direction**: 346 Voxels, 138.4 µm

**Y-Direction** 300 Voxels 120 µm

**Z-Direction** 300 Voxels 120 µm

**Anode Current Collector** 3 Voxels 1.2 µm

**Anode** Voxel length: 400 nm Size: 150x300x300 Voxels

Load Structure

**Separator / (Voxel)** 40 16 µm

**Cathode** Voxel length: 400 nm Size: 150x300x300 Voxels

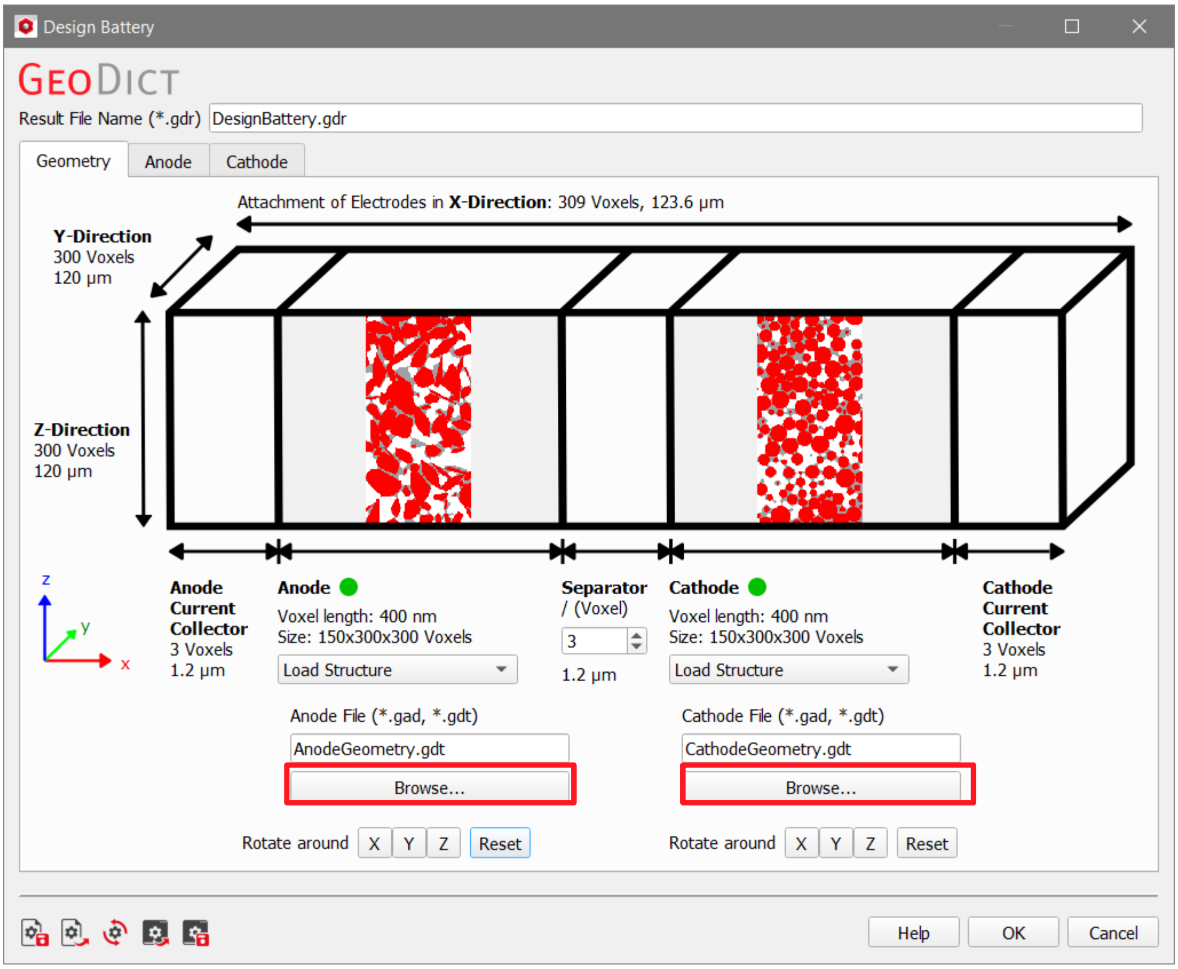
Load Structure

**Cathode Current Collector** 3 Voxels 1.2 µm

Anode File (*.gad, *.gdt) AnodeGeometry.gdt

Cathode File (*.gad, *.gdt) CathodeGeometry.gdt

Choose **Load Structure** and use the **Browse...** buttons to select an input file for anode and cathode, in *.gad or *.gdt GeoDict formats. If the built-in default settings are used for the dialog, a default structure for anode and cathode from the BatteryDict/DesignBattery folder is loaded.



Result File Name (*.gdr) DesignBattery.gdr

Attachment of Electrodes in **X-Direction**: 309 Voxels, 123.6 µm

**Y-Direction** 300 Voxels 120 µm

**Z-Direction** 300 Voxels 120 µm

**Anode Current Collector** 3 Voxels 1.2 µm

**Anode** Voxel length: 400 nm Size: 150x300x300 Voxels

**Separator** / (Voxel) 3 1.2 µm

**Cathode** Voxel length: 400 nm Size: 150x300x300 Voxels

**Cathode Current Collector** 3 Voxels 1.2 µm

Anode File (*.gad, *.gdt) AnodeGeometry.gdt

Cathode File (*.gad, *.gdt) CathodeGeometry.gdt

After selecting electrode files, a 2D representation of the anode and of the cathode appears in the dialog. For the example battery shown here, anode and cathode structure are created with the GeoApps Bimodal Anode and Bimodal Cathode.

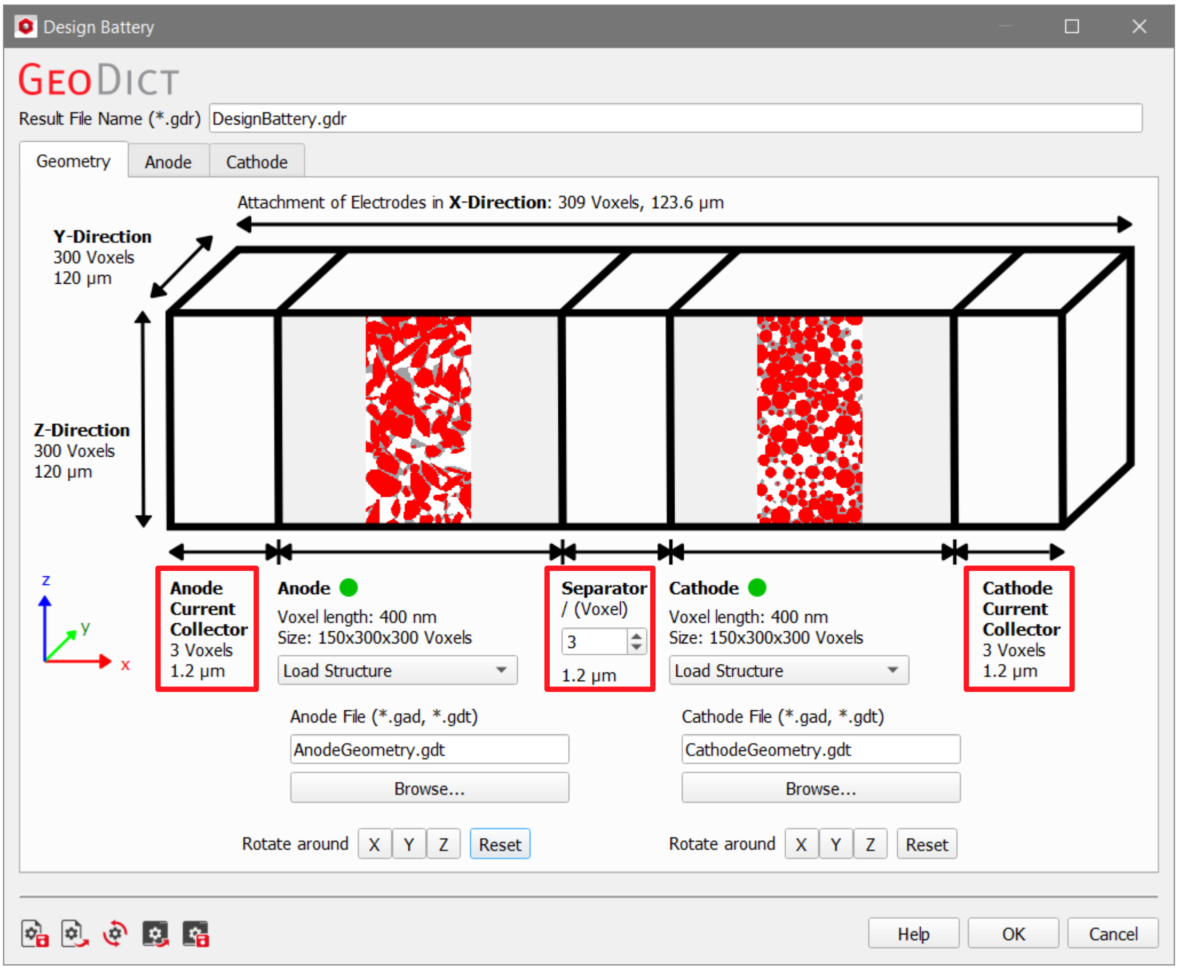
For details using this GeoApps, see the GeoApp handbook.

- A red dot is visible for the anode and cathode, if no files are loaded at all.
- A yellow dot appears if a file is loaded but the dimensions or voxel length of the anode and the cathode do not match.
- A green dot appears if the anode and cathode files are loaded successfully, the dimensions of the two match each other, and the voxel length is the same for both microstructures.

The **Size** of anode and cathode are shown as the number of voxels in each direction below the diagram of the battery, and the **Voxel Length** is also displayed. After choosing anode and cathode, the total number of voxels and total length of the complete battery structure are displayed for each direction above and to the left of the diagram.

The **Rotate around X**, **Y** and **Z** buttons are used to rotate the structure 90° around the X, Y, or Z-axis. Click **Reset** to go back to the original orientation of anode and cathode in the battery structure.

The number of voxels of the separator can be defined in the dialog. The default is 40 voxels (≙ 10 µm for 250 nm voxel length). The length of anode and cathode current collector is fixed to be three voxels and cannot be changed.



Result File Name (*.gdr) DesignBattery.gdr

Attachment of Electrodes in **X-Direction**: 309 Voxels, 123.6 µm

**Y-Direction** 300 Voxels 120 µm

**Z-Direction** 300 Voxels 120 µm

**Anode Current Collector** 3 Voxels 1.2 µm

**Anode** ●
Voxel length: 400 nm
Size: 150x300x300 Voxels
Load Structure

**Separator** / (Voxel) 3 1.2 µm

**Cathode** ●
Voxel length: 400 nm
Size: 150x300x300 Voxels
Load Structure

**Cathode Current Collector** 3 Voxels 1.2 µm

Anode File (*.gad, *.gdt) AnodeGeometry.gdt

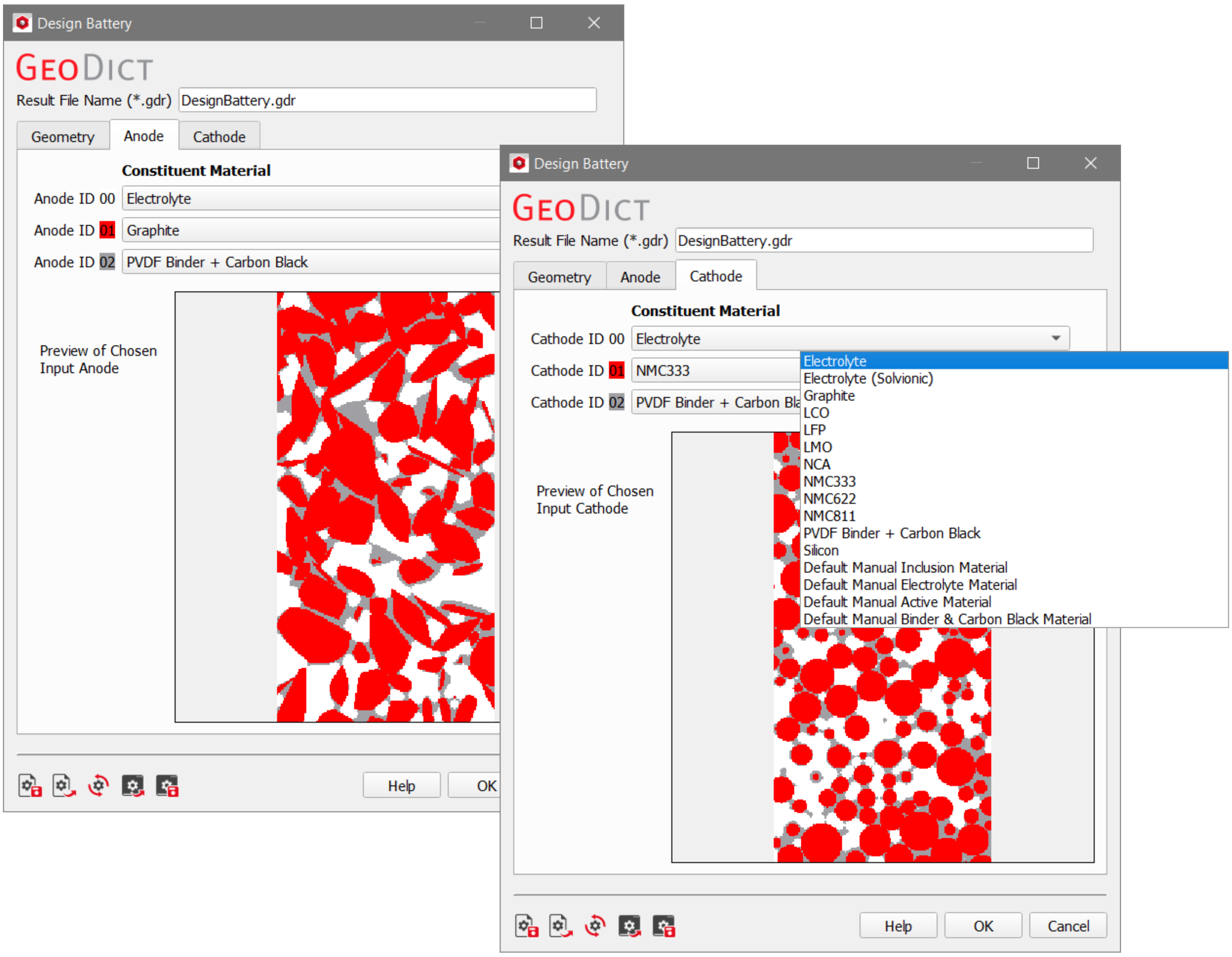
Cathode File (*.gad, *.gdt) CathodeGeometry.gdt

## ANODE AND CATHODE

The next step is to assign electrolyte and active materials, as well as binder and carbon black to the materials available in the structures of anode and cathode.

Under the **Anode** and **Cathode** tabs all Material IDs of the anode and cathode structure are assigned to a material (electrolyte, binder & carbon black, up to four different active materials per electrode, or inclusion). In the example shown here, both anode and cathode consist of one active material only.

Built-in default materials from the GeoDict Material Database can be selected from the pull-down menu. Materials and corresponding parameters can be changed when performing a charging simulation later on.



Result File Name (*.gdr) DesignBattery.gdr

Anode ID 00 Electrolyte
Anode ID 01 Graphite
Anode ID 02 PVDF Binder + Carbon Black

Result File Name (*.gdr) DesignBattery.gdr

Cathode ID 00 Electrolyte
Cathode ID 01 NMC333
Cathode ID 02 PVDF Binder + Carbon Bla

If one of the materials should have no active role in the battery charging process, assign it to the **Default Manual Inclusion Material**. Like this, no conduction is possible in this material, it has no potential, and does not contain lithium.

Click **OK** in the Design Battery dialog, to keep the parameters selected in memory, or **Cancel** to discard the parameters.

Click **Design** in the **BatteryDict** section of the GUI to create the battery.

If the battery is created successfully, a result file with the default name DesignBattery.gdr is created in the selected project folder, as well as a structure file (*.gdt) in the subfolder DesignBattery.

The Result Viewer of the result file opens automatically after the generation, showing the information of DesignBattery.gdr (see Results of Design Battery below).

## ALL SOLID STATE BATTERIES

In GeoDict 2024, it is also possible to simulate the charging of all solid state batteries. The geometry is designed in the same way as for batteries with fluid electrolyte, explained above, however we recommend some adjustments after using the battery designer.

To avoid issues in the charging simulation, make sure to reassign the material ID of the separator with the same material ID as for the solid electrolyte (see page 46). Also make sure that the transference number for the electrolyte is set to 1 (see page 49).

## MORE FLEXIBLE GEOMETRIES

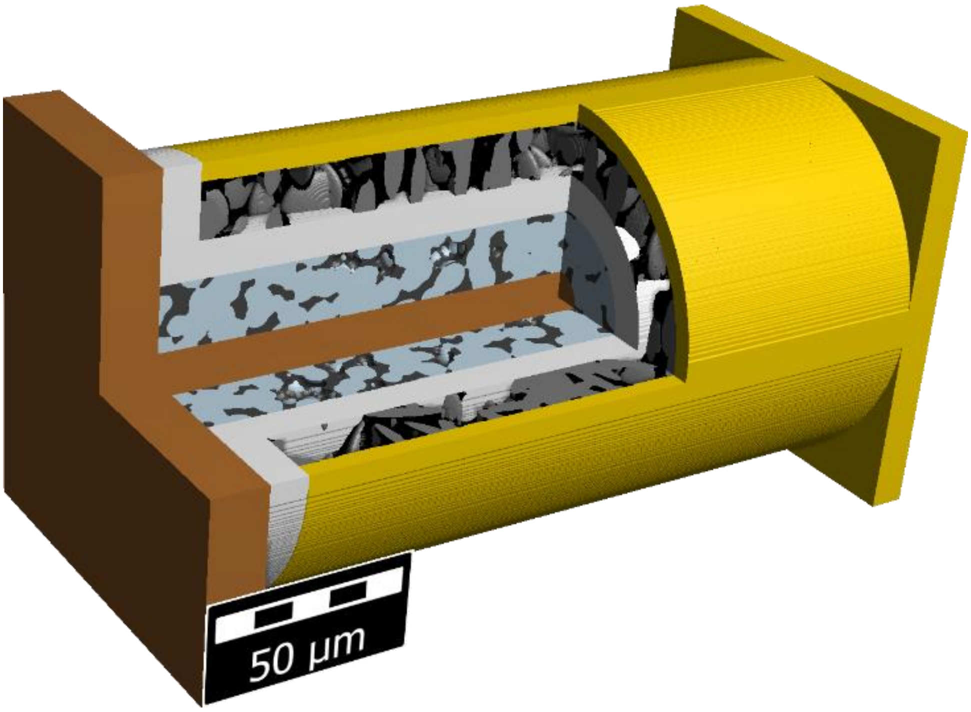
For charging simulations, it is possible to use arbitrary battery geometries, not only cuboid ones, as shown in the **Geometry** on page 31.

Since GeoDict 2022, to use arbitrary geometries, no additional expert setting is necessary anymore.

Regarding the current collectors of non-cuboid geometries, it is necessary that they cover the whole surface of the structure in x-direction.

That is, the anode current collector needs to cover the whole structure in negative x-direction. The cathode current collector needs to cover the whole structure in positive x-direction.

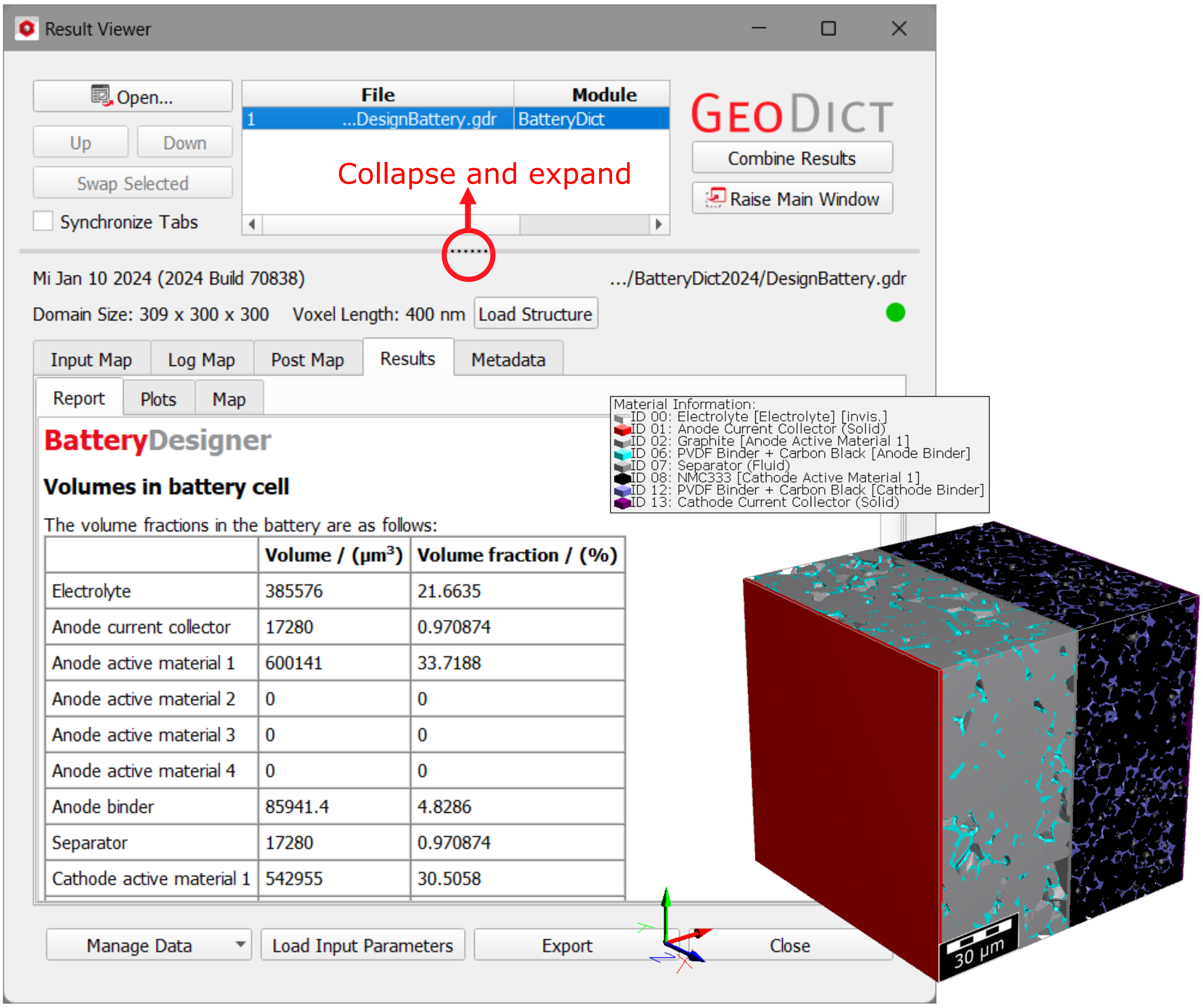
For geometries with circular cross sections, current collectors can be positioned like shown in the figure below.



Additionally, the geometry needs to be chosen in such a way that no short-circuit of both current collectors exists. I.e., the cathode and anode current collectors must not touch each other and must also not be connected directly via active material.

## RESULTS OF DESIGN BATTERY

After running Design Battery successfully, a GeoDict result file (.gdr) is written and the **Result Viewer** for this result file opens automatically. The created battery structure is available in memory and shown in the visualization area of the GeoDict GUI.



| | File | Module |
|---|---|---|
| 1 | ...DesignBattery.gdr | BatteryDict |

Mi Jan 10 2024 (2024 Build 70838) .../BatteryDict2024/DesignBattery.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm ●

**BatteryDesigner**

**Volumes in battery cell**

The volume fractions in the battery are as follows:

| | Volume / (µm³) | Volume fraction / (%) |
|---|---|---|
| Electrolyte | 385576 | 21.6635 |
| Anode current collector | 17280 | 0.970874 |
| Anode active material 1 | 600141 | 33.7188 |
| Anode active material 2 | 0 | 0 |
| Anode active material 3 | 0 | 0 |
| Anode active material 4 | 0 | 0 |
| Anode binder | 85941.4 | 4.8286 |
| Separator | 17280 | 0.970874 |
| Cathode active material 1 | 542955 | 30.5058 |

Material Information:
ID 00: Electrolyte [Electrolyte] [invis.]
ID 01: Anode Current Collector (Solid)
ID 02: Graphite [Anode Active Material 1]
ID 06: PVDF Binder + Carbon Black [Anode Binder]
ID 07: Separator (Fluid)
ID 08: NMC333 [Cathode Active Material 1]
ID 12: PVDF Binder + Carbon Black [Cathode Binder]
ID 13: Cathode Current Collector (Solid)

The .gdr file can be reopened at any time by choosing **File → Open Results (*.gdr)...** in the menu bar. The **Result Viewer** opens at the **Results** tab.

In the **Result Viewer**, the list of all open result files is shown in a box in the upper part. The name of the result file currently displayed is highlighted in blue. This box can be collapsed (and expanded) by pulling up (or down) the dotted line under the box.

The green dot in the upper right part of the result viewer, indicates that the structure from that these results were obtained is loaded in the visualization area. This is always the case directly after creating the battery structure. If a result file (*.gdr) is reloaded later through **File → Open Results (*.gdr)...** or through clicking the **Open** button in the upper left part of the Result Viewer, the dot is red. The structure can be loaded into GeoDict memory and the visualization area by clicking the **Load Structure** button in the result viewer.

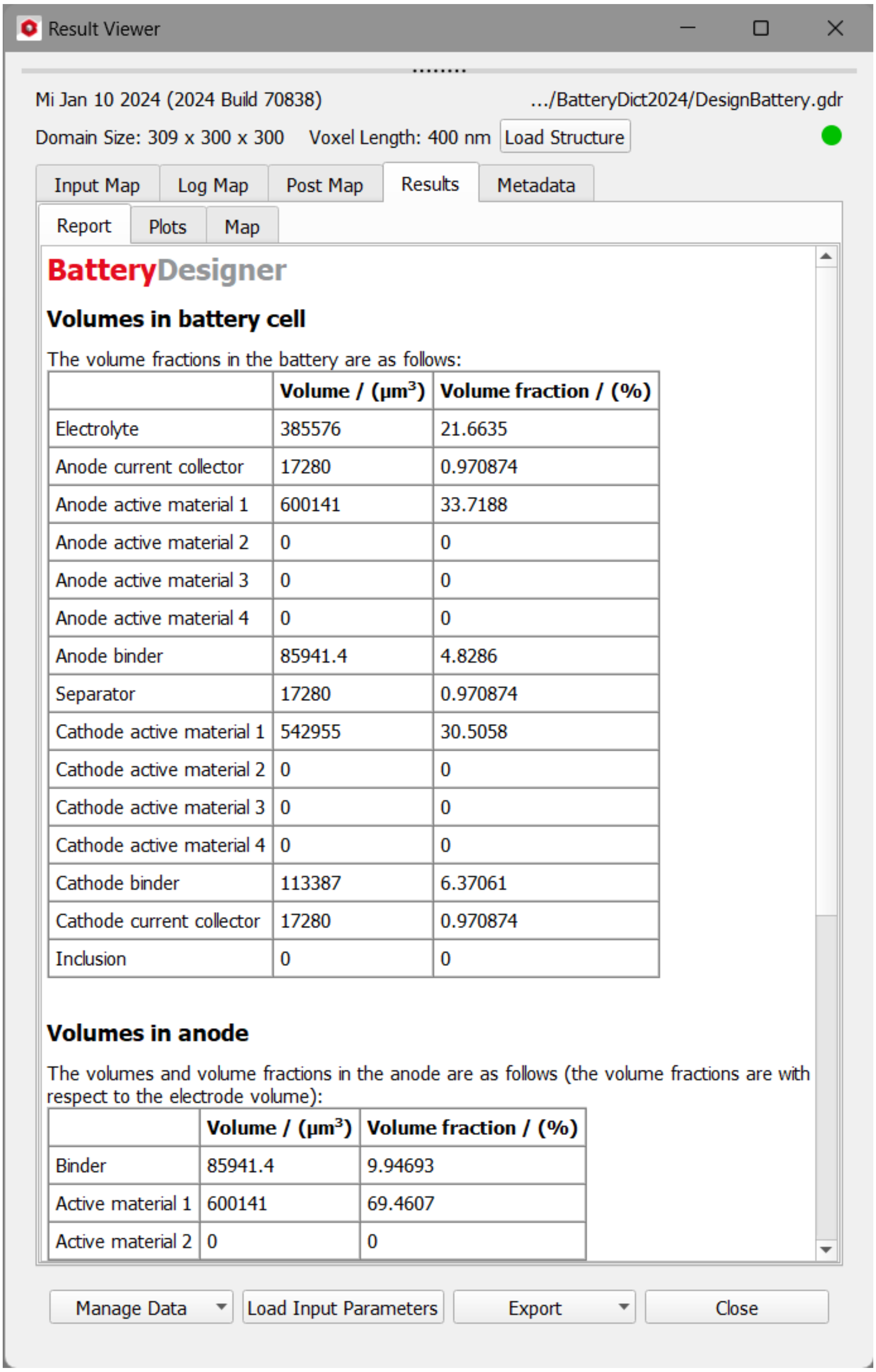
With the **Combine Results** button in the upper right part of the result viewer, the results of several selected .gdr files can be combined and shown in one plot in the result viewer. More details can be found in the Result Viewer handbook.

The **Input Map** tab contains all the input parameters of the battery creation.

The **Log Map** tab shows the runtime and memory used as well as the information about the system on which the battery structure was created.

The **Post Map** tab shows parameter and graph data used for the plots on the **Results** tab.

The **Results - Report** subtab lists the information on the volume fractions of the different materials for the whole battery, as well as for anode and cathode separately.



Mi Jan 10 2024 (2024 Build 70838) .../BatteryDict2024/DesignBattery.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

**BatteryDesigner**

**Volumes in battery cell**

The volume fractions in the battery are as follows:

| | Volume / (μm³) | Volume fraction / (%) |
|---|---|---|
| Electrolyte | 385576 | 21.6635 |
| Anode current collector | 17280 | 0.970874 |
| Anode active material 1 | 600141 | 33.7188 |
| Anode active material 2 | 0 | 0 |
| Anode active material 3 | 0 | 0 |
| Anode active material 4 | 0 | 0 |
| Anode binder | 85941.4 | 4.8286 |
| Separator | 17280 | 0.970874 |
| Cathode active material 1 | 542955 | 30.5058 |
| Cathode active material 2 | 0 | 0 |
| Cathode active material 3 | 0 | 0 |
| Cathode active material 4 | 0 | 0 |
| Cathode binder | 113387 | 6.37061 |
| Cathode current collector | 17280 | 0.970874 |
| Inclusion | 0 | 0 |

**Volumes in anode**

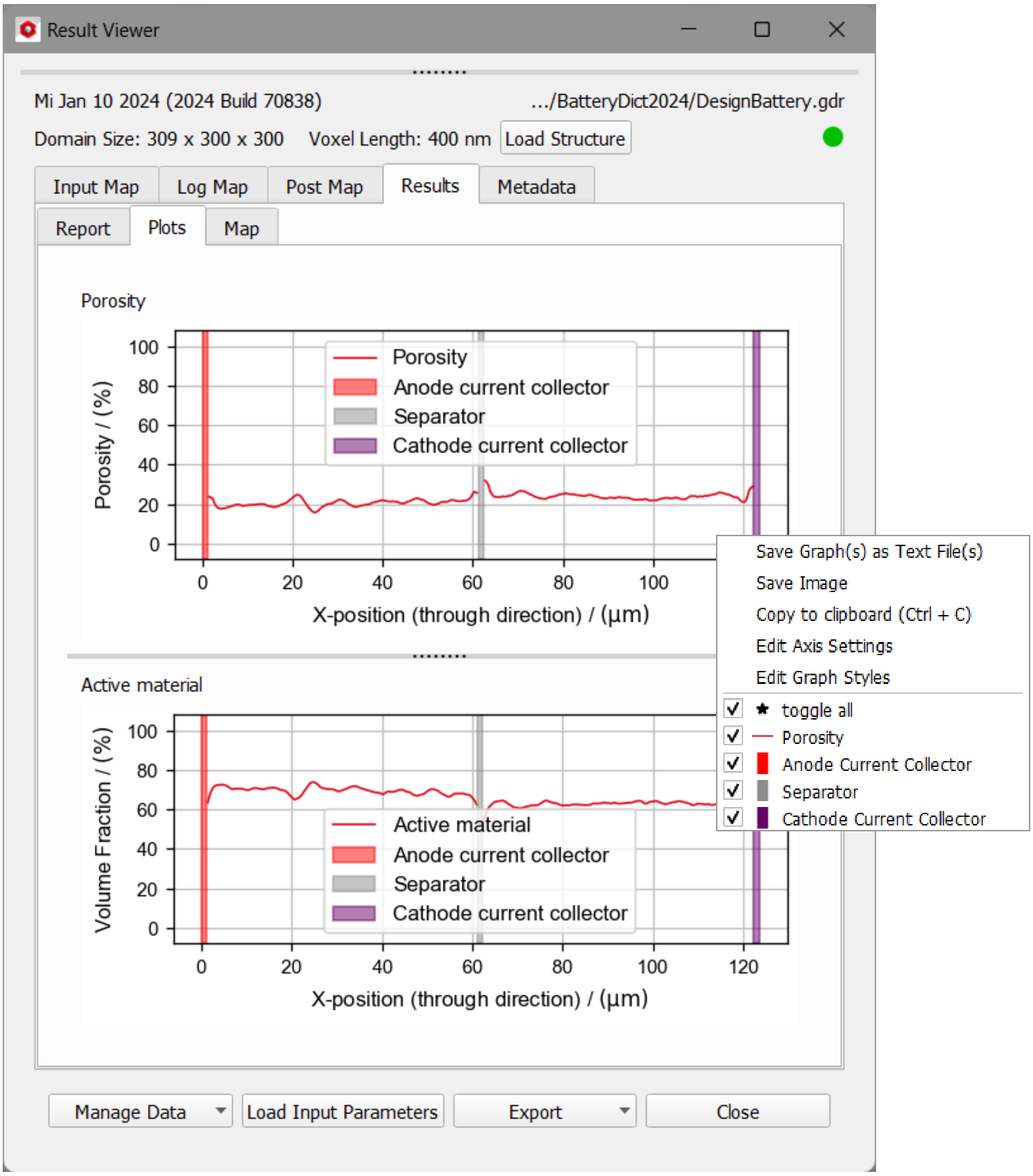
The volumes and volume fractions in the anode are as follows (the volume fractions are with respect to the electrode volume):

| | Volume / (μm³) | Volume fraction / (%) |
|---|---|---|
| Binder | 85941.4 | 9.94693 |
| Active material 1 | 600141 | 69.4607 |
| Active material 2 | 0 | 0 |

Under the **Results - Plots** subtab, the porosity and the distribution of active material over the whole battery are shown as averaged values over each slice in y- and z-direction.

At the separator and both current collectors, no values are shown for porosity and active material since these structures do not contain active material and are not resolved into a microstructure in the Battery Designer. Also, the binder is considered as solid material in the computation of the porosity. Later, in the analysis of the battery or a charging simulation, binder can be considered as porous material.

By right-clicking with the mouse in one of the plots, axis and graph settings can be changed, the components can be set to visible or invisible, and the graph can be saved as image, text file, or be copied to the clipboard.



Mi Jan 10 2024 (2024 Build 70838) .../BatteryDict2024/DesignBattery.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

The **Results - Map** subtab displays information on the volumes and volume fractions of the different materials of the whole battery, as well as for anode and cathode alone. These are the values shown under the **Results – Report** subtab.

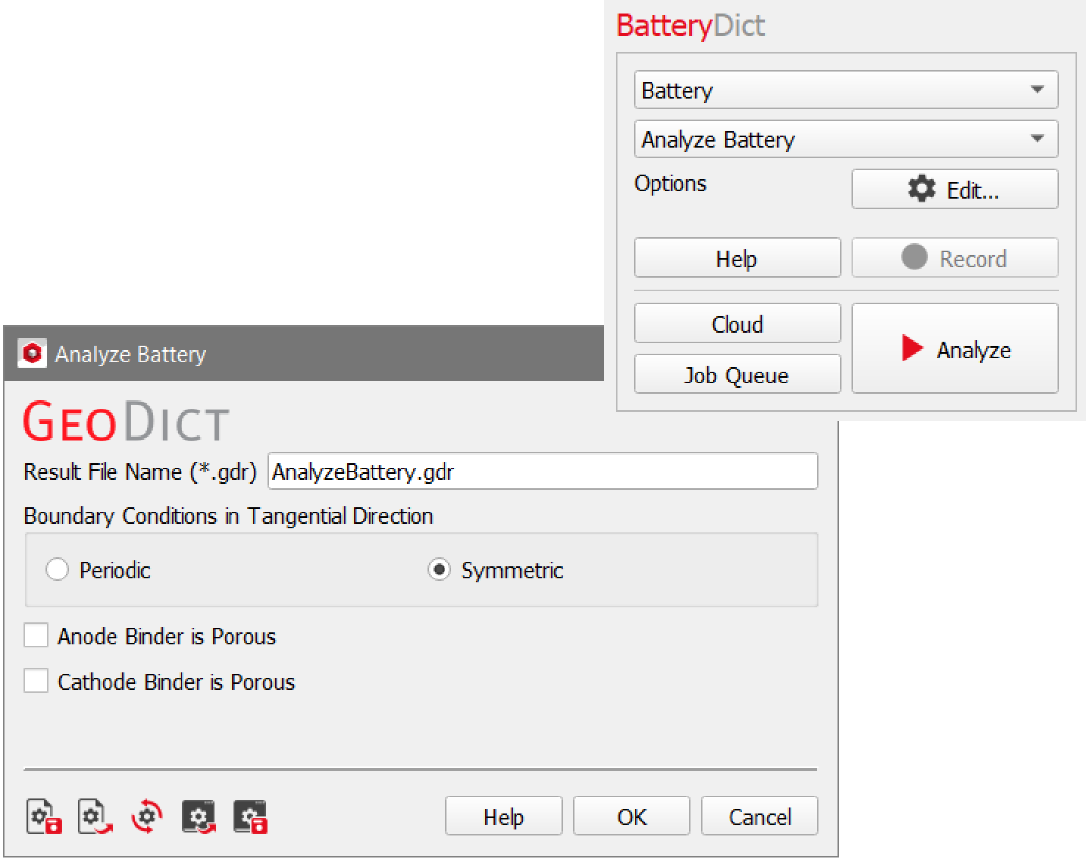
The **Metadata** tab displays a description of the .gdr file. The text can be modified here, and the modification can be saved to the .gdr file.

As usual for all GeoDict result files, several buttons for further processing are available at the bottom of the **Result Viewer**, see the Result Viewer handbook for more details.

## BATTERY - ANALYZE BATTERY

To analyze the connection and volume of the different materials for the designed battery structure, choose **Analyze Battery** from the second pull-down menu in the **BatteryDict** section.

Click **Edit** to open the options dialog.



Result File Name (*.gdr) AnalyzeBattery.gdr

Boundary Conditions in Tangential Direction

○ Periodic ● Symmetric

☐ Anode Binder is Porous

☐ Cathode Binder is Porous

First, define the result file name and the tangential boundary conditions.

**Periodic** or **Symmetric** boundary conditions can be selected. For periodic boundary conditions the structure is assumed to repeat periodically in y- and z-direction and for symmetric boundary conditions, the $Li^+$ ions and electrons are reflected at the boundary in y- and z-direction.

Boundary conditions are applied while identifying connected and unconnected material, since this depends on the continuation of the material in y- and z-direction. For a charging simulation, it can be chosen independent of the value selected here. Connected and unconnected material is identified again during charging simulation dependent on the boundary conditions selected then.

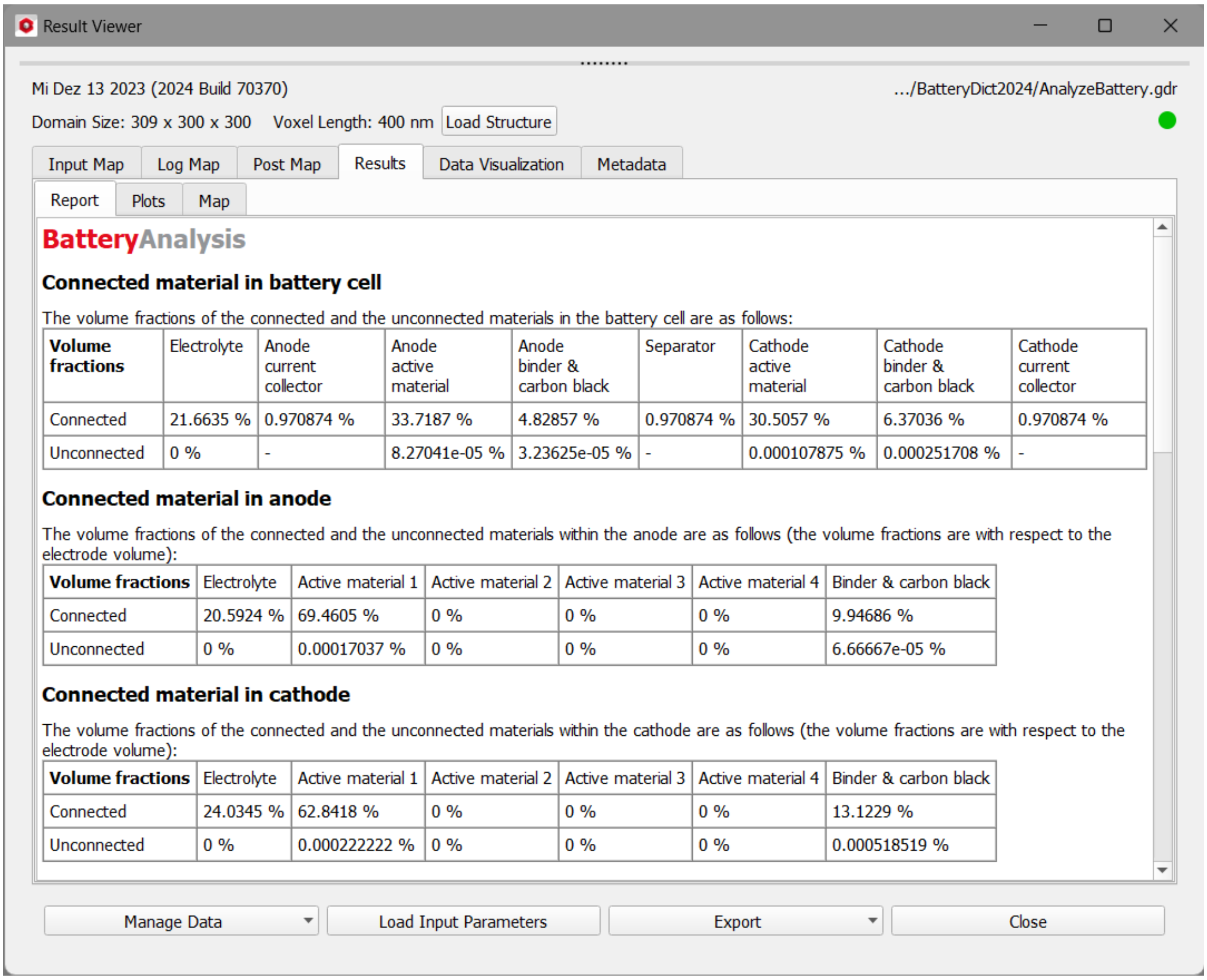
Check **Anode Binder is Porous** or/and **Cathode Binder is Porous** if the binder of one or both electrode(s) is a porous material with micropores that are filled with electrolyte and not resolved in the electrode structure.

Click **Analyze** in the BatteryDict section to start the analysis. If it is finished, the Result Viewer opens.

## RESULTS OF ANALYZE BATTERY

After successful completion of a battery analysis, the GeoDict Result Viewer opens for the results.

The **Results – Report** subtab lists the information on the volume fractions of the connected and unconnected part for the different battery components. First, these volume fractions are shown for the whole battery cell, then for anode and cathode separately. The unconnected parts do not contribute to the performance of the battery, a small fraction of unconnected material is therefore desired.



**BatteryAnalysis**

**Connected material in battery cell**

The volume fractions of the connected and the unconnected materials in the battery cell are as follows:

| **Volume fractions** | Electrolyte | Anode current collector | Anode active material | Anode binder & carbon black | Separator | Cathode active material | Cathode binder & carbon black | Cathode current collector |
|---|---|---|---|---|---|---|---|---|
| Connected | 21.6635 % | 0.970874 % | 33.7187 % | 4.82857 % | 0.970874 % | 30.5057 % | 6.37036 % | 0.970874 % |
| Unconnected | 0 % | - | 8.27041e-05 % | 3.23625e-05 % | - | 0.000107875 % | 0.000251708 % | - |

**Connected material in anode**

The volume fractions of the connected and the unconnected materials within the anode are as follows (the volume fractions are with respect to the electrode volume):

| **Volume fractions** | Electrolyte | Active material 1 | Active material 2 | Active material 3 | Active material 4 | Binder & carbon black |
|---|---|---|---|---|---|---|
| Connected | 20.5924 % | 69.4605 % | 0 % | 0 % | 0 % | 9.94686 % |
| Unconnected | 0 % | 0.00017037 % | 0 % | 0 % | 0 % | 6.66667e-05 % |

**Connected material in cathode**

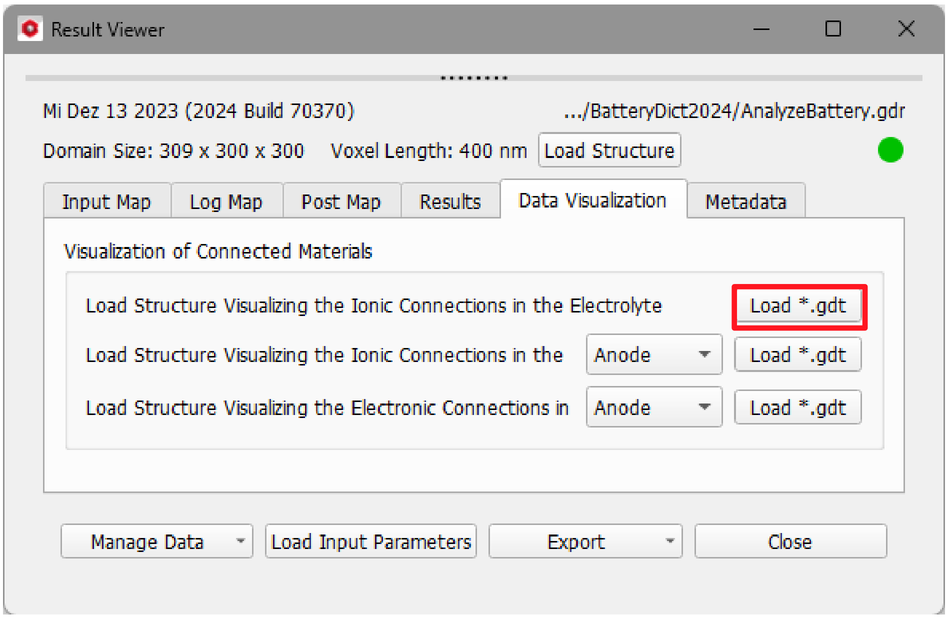
The volume fractions of the connected and the unconnected materials within the cathode are as follows (the volume fractions are with respect to the electrode volume):

| **Volume fractions** | Electrolyte | Active material 1 | Active material 2 | Active material 3 | Active material 4 | Binder & carbon black |
|---|---|---|---|---|---|---|
| Connected | 24.0345 % | 62.8418 % | 0 % | 0 % | 0 % | 13.1229 % |
| Unconnected | 0 % | 0.000222222 % | 0 % | 0 % | 0 % | 0.000518519 % |

After the information about connected and unconnected parts of the battery, in the **Results - Report** tab follows a list of the volume and volume fractions of each component for the whole battery cell as well as for anode and cathode separately. This is the same information also shown in the result file of the Battery Designer, see page 36.

Under the **Results - Plots** subtab, the porosity, and the distribution of active material over the whole battery are shown as averaged values over each slice in y- and z-direction. This is the same plot as shown for a result file of the battery designer, see page 36.

To visualize the location of connected and unconnected parts of the battery components, load structure files located in the Analyze Battery result folder from the **Data Visualization** tab.



Result Viewer

Mi Dez 13 2023 (2024 Build 70370) .../BatteryDict2024/AnalyzeBattery.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

Visualization of Connected Materials

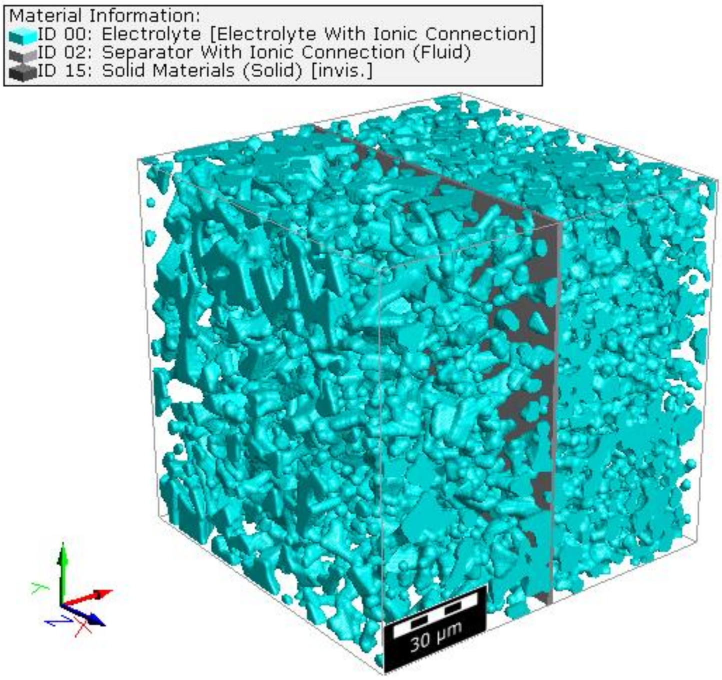
Load Structure Visualizing the Ionic Connections in the Electrolyte

Load Structure Visualizing the Ionic Connections in the: Anode

Load Structure Visualizing the Electronic Connections in: Anode

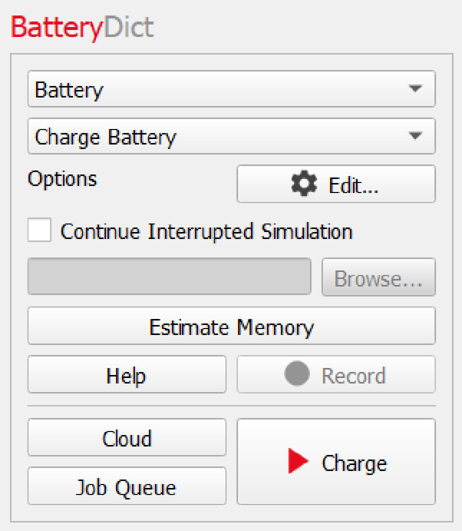
Structure files containing the electronic as well as the ionic connections are available for anode and cathode and for the electrolyte connections, see page 105.

As an example, here the structure for the ionic connection in the Electrolyte is shown. No unconnected electrolyte exists in the example battery shown here.



## BATTERY - CHARGE BATTERY

To simulate the charging or discharging of a battery, choose **Battery** and **Charge Battery** from the pull-down menus in the **BatteryDict** section. Then, click **Edit** to adjust the solver options.


BatteryDict

Battery

Charge Battery

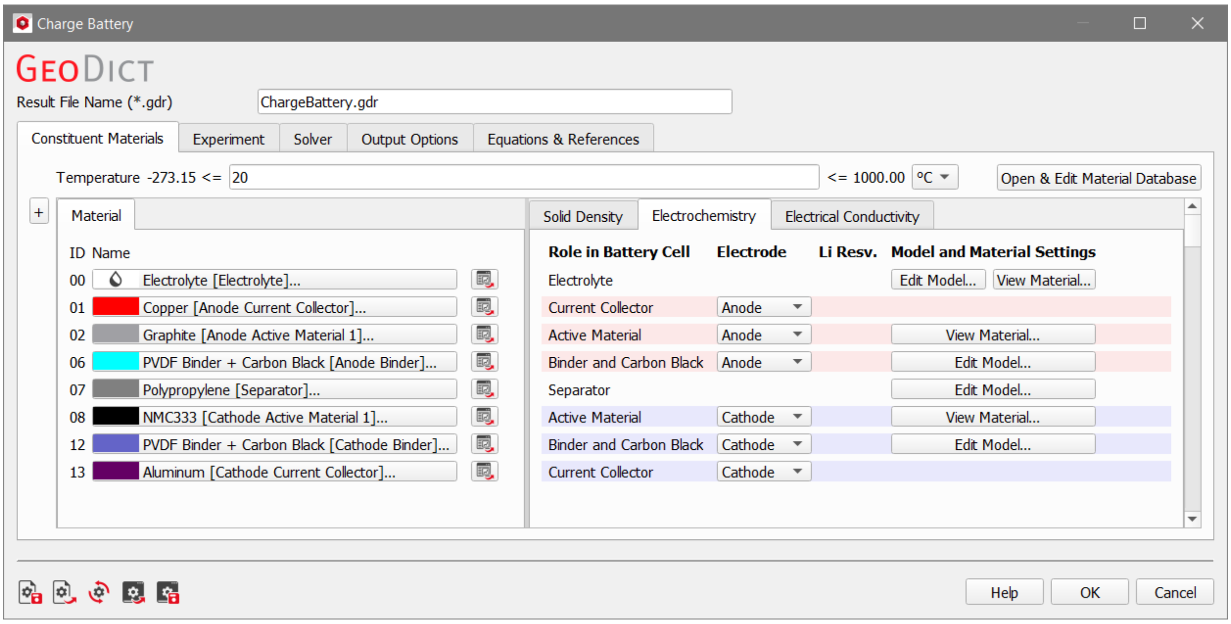
Options

☐ Continue Interrupted Simulation

The **BatteryDict** dialog opens, containing five tabs.

### CONSTITUENT MATERIALS

The properties of all materials of the battery structure are defined on the **Constituent Materials** tab.


Charge Battery

GeoDict

Result File Name (*.gdr): ChargeBattery.gdr

Temperature -273.15 <= 20 <= 1000.00 °C

| ID | Name |
|---|---|
| 00 | Electrolyte [Electrolyte]... |
| 01 | 🟥 Copper [Anode Current Collector]... |
| 02 | Graphite [Anode Active Material 1]... |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... |
| 07 | Polypropylene [Separator]... |
| 08 | NMC333 [Cathode Active Material 1]... |
| 12 | PVDF Binder + Carbon Black [Cathode Binder]... |
| 13 | Aluminum [Cathode Current Collector]... |

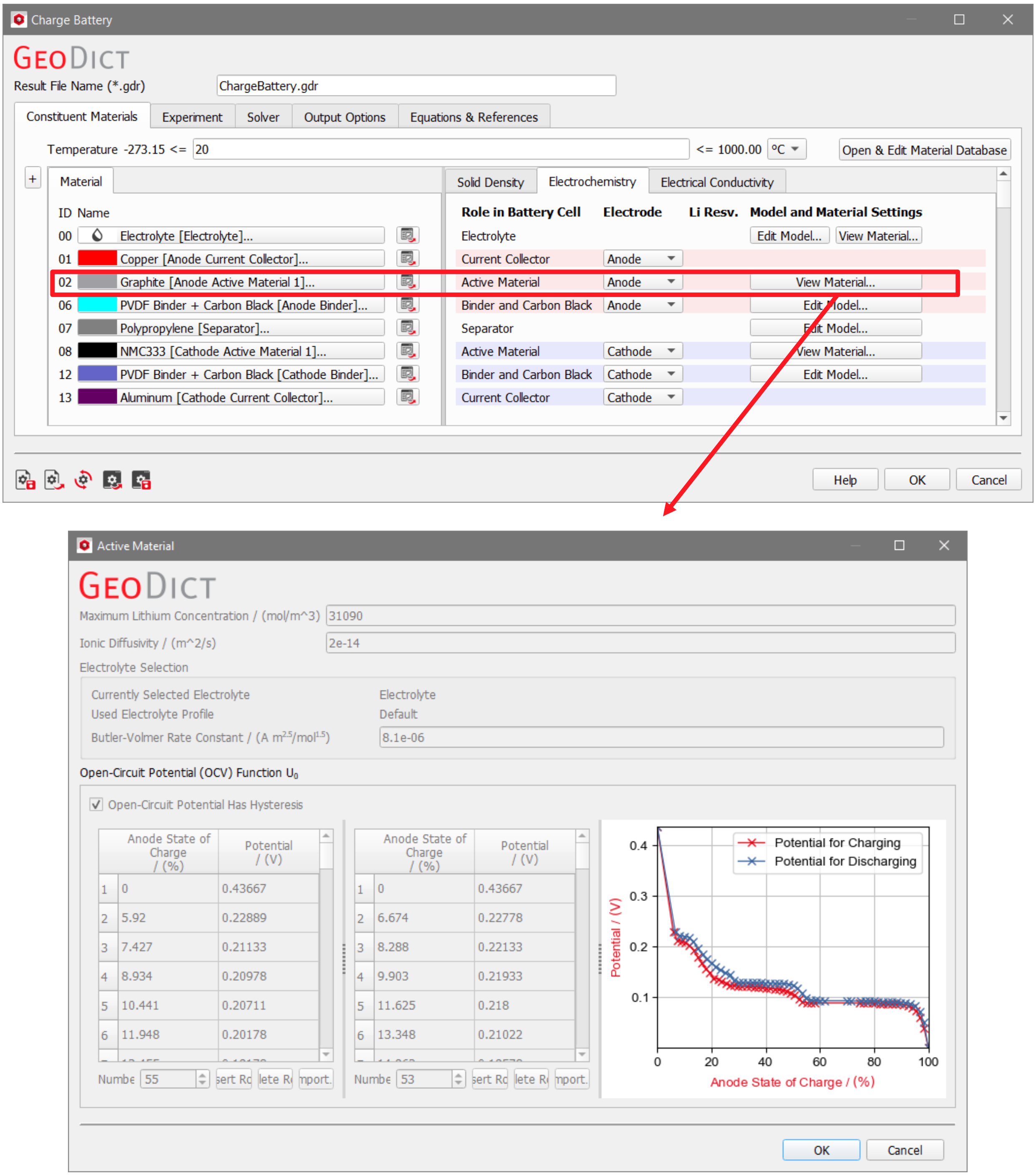
| Role in Battery Cell | Electrode | Li Resv. | Model and Material Settings |
|---|---|---|---|
| Electrolyte | | | Edit Model... View Material... |
| Current Collector | Anode | | |
| Active Material | Anode | | View Material... |
| Binder and Carbon Black | Anode | | Edit Model... |
| Separator | | | Edit Model... |
| Active Material | Cathode | | View Material... |
| Binder and Carbon Black | Cathode | | Edit Model... |
| Current Collector | Cathode | | |

The **Temperature** defines the temperature during simulation in Kelvin (K), Celsius (°C) or Fahrenheit (°F). The material properties of active materials and electrolyte can strongly depend on the temperature. Because this temperature-dependence of the electrochemical material parameters is not considered in the equations solved during charging or discharging, the temperature defined here needs to be consistent with the material properties defined for the materials below.

Material IDs of the structure and the assigned materials are listed on the left of the tab under **Material**.

Material properties are organized on three different subtabs on the right, **Solid Density**, **Electrochemistry**, and **Electrical Conductivity**.

In the **Electrochemistry** subtab, materials are highlighted according to the electrode they belong to. All anode materials (active materials, binder and carbon black, and the current collector) are highlighted in pink, all cathode materials in purple.



Result File Name (*.gdr): ChargeBattery.gdr

Temperature -273.15 <= 20 <= 1000.00 °C

| ID | Name |
|---|---|
| 00 | Electrolyte [Electrolyte]... |
| 01 | 🟥 Copper [Anode Current Collector]... |
| 02 | Graphite [Anode Active Material 1]... |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... |
| 07 | Polypropylene [Separator]... |
| 08 | NMC333 [Cathode Active Material 1]... |
| 12 | PVDF Binder + Carbon Black [Cathode Binder]... |
| 13 | Aluminum [Cathode Current Collector]... |

| Role in Battery Cell | Electrode | Li Resv. | Model and Material Settings |
|---|---|---|---|
| Electrolyte | | | Edit Model... View Material... |
| Current Collector | Anode | | |
| Active Material | Anode | | View Material... |
| Binder and Carbon Black | Anode | | Edit Model... |
| Separator | | | Edit Model... |
| Active Material | Cathode | | View Material... |
| Binder and Carbon Black | Cathode | | Edit Model... |
| Current Collector | Cathode | | |

Maximum Lithium Concentration / (mol/m^3): 31090

Ionic Diffusivity / (m^2/s): 2e-14

Electrolyte Selection

Currently Selected Electrolyte: Electrolyte

Used Electrolyte Profile: Default

Butler-Volmer Rate Constant / (A $m^{2.5}$/$mol^{1.5}$): 8.1e-06

Open-Circuit Potential (OCV) Function $U_0$

☑ Open-Circuit Potential Has Hysteresis

| | Anode State of Charge / (%) | Potential / (V) |
|---|---|---|
| 1 | 0 | 0.43667 |
| 2 | 5.92 | 0.22889 |
| 3 | 7.427 | 0.21133 |
| 4 | 8.934 | 0.20978 |
| 5 | 10.441 | 0.20711 |
| 6 | 11.948 | 0.20178 |

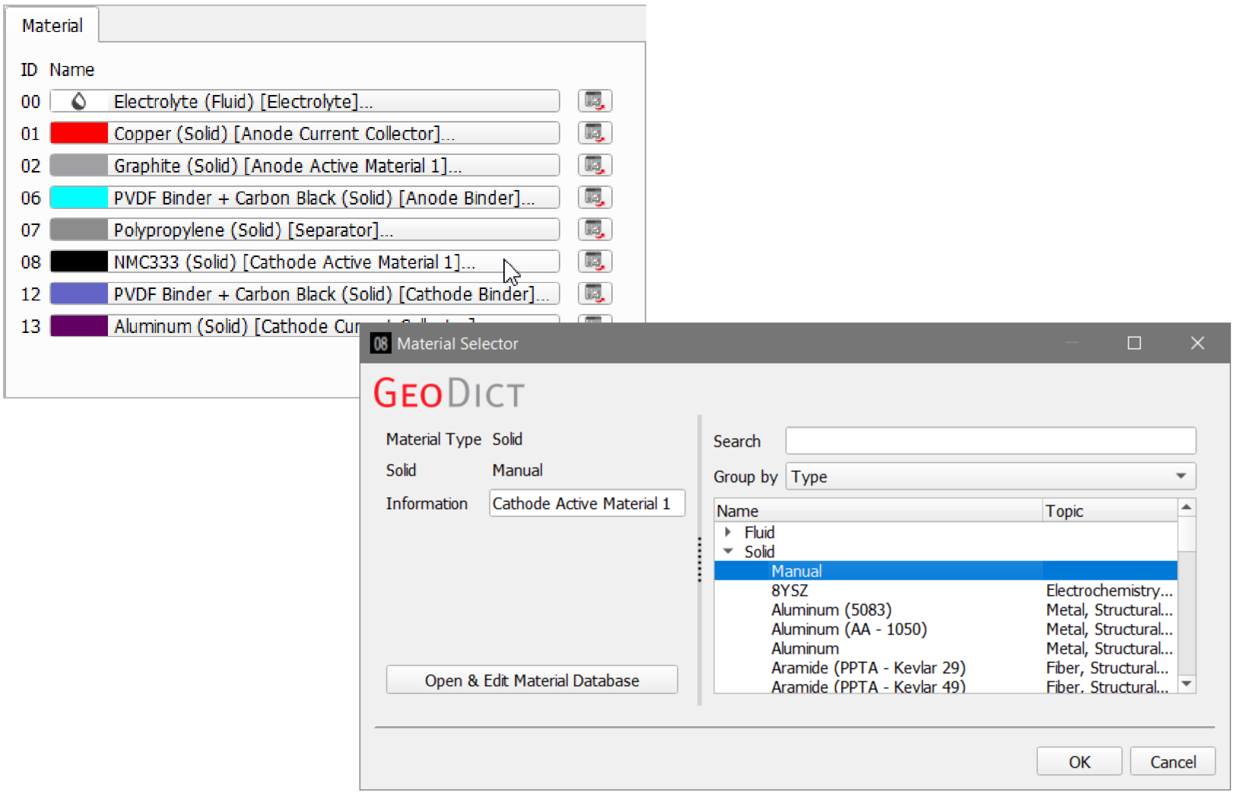
Numbe 55

| | Anode State of Charge / (%) | Potential / (V) |
|---|---|---|
| 1 | 0 | 0.43667 |
| 2 | 6.674 | 0.22778 |
| 3 | 8.288 | 0.22133 |
| 4 | 9.903 | 0.21933 |
| 5 | 11.625 | 0.218 |
| 6 | 13.348 | 0.21022 |

Numbe 53

If a material from the GeoDict Material Database is selected for a Material ID (e.g. for ID 02 in the example shown), all parameters are set according to the database values. The electrochemical role of the material (here: Anode Active Material) is shown and the electrochemical parameters can be displayed by clicking the **View Material** button for electrolyte and active materials. For all electrochemical roles of the materials, the database values for Solid Density and Electrical Conductivity are shown on the correspondent subtabs. For more details on the parameters displayed and selectable see Parameter Options Dialogs section below.

The assigned material can be changed by clicking the material of an ID to open the **Material Selector** dialog. Choose another material from the database, or select **Manual**, to edit the material's properties.


Material

| ID | Name |
|---|---|
| 00 | Electrolyte (Fluid) [Electrolyte]... |
| 01 | Copper (Solid) [Anode Current Collector]... |
| 02 | Graphite (Solid) [Anode Active Material 1]... |
| 06 | PVDF Binder + Carbon Black (Solid) [Anode Binder]... |
| 07 | Polypropylene (Solid) [Separator]... |
| 08 | NMC333 (Solid) [Cathode Active Material 1]... |
| 12 | PVDF Binder + Carbon Black (Solid) [Cathode Binder]... |
| 13 | Aluminum (Solid) [Cathode Cur |

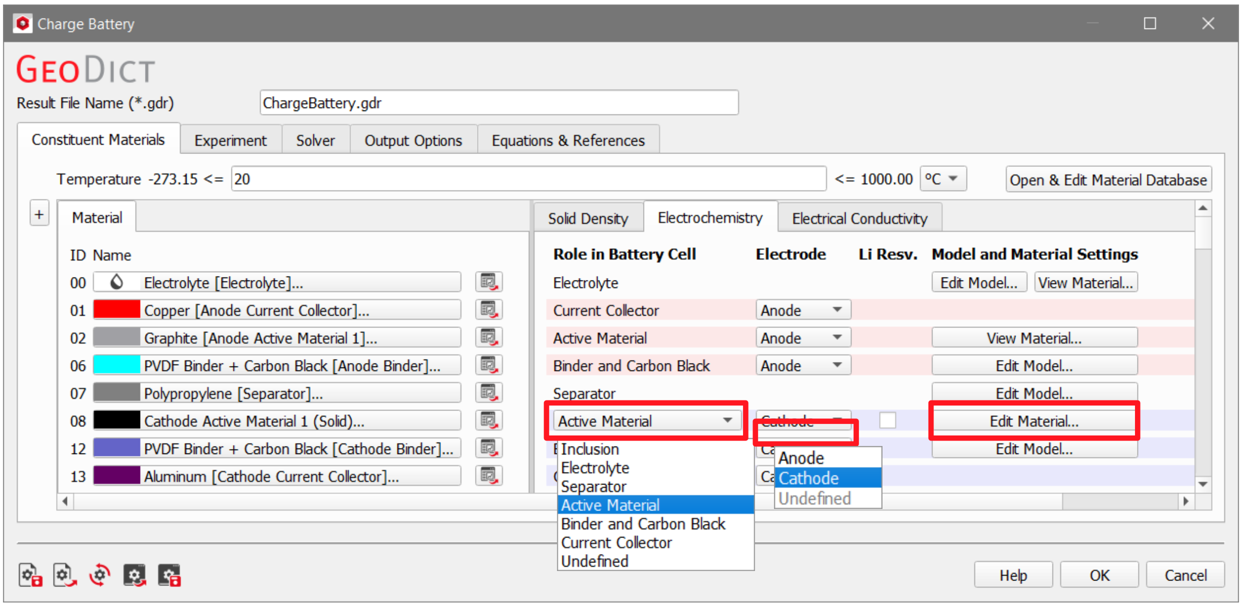
08 Material Selector

Material Type: Solid
Solid: Manual
Information: Cathode Active Material 1

Search:
Group by: Type

| Name | Topic |
|---|---|
| Fluid | |
| Solid | |
| Manual | |
| 8YSZ | Electrochemistry... |
| Aluminum (5083) | Metal, Structural... |
| Aluminum (AA - 1050) | Metal, Structural... |
| Aluminum | Metal, Structural... |
| Aramide (PPTA - Kevlar 29) | Fiber, Structural... |
| Aramide (PPTA - Kevlar 49) | Fiber, Structural... |

Now, the electrochemical role of the material and the electrode it belongs to can be selected or changed, and the electrochemical parameters can be modified.


Charge Battery

Result File Name (*.gdr): ChargeBattery.gdr

Temperature -273.15 <= 20 <= 1000.00 °C

| ID | Name |
|---|---|
| 00 | Electrolyte [Electrolyte]... |
| 01 | Copper [Anode Current Collector]... |
| 02 | Graphite [Anode Active Material 1]... |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... |
| 07 | Polypropylene [Separator]... |
| 08 | Cathode Active Material 1 (Solid)... |
| 12 | PVDF Binder + Carbon Black [Cathode Binder]... |
| 13 | Aluminum [Cathode Current Collector]... |

| Role in Battery Cell | Electrode | Li Resv. | Model and Material Settings |
|---|---|---|---|
| Electrolyte | | | Edit Model... View Material... |
| Current Collector | Anode | | |
| Active Material | Anode | | View Material... |
| Binder and Carbon Black | Anode | | Edit Model... |
| Separator | | | Edit Model... |
| Active Material | Cathode | ☐ | Edit Material... |
| Inclusion | | | Edit Model... |

The electrochemical roles Separator, Binder and Carbon Black for each electrode and Current Collector for each electrode, can each be selected only for one material in the structure.

For all solid state batteries, the separator should be reassigned to the same material ID as the solid electrolyte using **Model** → **ProcessGeo** → **Reassign Materials & IDs**, and selecting the command Reassign Material ID.

The simulation cannot be started if one of the materials has the role Undefined or if the electrode type is Undefined for an active material, binder & carbon black or a current collector. If one of the materials has no active role in the charging process, assign the electrochemical role Inclusion to it. No conduction is possible for a material defined as Inclusion, it has no potential, and does not contain lithium.

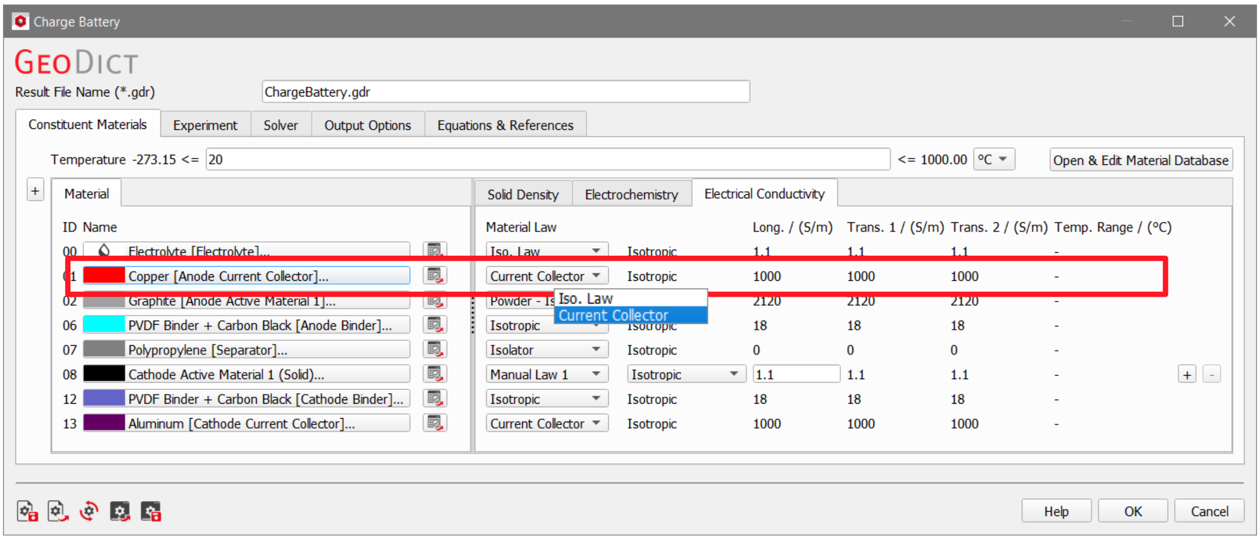
Clicking **Edit Material** opens the property dialog for active materials or electrolyte for editing the values, **Edit Model** allows to change the binder and carbon black or separator model. See Parameter Options Dialogs section below for more details.

If the box **Lithium reservoir** is checked for a Cathode Active Material or an Anode Active Material, the **Edit Material** button changes to an **Edit Model** button and allows to change the Butler-Volmer rate constant. The active material is in this case modelled as a lithium reservoir (necessary for half cell simulations). The solver will treat this material as a never-ending reservoir, not limiting the battery performance. Only one material can be modelled as lithium reservoir. Note that the lithium reservoir is modelled as a Manual material. Assigning lithium from the material database will not work to model a lithium reservoir in BatteryDict.

In the same way, on the other subtabs, the **Solid Density** and the **Electrical Conductivity** are shown (for materials from the Material Database) or can be selected (for Manual materials).

For numerical reasons, the electrical conductivity of the current collectors and the lithium reservoir used in the simulations should be limited to 1000 S/m instead of using the physical conductivities of the metals, to avoid large contrasts in electrical conductivities in the battery structure. 1000 S/m is a sufficiently high value for the electrical conductivity to not be a limiting factor during the charging simulations. Reducing the electrical conductivities to this value will not influence the overall battery performance but allowing a faster convergence of the solver.

Therefore, the lithium reservoir and Manual materials for the current collectors have 1000 S/m as electrical conductivity by default. If the material for the current collector is not set to Manual, but to a material from the Material Database (e.g. copper or aluminum), make sure that the **Material Law Current Collector** is selected for the electrical conductivity to limit the electrical conductivity to 1000 S/m.



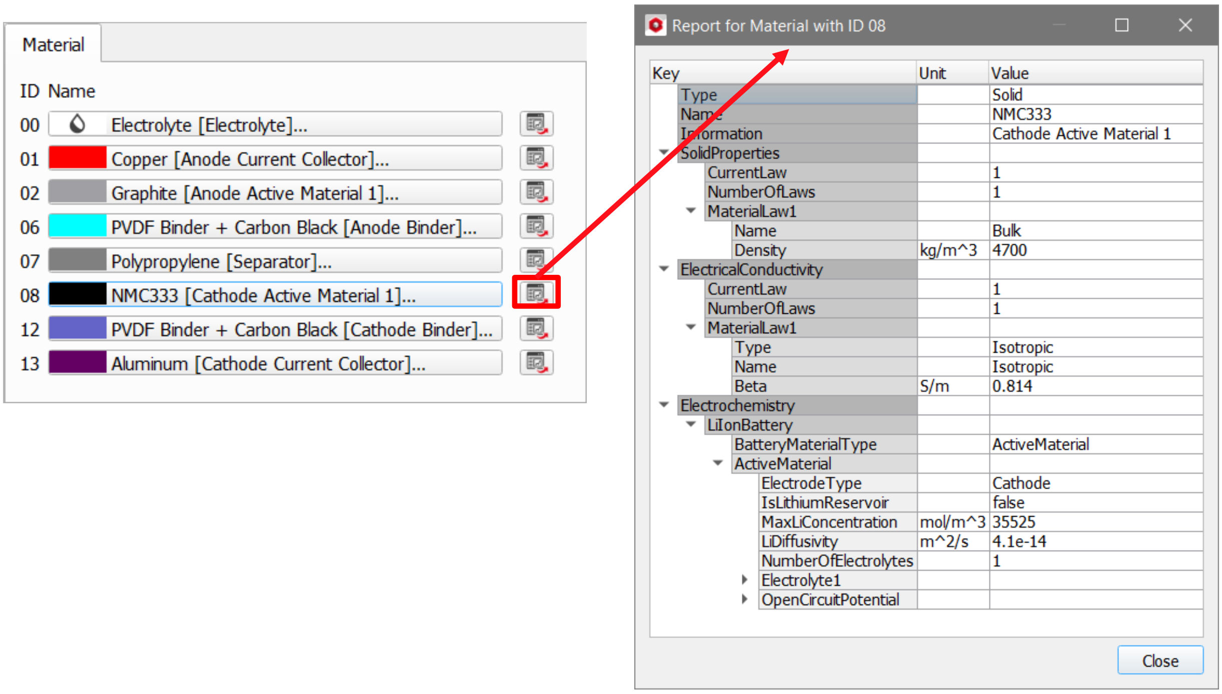
Result File Name (*.gdr): ChargeBattery.gdr

Temperature -273.15 <= 20 <= 1000.00 °C

| ID | Name | Material Law | | Long. / (S/m) | Trans. 1 / (S/m) | Trans. 2 / (S/m) | Temp. Range / (°C) |
|---|---|---|---|---|---|---|---|
| 00 | Electrolyte [Electrolyte]... | Iso. Law | Isotropic | 1.1 | 1.1 | 1.1 | - |
| 01 | Copper [Anode Current Collector]... | Current Collector | Isotropic | 1000 | 1000 | 1000 | - |
| 02 | Graphite [Anode Active Material 1]... | Powder - Is | | 2120 | 2120 | 2120 | - |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... | Isotropic | Isotropic | 18 | 18 | 18 | - |
| 07 | Polypropylene [Separator]... | Isolator | Isotropic | 0 | 0 | 0 | - |
| 08 | Cathode Active Material 1 (Solid)... | Manual Law 1 | Isotropic | 1.1 | 1.1 | 1.1 | - |
| 12 | PVDF Binder + Carbon Black [Cathode Binder]... | Isotropic | Isotropic | 18 | 18 | 18 | - |
| 13 | Aluminum [Cathode Current Collector]... | Current Collector | Isotropic | 1000 | 1000 | 1000 | - |

For the separator, always 0 S/m is shown as a default value on this tab. Actually, this value has no influence on the simulation. In case the porosity of the separator is not modelled, it gets the same ionic conductivity as the electrolyte. In case the separator is modelled as porous material, it is defined by the user settings in the dialog **Separator Model Parameters**, see page 51.

Click the **Material Report** button, available on the right of each material, to access all parameters of the material, relevant for the charging simulation.



| ID | Name |
|---|---|
| 00 | Electrolyte [Electrolyte]... |
| 01 | Copper [Anode Current Collector]... |
| 02 | Graphite [Anode Active Material 1]... |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... |
| 07 | Polypropylene [Separator]... |
| 08 | NMC333 [Cathode Active Material 1]... |
| 12 | PVDF Binder + Carbon Black [Cathode Binder]... |
| 13 | Aluminum [Cathode Current Collector]... |

| Key | Unit | Value |
|---|---|---|
| Type | | Solid |
| Name | | NMC333 |
| Information | | Cathode Active Material 1 |
| SolidProperties | | |
| CurrentLaw | | 1 |
| NumberOfLaws | | 1 |
| MaterialLaw1 | | |
| Name | | Bulk |
| Density | kg/m^3 | 4700 |
| ElectricalConductivity | | |
| CurrentLaw | | 1 |
| NumberOfLaws | | 1 |
| MaterialLaw1 | | |
| Type | | Isotropic |
| Name | | Isotropic |
| Beta | S/m | 0.814 |
| Electrochemistry | | |
| LiIonBattery | | |
| BatteryMaterialType | | ActiveMaterial |
| ActiveMaterial | | |
| ElectrodeType | | Cathode |
| IsLithiumReservoir | | false |
| MaxLiConcentration | mol/m^3 | 35525 |
| LiDiffusivity | m^2/s | 4.1e-14 |
| NumberOfElectrolytes | | 1 |
| Electrolyte1 | | |
| OpenCircuitPotential | | |

## PARAMETER OPTIONS DIALOGS

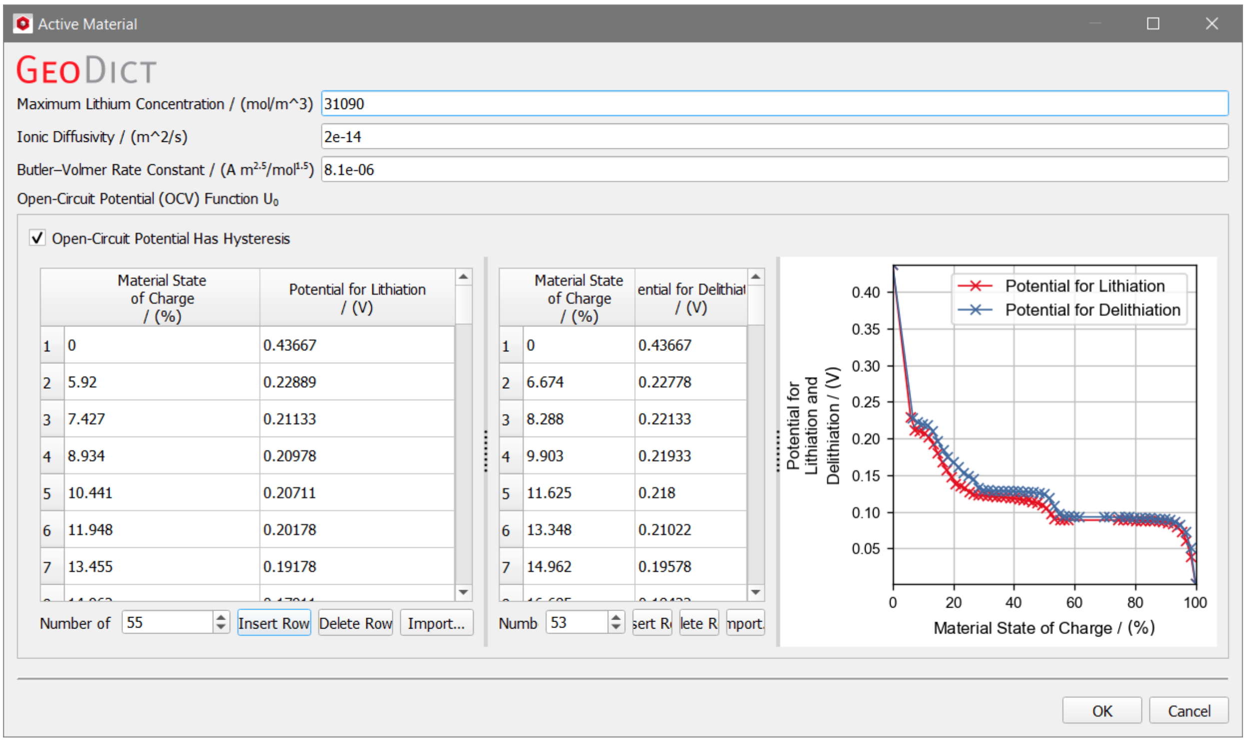
Parameter dialogs for active materials, binder and carbon black, separator, and electrolyte are explained in the following. For an explanation of the meaning of the parameters, see Simulation Parameters above.

### ACTIVE MATERIAL PARAMETER DIALOG

For all active materials, the simulation parameters **Maximum Lithium Concentration**, **Ionic Diffusivity**, **Butler-Volmer Rate Constant**, and **Open-Circuit Potential Function** (OCV) need to be defined.

If a material from the GeoDict Material Database is used for an active material, values are shown in the **Active Material** dialog. They are shown in gray and cannot be changed.

In case **Manual (Solid)** is selected as active material, the simulation parameters can be set in the **Active Material** dialog.



Maximum Lithium Concentration / (mol/m^3) 31090

Ionic Diffusivity / (m^2/s) 2e-14

Butler–Volmer Rate Constant / (A $m^{2.5}/mol^{1.5}$) 8.1e-06

Open-Circuit Potential (OCV) Function $U_0$

☑ Open-Circuit Potential Has Hysteresis

| | Material State of Charge / (%) | Potential for Lithiation / (V) |
|---|---|---|
| 1 | 0 | 0.43667 |
| 2 | 5.92 | 0.22889 |
| 3 | 7.427 | 0.21133 |
| 4 | 8.934 | 0.20978 |
| 5 | 10.441 | 0.20711 |
| 6 | 11.948 | 0.20178 |
| 7 | 13.455 | 0.19178 |

Number of 55

| | Material State of Charge / (%) | ential for Delithiat / (V) |
|---|---|---|
| 1 | 0 | 0.43667 |
| 2 | 6.674 | 0.22778 |
| 3 | 8.288 | 0.22133 |
| 4 | 9.903 | 0.21933 |
| 5 | 11.625 | 0.218 |
| 6 | 13.348 | 0.21022 |
| 7 | 14.962 | 0.19578 |

Numb 53

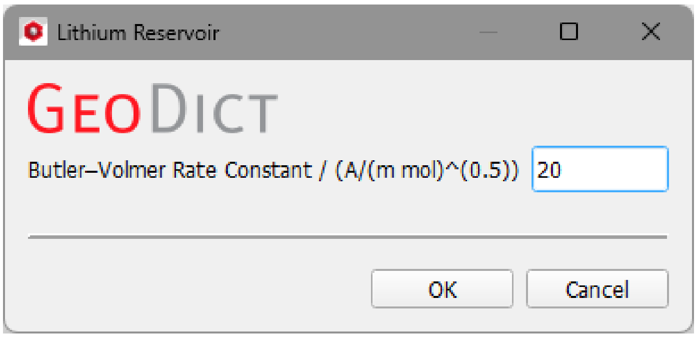
Parameters of the material from the Material Database, that was last selected for the ID, are shown, and can be modified.

Values defining the **Open-Circuit Potential Function** can be modified directly in the table. Additionally, the number of value points can be changed by deleting or inserting new rows. Another possibility is to import the **Open-Circuit Potential Function** from a text file with two columns. The first column contains the material state of charge in percent, and the second column shows the related potential.

The chosen function is displayed as **Potential for Lithiation and Delithiation** over **Material State of Charge** in the plot on the right of the table.

If the Open-Circuit Potential Function is different for lithiation and delithiation, check the box **Open-Circuit Potential Has Hysteresis** and define one OCV function for lithiation and a different one for delithiation.

In case the active material of an electrode is defined as Lithium reservoir, with **Edit Model ...**, the Butler-Volmer Rate Constant can be defined.



Butler–Volmer Rate Constant / (A/(m mol)^(0.5)) 20

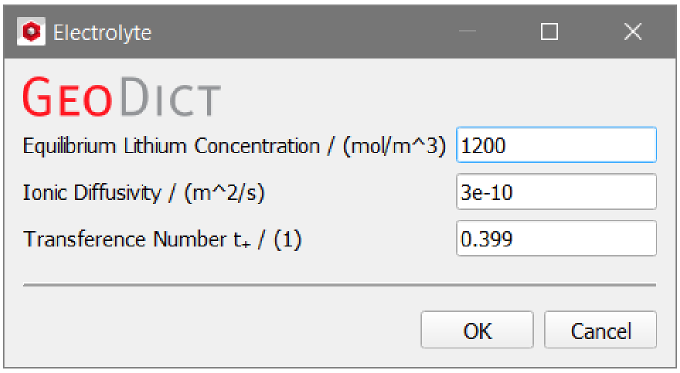
No other parameters need to be set for a lithium reservoir, since it will be considered as a never-ending reservoir of lithium, not limiting the battery performance.

### Electrolyte Parameter Dialog

For the electrolyte, the **Equilibrium Lithium Concentration**, **Ionic Diffusivity**, and **Transference Number** need to be defined (see Simulation Parameters above).

If a material from the GeoDict Material Database is selected for the electrolyte, values are shown in the **Electrolyte** dialog, but cannot be changed.

Set the electrolyte to **Manual (Fluid)** or **Manual (Solid)** and click **Edit Material** to modify the parameters.



Equilibrium Lithium Concentration / (mol/m^3) 1200

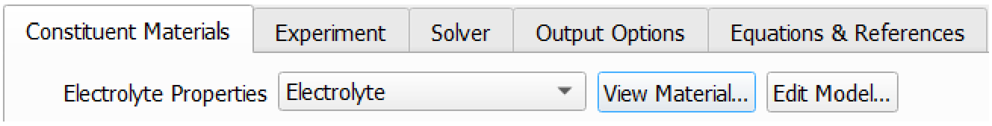
Ionic Diffusivity / (m^2/s) 3e-10

Transference Number $t_+$ / (1) 0.399

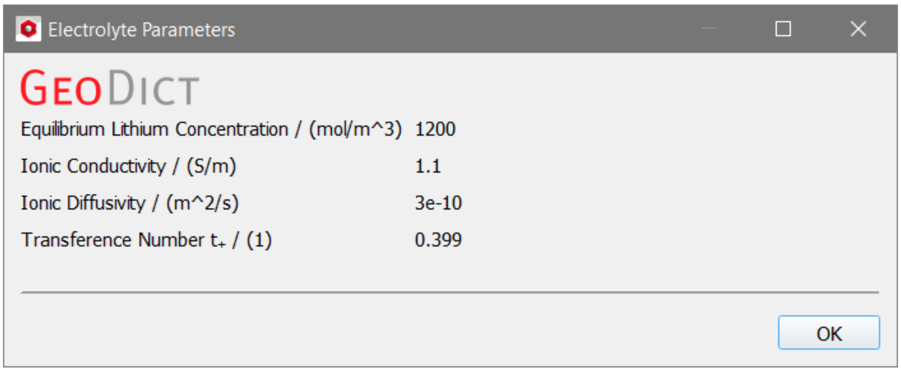
The ionic conductivity of the electrolyte is the value for the electrical conductivity defined on the **Electrical Conductivity** tab. In the case of electrolyte materials, the electrical conductivity corresponds to the ionic conductivity, since they have no electronic conductivity.

For solid electrolyte, use the LIR solver (see page 59) and set the transference number to 1, to switch off the term of electron migration due to concentration differences in (8).

If no material ID with material defined as electrolyte exists, the electrolyte can be defined in the upper part of the Constituent Materials tab. In this case, no electrolyte exists in both electrodes, but only in the separator and in the binder, if it is modelled as porous material.

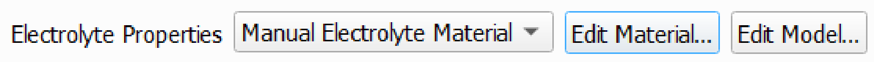


Electrolyte Properties Electrolyte

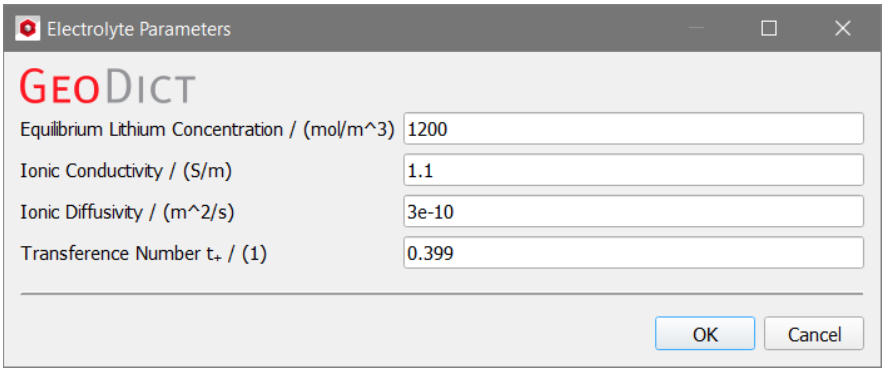


Equilibrium Lithium Concentration / (mol/m^3) 1200
Ionic Conductivity / (S/m) 1.1
Ionic Diffusivity / (m^2/s) 3e-10
Transference Number $t_+$ / (1) 0.399

In this case, the ionic conductivity is shown additionally in the Electrolyte dialog, and can be set here, like the other parameters, if Manual Electrolyte Material is selected.



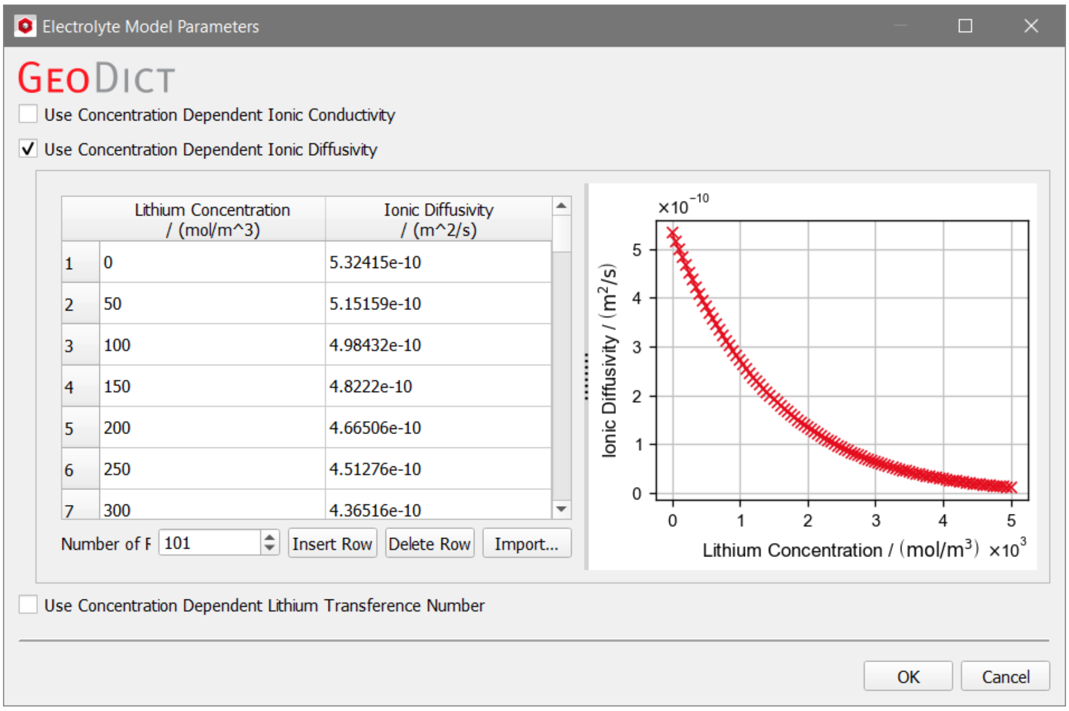
Electrolyte Properties: Manual Electrolyte Material



Equilibrium Lithium Concentration / (mol/m^3) 1200
Ionic Conductivity / (S/m) 1.1
Ionic Diffusivity / (m^2/s) 3e-10
Transference Number $t_+$ / (1) 0.399

Since GeoDict 2023, electrolyte parameters can be modelled depending on the lithium concentration.

Click the **Edit Model** button for the electrolyte to open the Electrolyte Model Parameters dialog. Check the parameter that should be modelled concentration dependent.



☐ Use Concentration Dependent Ionic Conductivity
☑ Use Concentration Dependent Ionic Diffusivity

| | Lithium Concentration / (mol/m^3) | Ionic Diffusivity / (m^2/s) |
|---|---|---|
| 1 | 0 | 5.32415e-10 |
| 2 | 50 | 5.15159e-10 |
| 3 | 100 | 4.98432e-10 |
| 4 | 150 | 4.8222e-10 |
| 5 | 200 | 4.66506e-10 |
| 6 | 250 | 4.51276e-10 |
| 7 | 300 | 4.36516e-10 |

Number of F 101

☐ Use Concentration Dependent Lithium Transference Number

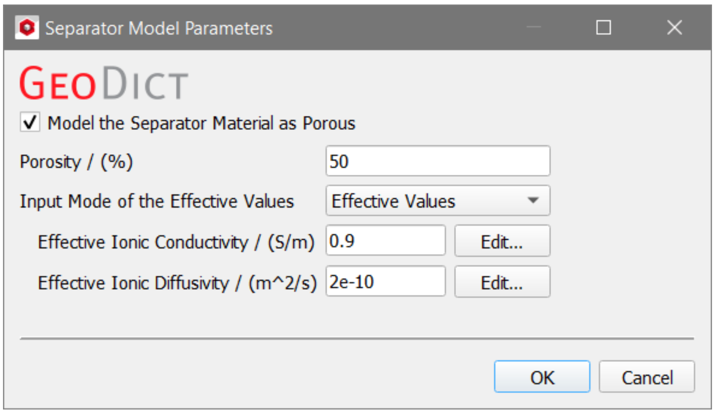
Note that concentration dependent parameters are not yet available for the LIR solver. Therefore, if the LIR solver is selected, the **Edit Model** button is grayed out and a warning is shown if values are selected anyway, ⚠ Edit Model... .

### SEPARATOR MODEL PARAMETERS

If the box **Model the Separator Material as Porous** is unchecked, the porosity of the separator is not considered and the separator gets the same properties as the electrolyte. Since it is filled with electrolyte, this assumption is reasonable if the properties are not influenced by the microstructure of the separator. In the case of solid state batteries, the separator is composed of solid electrolyte. We recommend to reassign the separator material ID with the material ID of the solid electrolyte (see page 46).

If separator properties are influenced by the separator microstructure, check **Model the Separator Material as Porous** and define the porosity of the separator. An **Effective Ionic Conductivity** and an **Effective Ionic Diffusivity** to account for the influence of the separator microstructure are in this case necessary.

To define the effective values directly, choose **Effective Values** as **Input Mode of the Effective Values**.



☑ Model the Separator Material as Porous

Porosity / (%): 50

Input Mode of the Effective Values: Effective Values

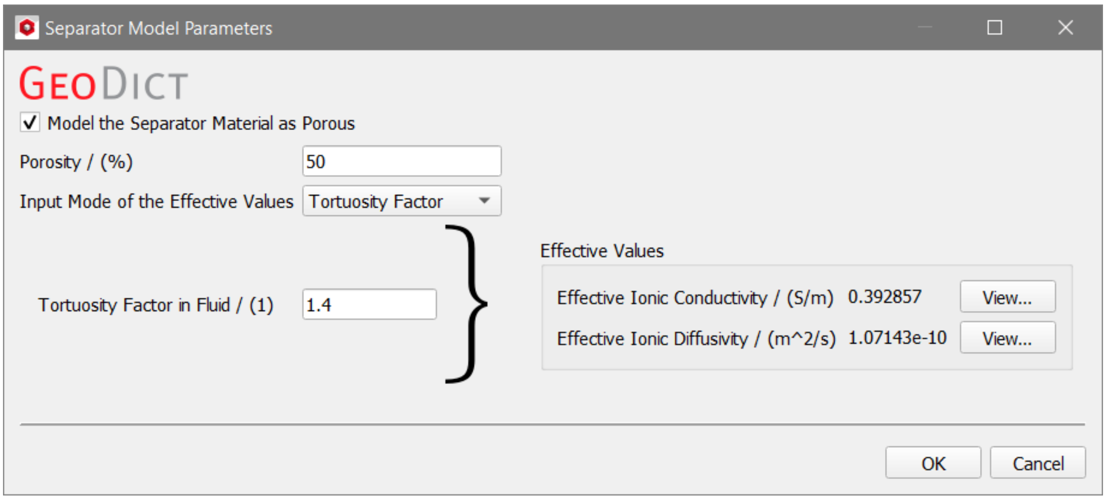
Effective Ionic Conductivity / (S/m): 0.9

Effective Ionic Diffusivity / (m^2/s): 2e-10

Set the **Input Mode of the Effective Values** to **Tortuosity Factor** to define the tortuosity factor in the fluid instead. The effective values are computed from the tortuosity factor, the porosity and the electrolyte properties. The effective diffusivity $D_{eff}$ (and analogous the ionic conductivity) is calculated by the equation

$$D_{eff} = \frac{\varepsilon}{\kappa_{fluid}} \cdot D_0$$

where $\varepsilon$ is the porosity, $\kappa_{fluid}$ the tortuosity factor in the fluid, and $D_0$ the diffusivity of the electrolyte (see also the section *Compute Tortuosity* in the GeoApp handbook). In case the electrolyte properties are not concentration dependent (see page 50), effective values are displayed directly in the dialog.



☑ Model the Separator Material as Porous

Porosity / (%): 50

Input Mode of the Effective Values: Tortuosity Factor

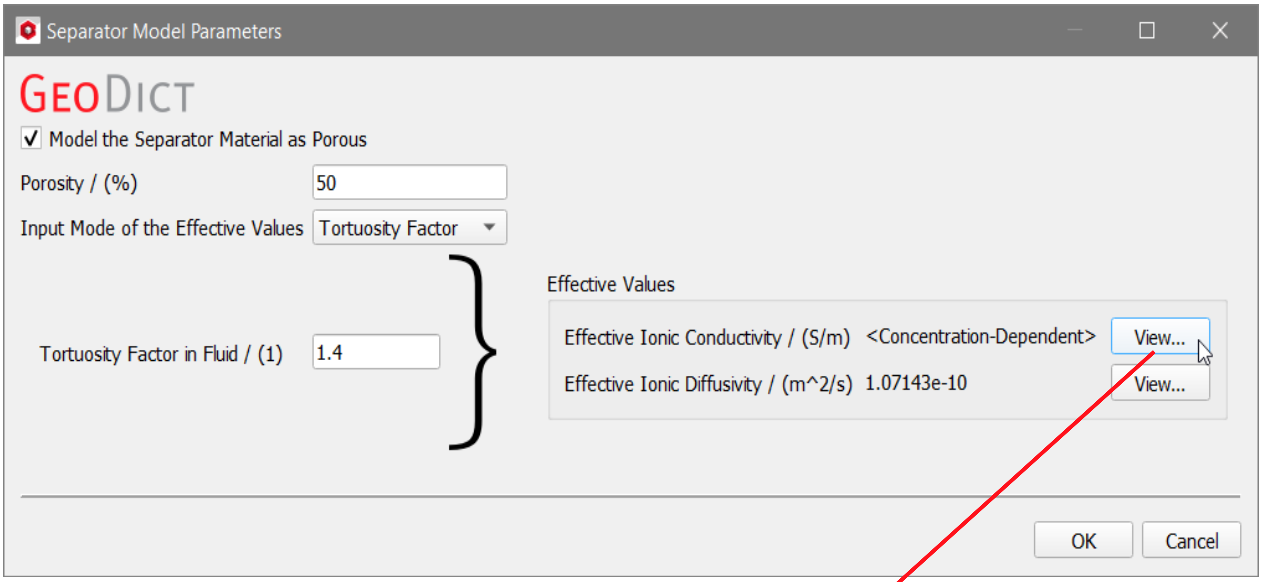
Tortuosity Factor in Fluid / (1): 1.4

Effective Values

Effective Ionic Conductivity / (S/m): 0.392857

Effective Ionic Diffusivity / (m^2/s): 1.07143e-10

For concentration dependent electrolyte properties (here ionic conductivity), also the effective parameters of the separator depend on the lithium concentration. Click **View** to show the concentration dependence of the effective values.



☑ Model the Separator Material as Porous

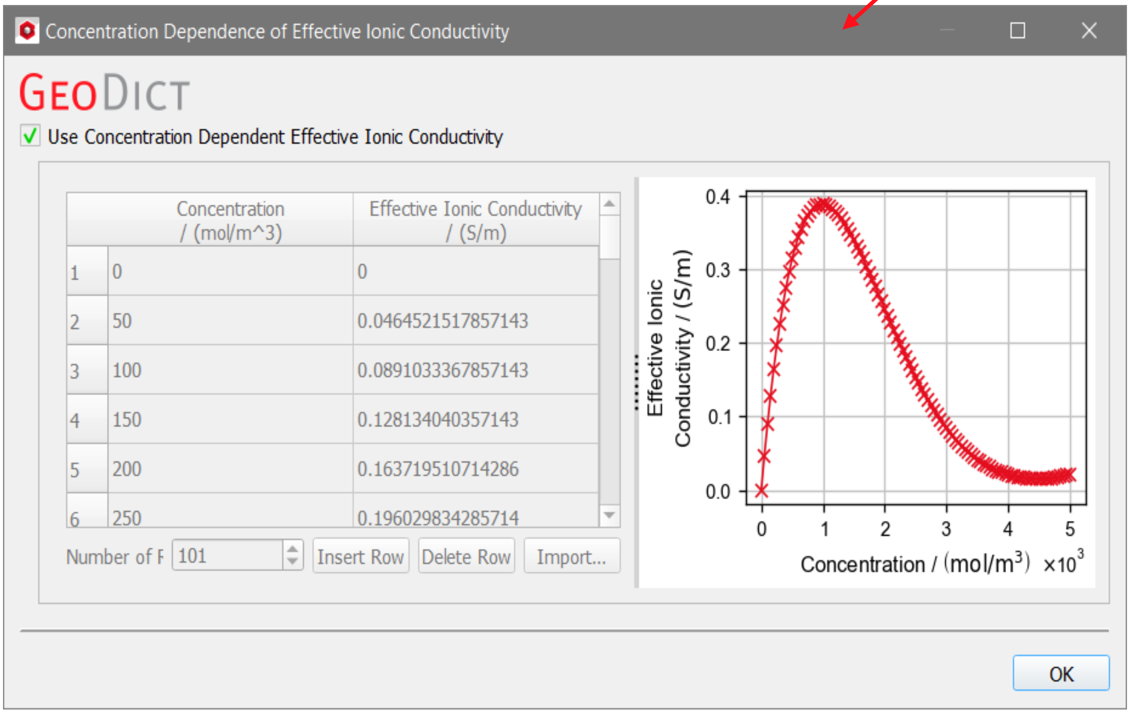
Porosity / (%) 50

Input Mode of the Effective Values Tortuosity Factor

Tortuosity Factor in Fluid / (1) 1.4

Effective Ionic Conductivity / (S/m) <Concentration-Dependent>

Effective Ionic Diffusivity / (m^2/s) 1.07143e-10



☑ Use Concentration Dependent Effective Ionic Conductivity

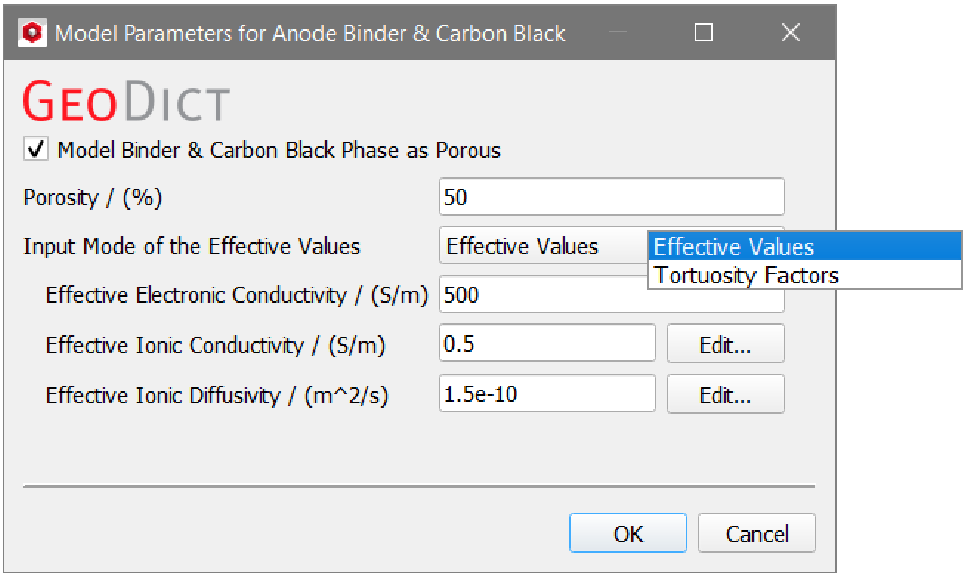
| | Concentration / (mol/m^3) | Effective Ionic Conductivity / (S/m) |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 50 | 0.0464521517857143 |
| 3 | 100 | 0.0891033367857143 |
| 4 | 150 | 0.128134040357143 |
| 5 | 200 | 0.163719510714286 |
| 6 | 250 | 0.196029834285714 |

Number of F 101

## BINDER & CARBON BLACK PARAMETER DIALOG

If the binder is modelled as solid material, leave the box **Model Binder & Carbon Black Phase as Porous** unchecked. In this case, only the electronic conductivity of the binder and carbon black material is used for the simulation. This value is defined by the electrical conductivity on the **Electrical Conductivity** tab. For binder and carbon black material, with no ionic conductivity, electrical and electronic conductivity are equivalent.

To model binder and carbon black with unresolved electrolyte pores in the simulation, check **Model Binder & Carbon Black Phase as Porous**. In this case, define the **Porosity** of the binder and carbon black material.


Model Parameters for Anode Binder & Carbon Black

☑ Model Binder & Carbon Black Phase as Porous

Porosity / (%): 50

Input Mode of the Effective Values: Effective Values

Effective Electronic Conductivity / (S/m): 500

Effective Ionic Conductivity / (S/m): 0.5

Effective Ionic Diffusivity / (m^2/s): 1.5e-10

The **Effective Electronic Conductivity**, the **Effective Ionic Conductivity** and the **Effective Ionic Diffusivity** can be defined in two different ways by choosing the **Input Mode of the Effective Values**:

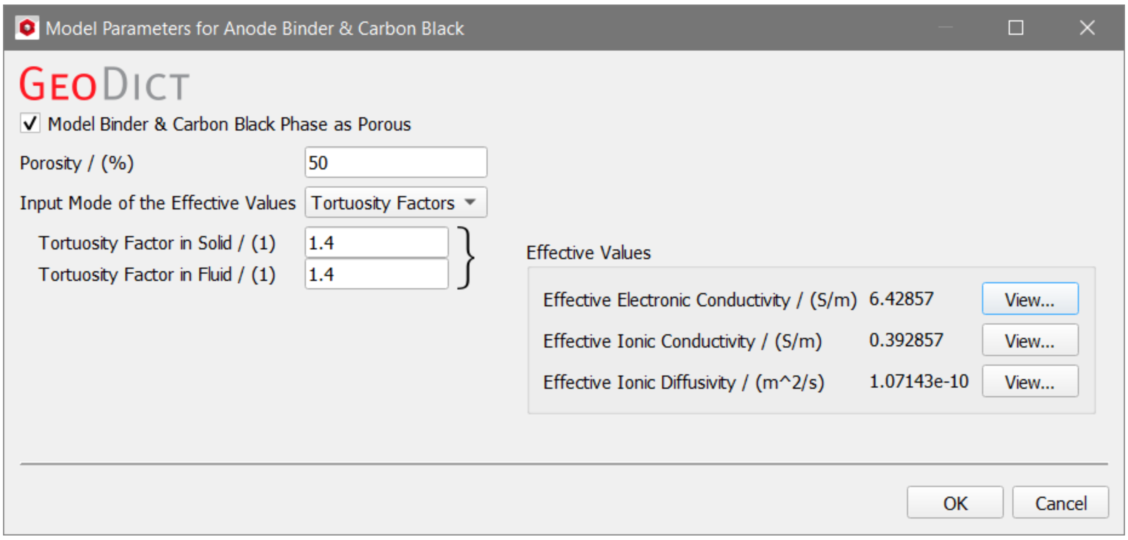
- Select **Effective Values** to define the properties directly.
- Or choose **Tortuosity Factors** to set tortuosity factor values for both solid and fluid. Effective values are computed and shown on the right of the dialog in case electrolyte values are not concentration dependent. They cannot be changed there.

  The effective electronic conductivity $\sigma_{eff}$ is calculated by the equation

  $$\sigma_{eff} = \frac{1-\varepsilon}{\kappa_{solid}} \cdot \sigma_0$$

  where $\varepsilon$ is the porosity, $\kappa_{solid}$ the tortuosity factor in the solid, and $\sigma_0$ the electronic conductivity of the (non-porous) Binder & Carbon Black material. The ionic conductivity and ionic diffusivity are calculated using the provided tortuosity factor in the fluid and the parameters from the electrolyte with the same equation as given above for the separator.

  For details, see also the section *Compute Tortuosity* in the GeoApp handbook.


Model Parameters for Anode Binder & Carbon Black

☑ Model Binder & Carbon Black Phase as Porous

Porosity / (%): 50

Input Mode of the Effective Values: Tortuosity Factors

Tortuosity Factor in Solid / (1): 1.4

Tortuosity Factor in Fluid / (1): 1.4

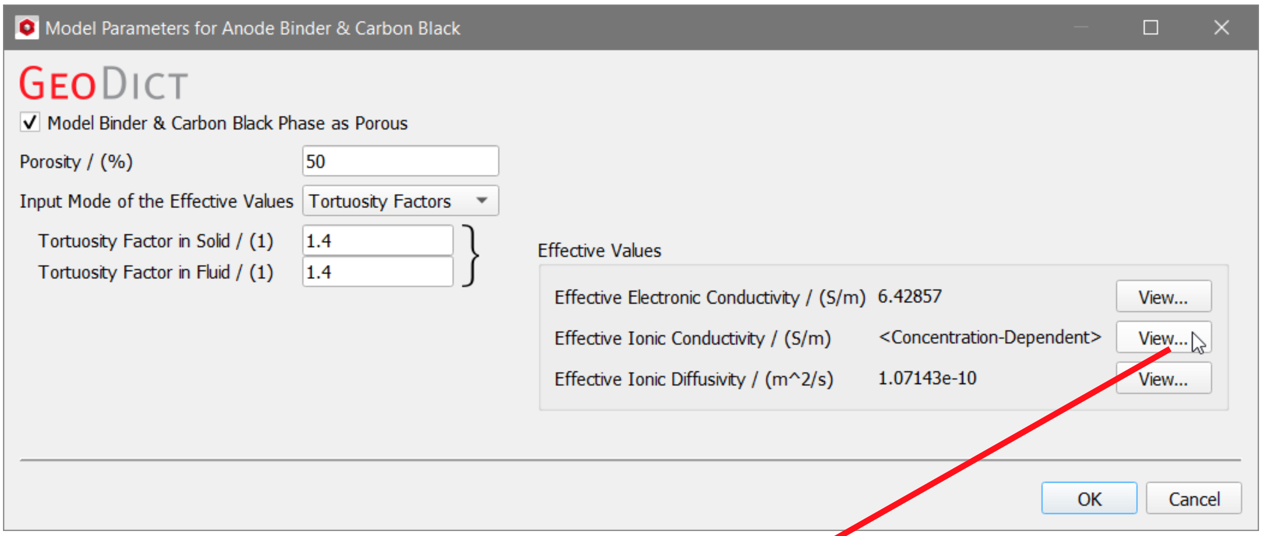
Effective Values

Effective Electronic Conductivity / (S/m): 6.42857

Effective Ionic Conductivity / (S/m): 0.392857

Effective Ionic Diffusivity / (m^2/s): 1.07143e-10

For concentration dependent electrolyte properties (here ionic conductivity), also the effective parameters of the separator depend on the lithium concentration. Click **View** to show the concentration dependence of the effective values.



Model Parameters for Anode Binder & Carbon Black

☑ Model Binder & Carbon Black Phase as Porous

Porosity / (%): 50

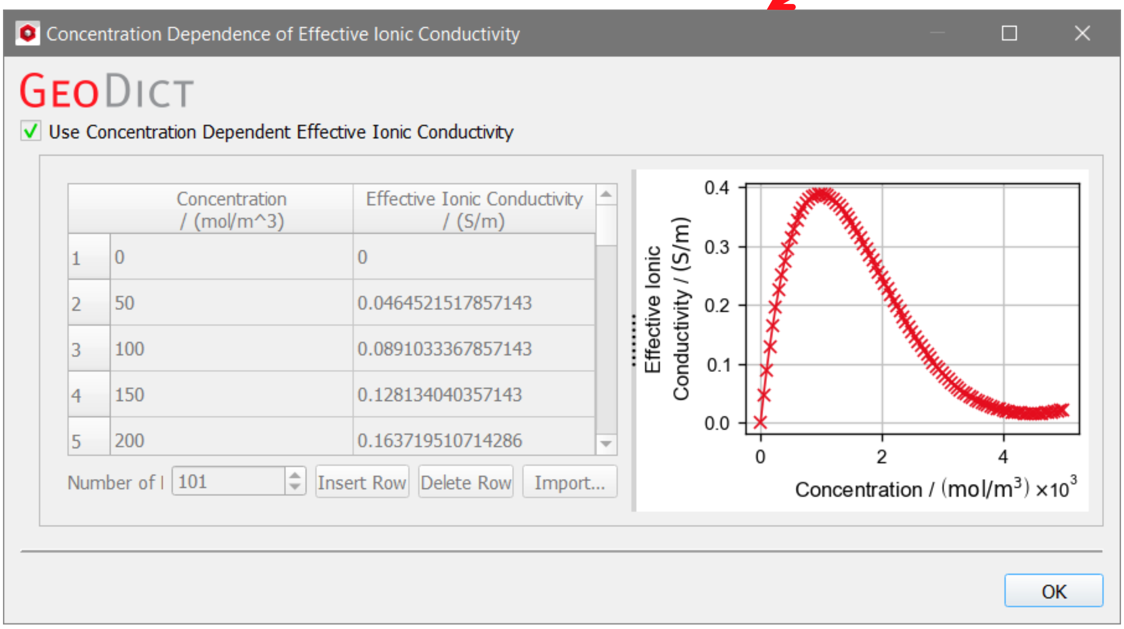
Input Mode of the Effective Values: Tortuosity Factors

Tortuosity Factor in Solid / (1): 1.4

Tortuosity Factor in Fluid / (1): 1.4

Effective Values

| | | |
|---|---|---|
| Effective Electronic Conductivity / (S/m) | 6.42857 | View... |
| Effective Ionic Conductivity / (S/m) | <Concentration-Dependent> | View... |
| Effective Ionic Diffusivity / (m^2/s) | 1.07143e-10 | View... |



Concentration Dependence of Effective Ionic Conductivity

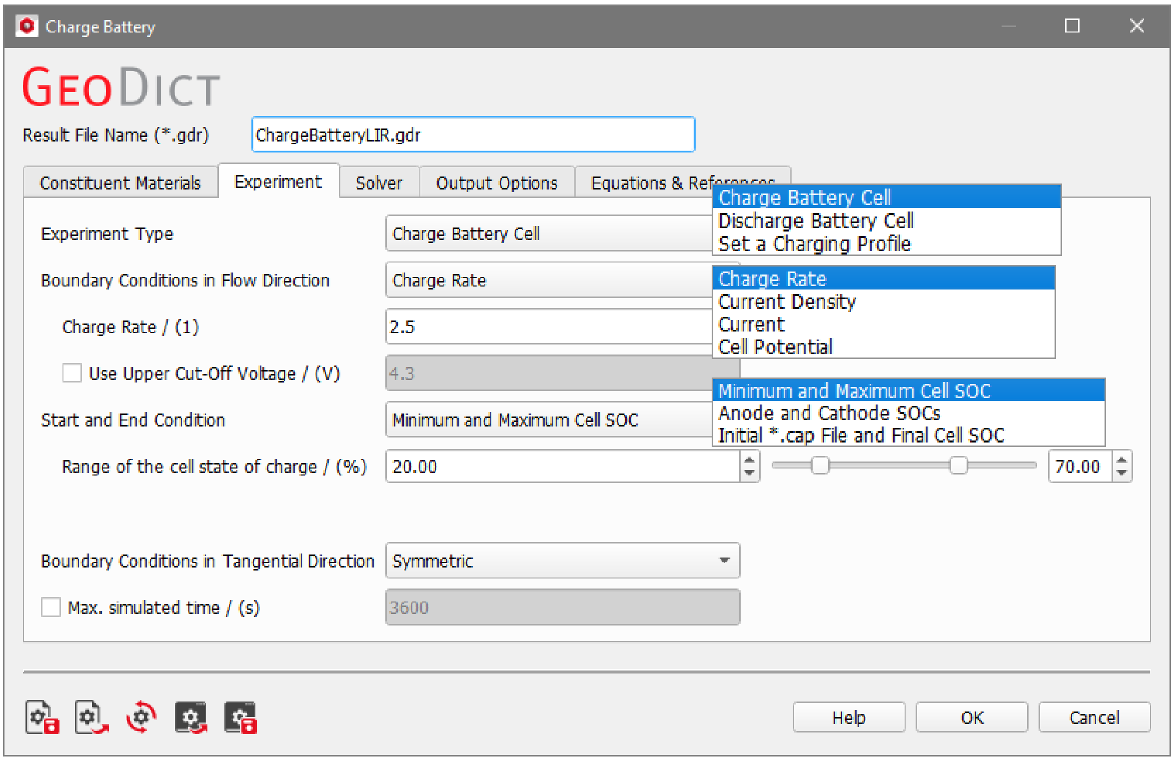
☑ Use Concentration Dependent Effective Ionic Conductivity

| | Concentration / (mol/m^3) | Effective Ionic Conductivity / (S/m) |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 50 | 0.0464521517857143 |
| 3 | 100 | 0.0891033367857143 |
| 4 | 150 | 0.128134040357143 |
| 5 | 200 | 0.163719510714286 |

Number of I: 101

## EXPERIMENT

All parameters defining the charging simulation of the battery are defined on this tab.



Result File Name (*.gdr): ChargeBatteryLIR.gdr

Experiment Type: Charge Battery Cell

Boundary Conditions in Flow Direction: Charge Rate

Charge Rate / (1): 2.5

☐ Use Upper Cut-Off Voltage / (V): 4.3

Start and End Condition: Minimum and Maximum Cell SOC

Range of the cell state of charge / (%): 20.00 – 70.00

Boundary Conditions in Tangential Direction: Symmetric

☐ Max. simulated time / (s): 3600

From the pull-down menu **Experiment Type**, select the appropriate entry to simulate the charging or discharging of the battery or to set a charging profile. Here, a charging simulation is chosen. Charging profiles will be explained below, see page 57.

The **Boundary Conditions in Flow Direction** can be specified by a **Charge Rate**, a **Charge Density,** by defining the **Current** in Ampere (A) or by defining the **Cell Potential**.

With a **Charge Rate** defined, the applied current is related to the cell's capacity and is a measure of the duration of the battery charging. For example, a charge rate of 1 for a battery with capacity of 1 Ah means that the battery is loaded completely in 1 hour with a constant current of 1 Ampere (A). This time is unrelated to the simulation time, but instead to the time that the charging process itself requires. A charge rate of 2 means that charging the same battery with a current of 2 Ampere takes ½ hour.

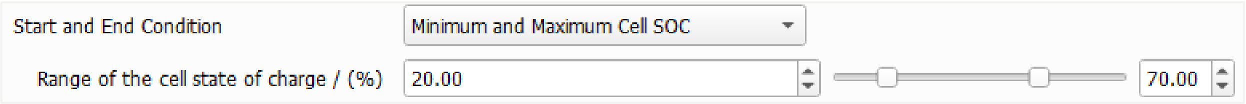
Defining the **Current** or the **Current Density** instead means that the applied current (in A) or the current density (in A/m²) is defined directly.

If **Cell Potential** is selected, the voltage is kept at a constant value during the simulation, and the current is a time-dependent value.

Check **Use Upper Cut-Off Voltage** to limit the voltage in a simulation with defined charge rate, current, or current density. The voltage will not rise above this limit. I.e., if the maximum voltage is reached, the charging will not continue with the charge rate, current, or current density defined above, but with a smaller one.

The **Start and End Condition** for the charging simulation, can be defined in several ways:

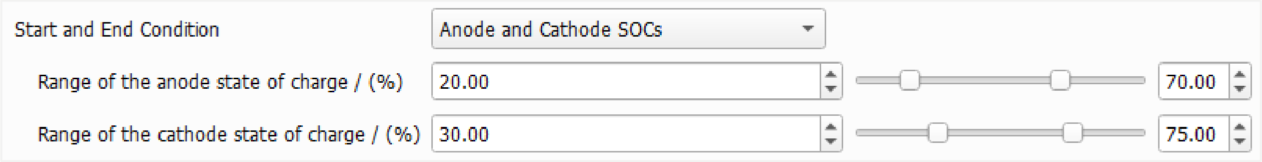
- as minimum and maximum percentage of the state of charge (SOC, see State of Charge above) of the whole cell



Start and End Condition: Minimum and Maximum Cell SOC

Range of the cell state of charge / (%): 20.00 – 70.00

- for the anode SOC and cathode SOC individually,

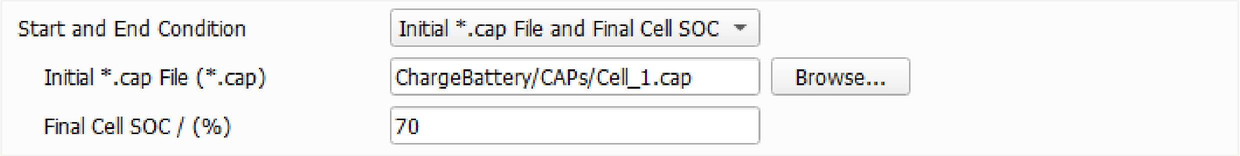


Start and End Condition: Anode and Cathode SOCs

Range of the anode state of charge / (%): 20.00 – 70.00

Range of the cathode state of charge / (%): 30.00 – 75.00

- or, by selecting an initial .cap file from a previous BatteryDict simulation and defining a final SOC.
  This option is especially useful for simulating a charging or discharging process, starting from a non-equilibrium condition after a previous discharging or charging simulation.



Start and End Condition: Initial *.cap File and Final Cell SOC

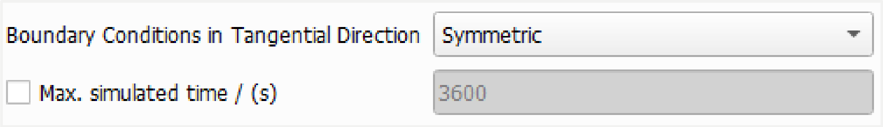
Initial *.cap File (*.cap): ChargeBattery/CAPs/Cell_1.cap

Final Cell SOC / (%): 70

Note that to get a numerically stable solution, the state of charge for the whole cell as well as for anode and cathode separately can be set only between 5% and 95%, see page 9.

**Periodic** or **Symmetric** boundary conditions can be selected for the **Boundary Conditions in Tangential Directions.**

For periodic boundary conditions, the structure is assumed to repeat periodically in y- and z-direction and for symmetric boundary conditions, the Li$^+$ ions and electrons are reflected at the boundary in y- and z-direction. Connected and unconnected parts of the active materials and of the electrolyte are dependent on the boundary conditions, and are, therefore, identified when the simulation is started.



Boundary Conditions in Tangential Direction: Symmetric

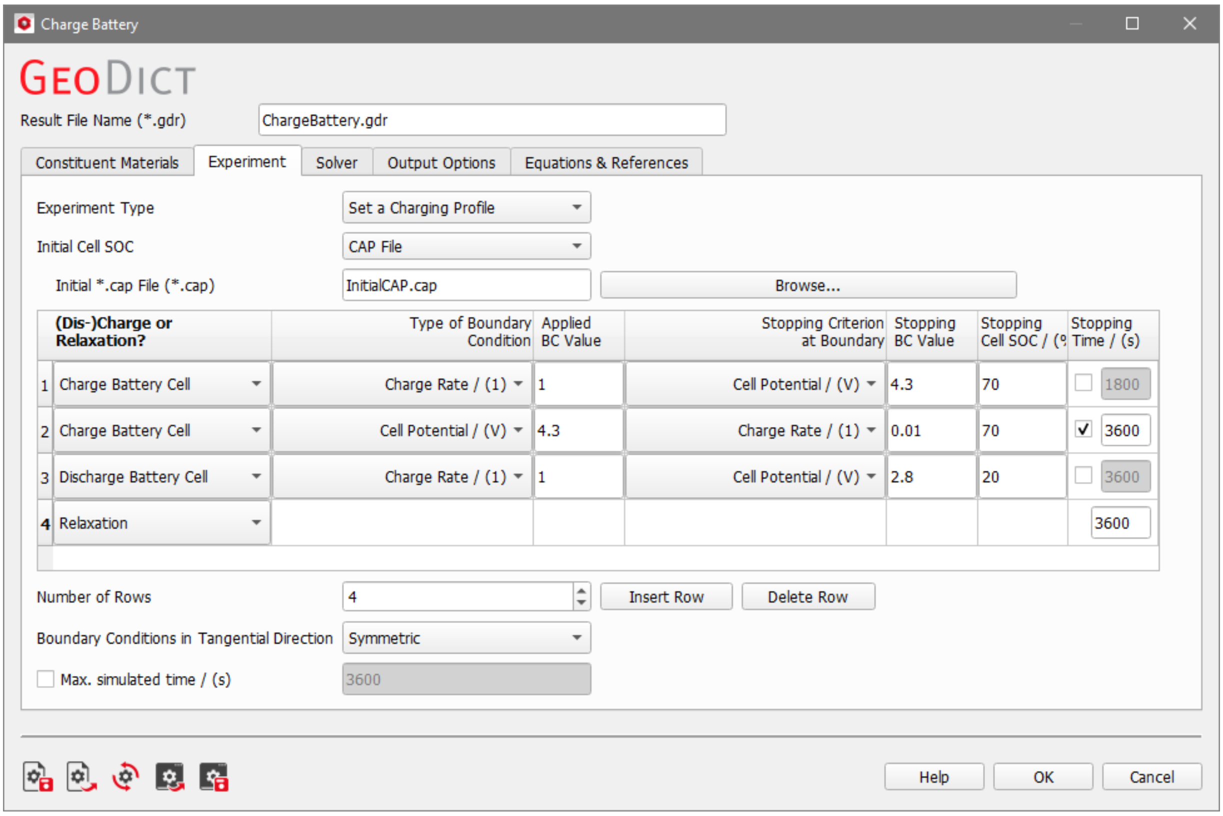
☐ Max. simulated time / (s): 3600

Checking **Max. simulated time**, the total time that the battery will be charged can be defined. The simulation ends if the charging process exceeds the **Max. simulated Time** even if the final state of charge for the simulation is not reached. Note that the **Max. simulated time** is not the time that the solver is given for its computation, but it is the time, the simulated battery is given for charging or discharging.

Example: Let us consider a battery that is charged from 20% state-of-charge to 70% state-of-charge at a charge rate of 1C. The battery takes 30 min to charge. If the **Max. simulated time** is set to 600 seconds (10 min), then in this example, the battery will only be charged from 20% to 36.67% state-of-charge.

## DEFINE CHARGING PROFILES

Charging Profiles are a series of charging, discharging, and relaxation simulations that are performed sequentially for the same structure.



Result File Name (*.gdr): ChargeBattery.gdr

Experiment Type: Set a Charging Profile

Initial Cell SOC: CAP File

Initial *.cap File (*.cap): InitialCAP.cap

| | (Dis-)Charge or Relaxation? | Type of Boundary Condition | Applied BC Value | Stopping Criterion at Boundary | Stopping BC Value | Stopping Cell SOC / ( | | Stopping Time / (s) |
|---|---|---|---|---|---|---|---|---|
| 1 | Charge Battery Cell | Charge Rate / (1) | 1 | Cell Potential / (V) | 4.3 | 70 | ☐ | 1800 |
| 2 | Charge Battery Cell | Cell Potential / (V) | 4.3 | Charge Rate / (1) | 0.01 | 70 | ☑ | 3600 |
| 3 | Discharge Battery Cell | Charge Rate / (1) | 1 | Cell Potential / (V) | 2.8 | 20 | ☐ | 3600 |
| 4 | Relaxation | | | | | | | 3600 |

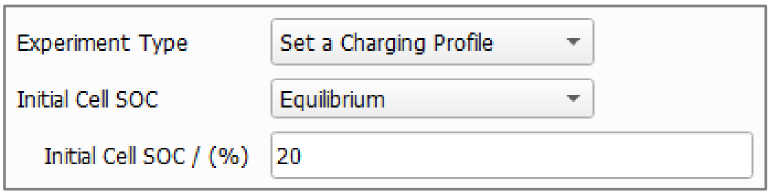
Number of Rows: 4

Boundary Conditions in Tangential Direction: Symmetric

☐ Max. simulated time / (s): 3600

If **Set a Charging Profile** is selected as **Experiment Type**, the starting point for the first simulation can be defined

- as an equilibrium state of charge,



Experiment Type: Set a Charging Profile

Initial Cell SOC: Equilibrium

Initial Cell SOC / (%): 20

- or, by selecting a .cap file of a previous simulation.

Experiment Type: Set a Charging Profile

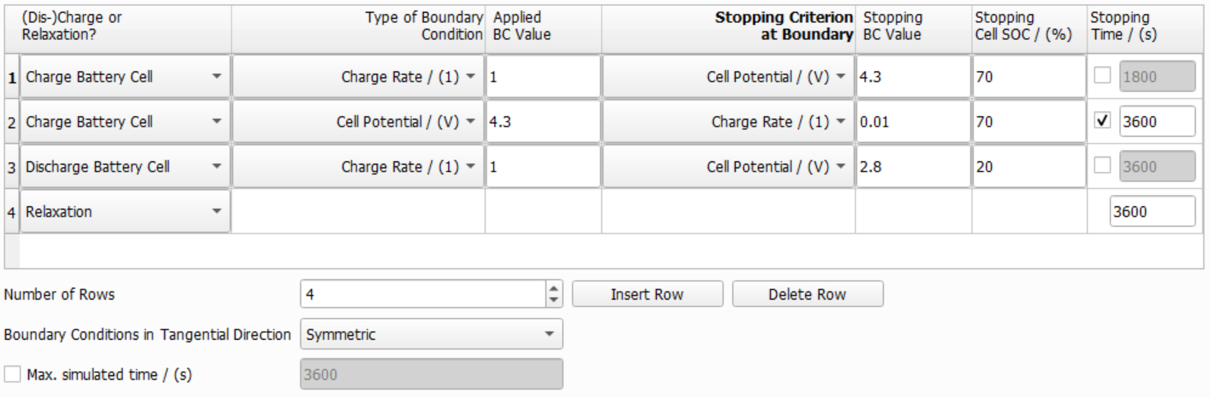
Initial Cell SOC: CAP File

Initial *.cap File (*.cap): InitialCAP.cap

The starting point for the following simulations is always the final state of the previous one.

To define a charging profile, choose as many rows for the table as simulation steps desired. Select for each step, if the battery is charged, discharged, or if relaxation is simulated. For charging or discharging, define the type of boundary condition and the corresponding value, in the same way as for simple charging simulations, see page 55. The same options for the boundary condition (Charge Rate, Current Density, Current, and Cell Potential) are available.

For charging or discharging, next, the stopping criterion for the selected boundary condition is chosen for each simulation step. The available options depend on the type of boundary condition (BC). If Charge Rate, Current Density, or Current is selected as BC, only Cell Potential is possible as stopping criterion. For Cell Potential as BC, the Stopping Criterion can be chosen between Charge Rate, Current Density, and Current.



| | (Dis-)Charge or Relaxation? | Type of Boundary Condition | Applied BC Value | **Stopping Criterion at Boundary** | Stopping BC Value | Stopping Cell SOC / (%) | Stopping Time / (s) |
|---|---|---|---|---|---|---|---|
| 1 | Charge Battery Cell | Charge Rate / (1) | 1 | Cell Potential / (V) | 4.3 | 70 | ☐ 1800 |
| 2 | Charge Battery Cell | Cell Potential / (V) | 4.3 | Charge Rate / (1) | 0.01 | 70 | ☑ 3600 |
| 3 | Discharge Battery Cell | Charge Rate / (1) | 1 | Cell Potential / (V) | 2.8 | 20 | ☐ 3600 |
| 4 | Relaxation | | | | | | 3600 |

Number of Rows: 4

Boundary Conditions in Tangential Direction: Symmetric

☐ Max. simulated time / (s): 3600

Enter the **Stopping BC Value** for the **Stopping Criterion**, a stopping state-of-charge for the whole cell (**Stopping Cell SOC / %**) and (optionally) a stopping time. For each simulation step, the computation will end, if the first one of the stopping criteria is reached. The next simulation step will continue from this state.

For relaxation, no boundary conditions need to be defined. In a relaxation step, the return of the battery cell to an equilibrium state after charging or discharging is simulated. The solver settings, like the time step, etc. are chosen in such a way that the simulation time necessary for the relaxation is optimal.

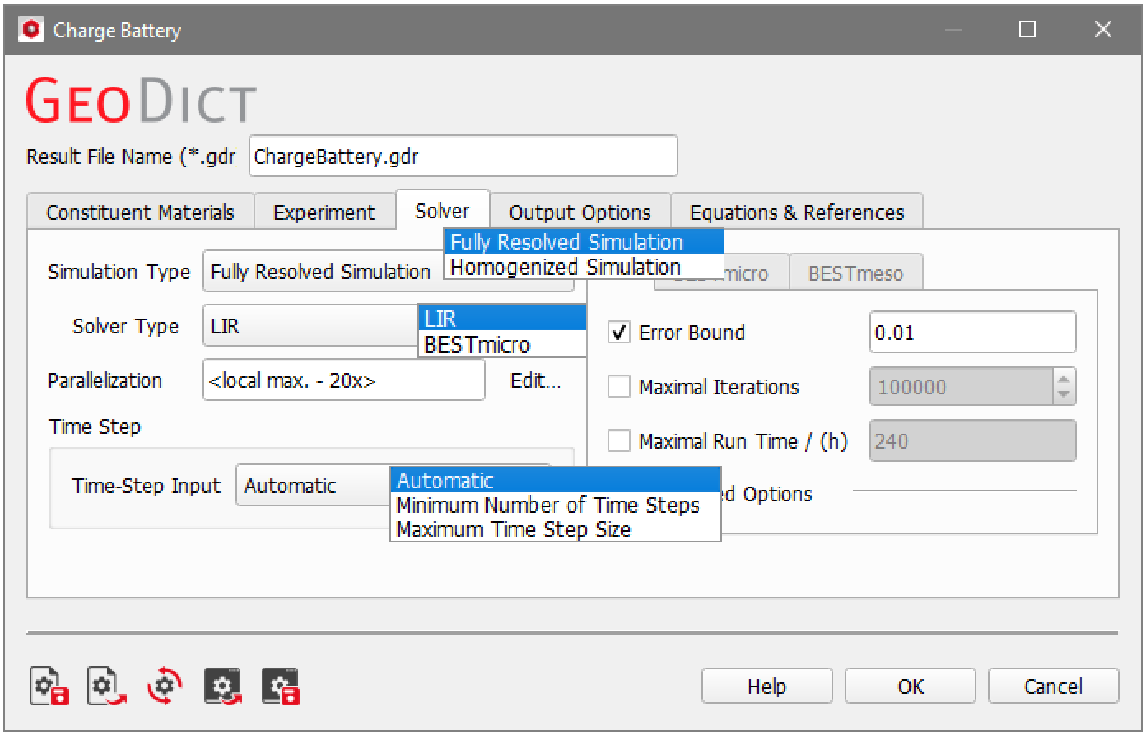
## SOLVER

Under the **Solver** tab, the type of simulation to run and the solver to use when solving the system of partial differential equations is selected, as well as the solver options.

Select the **Simulation Type Fully Resolved Simulation** or **Homogenized Simulation**.

The fully resolved simulation (see page 7) runs directly on the voxels of the battery structure. It is therefore very accurate, and, in addition to charge curves, also provides solution files with results resolved on the voxel scale and slice mean plots. The homogenized simulation (see page 11) is much faster than the fully resolved simulation. It uses a simplified model (an advanced 1D-Newman-model) that is created from the given battery structure. The effective parameters for this simulation are computed in GeoDict. It returns a charge curve as well, but no solution fields resolved on the voxel scale.

For a **Fully Resolved Simulation**, the **Solver Type LIR** or **BESTmicro** can be selected.



Result File Name (*.gdr ChargeBattery.gdr

Simulation Type: Fully Resolved Simulation

Solver Type: LIR

Parallelization: <local max. - 20x>

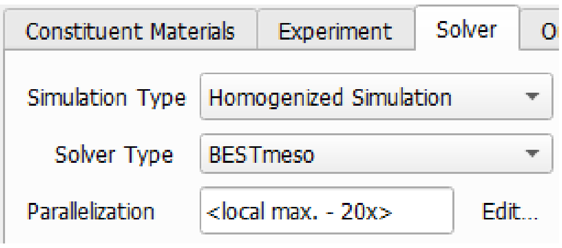
Time-Step Input: Automatic

☑ Error Bound: 0.01

☐ Maximal Iterations: 100000

☐ Maximal Run Time / (h): 240

For the **Homogenized Simulation**, the **BESTmeso** solver is available.



Simulation Type: Homogenized Simulation

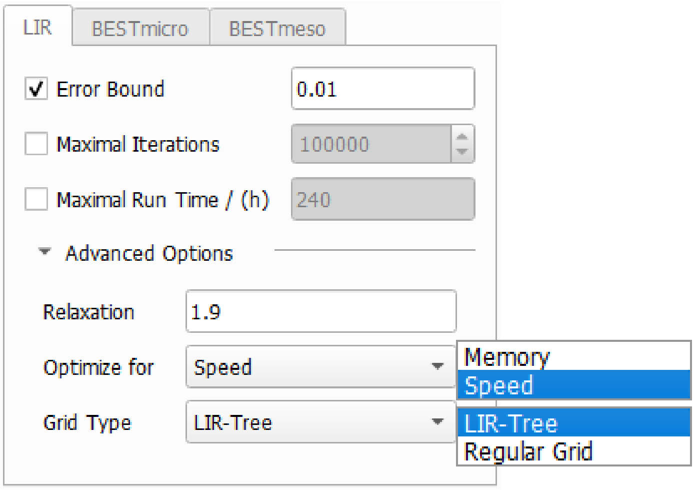
Solver Type: BESTmeso

Parallelization: <local max. - 20x>

Dependent on the choice of simulation and solver, the parameters for the computation need to be defined.

## FULLY RESOLVED SIMULATION - LIR SOLVER

With the LIR solver, the partial differential equations of each time step are solved iteratively with an adaptive tree structure. Several solver options can be chosen on the panel on the right.



☑ Error Bound: 0.01
☐ Maximal Iterations: 100000
☐ Maximal Run Time / (h): 240
Relaxation: 1.9
Optimize for: Speed
Grid Type: LIR-Tree

Stopping criteria **Error Bound, Maximal Iterations**, and **Maximal Run Time** can be selected. The stopping criteria **Error Bound** stops the solver if the relative difference between computed and predicted solution is smaller than the error bound defined.

Note that all stopping criteria selected are applied for each time step separately. I.e., the maximal run time defined is not the maximal run time for the whole charging simulation, but for each time step.

The balance between stable and fast simulation is managed for the LIR solver through the **Relaxation** value, that must be positive and should not be larger than 2: For a relaxation value smaller than 1, the simulation is more stable. For a value larger than 1, it is faster.

The LIR solver can **Optimize for** speed or memory.

- If **Speed** is chosen, the solver constructs additional optimization structures. The runtime is decreased but it requires more memory compared to the **Memory** option.
- If **Memory** is chosen, the runtime is increased but the solver requires less memory.

The **Grid Type** decides what kind of tree structure is used for the simulation.

The default option is **LIR-Tree** and should always be used. The solver uses an adaptive tree structure called LIR-tree and needs up to 10 times less runtime and memory compared to the **Regular Grid** option.

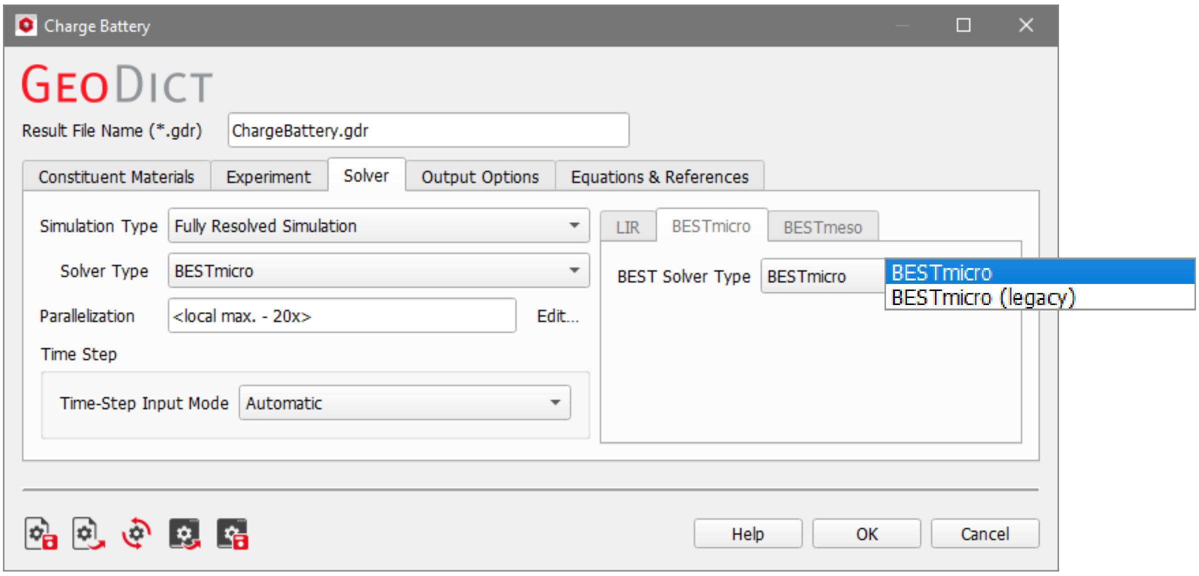
The solver can analyze the result field during the computation and improves the adaptive grid in places where more accuracy is needed. The LIR solver splits cells where a high gradient occurs.

## FULLY RESOLVED SIMULATION – BESTMICRO SOLVER

The BESTmicro solver uses algebraic multigrid methods to solve the system of partial differential equations of the battery charging process. Two implementations are available for the BESTmicro solver from the Battery and Electrochemistry Simulation Tools of Fraunhofer ITWM:

- BESTmicro (legacy): Implementation of BESTmicro solver available in GeoDict since GeoDict 2018. This implementation is very robust, with more than a decade of experience. However, it needs a lot of memory.
- BESTmicro: Reimplementation of BESTmicro, newly available in GeoDict 2023. It is faster than BESTmicro and needs less memory. In GeoDict 2023, it was known as BEST:er-micro.

For both implementations, apart from the parallelization and the Time-Step Input Mode, no additional solver options need to be defined on the panel on the right.



Result File Name (*.gdr): ChargeBattery.gdr

Simulation Type: Fully Resolved Simulation

Solver Type: BESTmicro

Parallelization: <local max. - 20x>

Time Step

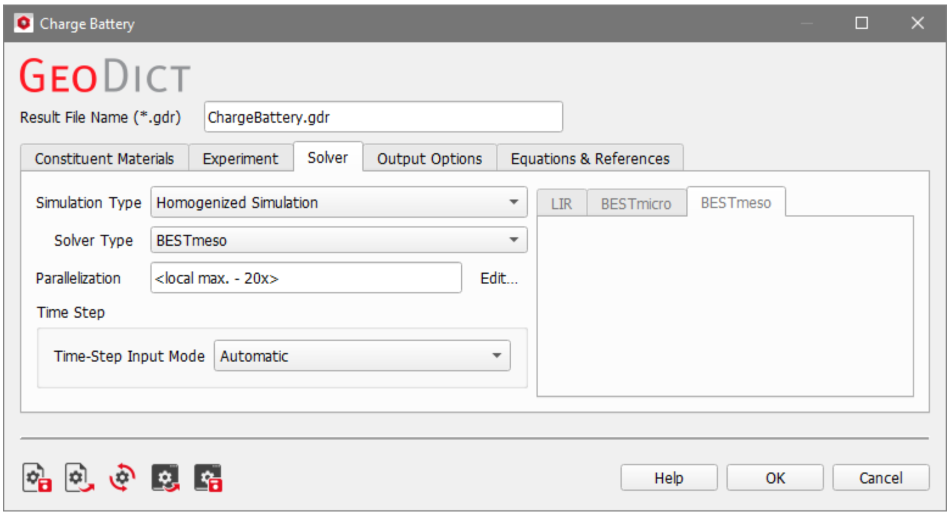
Time-Step Input Mode: Automatic

BEST Solver Type: BESTmicro

BESTmicro
BESTmicro (legacy)

## HOMOGENIZED SIMULATION – BESTMESO SOLVER

For the BESTmeso solver, only the parallelization and the Time-Step Input Mode need to be chosen, no further solver options need to be defined.



Result File Name (*.gdr): ChargeBattery.gdr

Simulation Type: Homogenized Simulation

Solver Type: BESTmeso

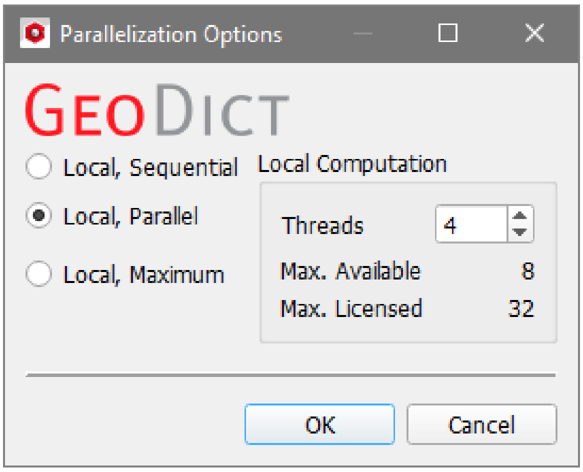
Parallelization: <local max. - 20x>

Time Step

Time-Step Input Mode: Automatic

## Parallelization and Time-Step

The **Parallelization Options** dialog box opens when clicking the **Edit ...** button, to choose between **Local, Sequential**, **Local, Parallel**, or **Local, Maximum**.



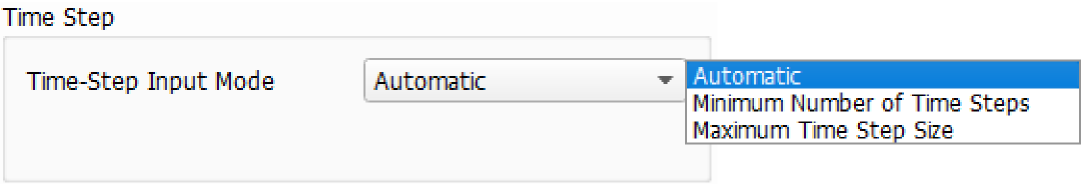
Threads 4
Max. Available 8
Max. Licensed 32

If **Local, Maximum** is selected, the maximum number of parallel processes is used. The maximum number depends on the available hardware and on the maximum number of processes licensed.

If **Local, Parallel** is selected, the number of threads can be selected. The maximum thread number available and licensed is shown.

With **Local, Sequential**, only one thread is used, and no parallel computation is done.

Finally, in the **Time-Step** panel an option for the **Time-Step Input Mode** may be selected.



Time-Step Input Mode Automatic

Any of the battery solvers calculates the time evolution of the given Li-ion battery. It starts at the initial state, which has time = 0 in the result plots (see page 67). It takes the time step defined as maximum time step size and tries to find the battery state at time = last time + time step by searching an equilibrium solution fulfilling the given system of differential equations. If no solution can be found for this time step size, it reduces the time step size, and the solver starts again. This procedure is repeated until an appropriate time step size is found. This time step size is used for the next steps in the simulation as well. After several successful steps with a certain time step size, the solver tries to increase this time step size again, to reduce overall computation time. With the **Time-Step Input Mode**, the maximum time-step size can be influenced.

- Choosing **Automatic**, the solver selects the time-step size without restrictions of the user.
- If a **Minimum Number of Time Steps** is defined, at least this number of points are computed for the solution and the maximum time-step size is selected accordingly. If your simulation does not produce enough points in the plots of the result file, then you might want to increase the **Minimum Number of Time Steps**.

- **Maximum Time Step Size** defines the maximum time step in seconds used in the simulation. If the size of the time step is oscillating a lot, the recommendation is to reduce this maximum value.

The time steps that were finally realized in the simulation are saved in the Result Map (see page 67) of the GeoDict result file (*.gdr file), created for the charging simulation, under the key **TimeDependentValues:TimeStep**.

If a new battery state is found, the solver computes the Cell-SOC step of the just found new battery state *i* via:

$$\Delta(SOC)_i = \Delta t_i \cdot C/(1h)$$

with $\Delta t_i$ the time step and *C* the charge rate. So, it is not clear from the start which is the next computed Cell-SOC in a simulation, this depends on the time step.

**Example:**

- Charge Rate $C = 5$
- Time Step Size $\Delta t_i = 2.5\ s$
- Cell-SOC step $\Delta(SOC)_i = 2.5\ s \cdot \frac{5}{1h} = 2.5\ s \cdot \frac{5}{3600\ s} = 0.00347 = 0.347\%$

If you choose to set the current density instead of the charge rate, then the calculation of the Cell-SOC step size depends on the given current density and the cell capacity. Thereby, the cell capacity depends on the cell-geometry and the maximum lithium concentration of the active materials.

In the GeoDict result file (*.gdr file), created for the charging simulation, you can find the time-evolution of the Cell-SOCs in percent as well as the corresponding times in seconds in the Result Map under the keys **TimeDependentValues:CellStateOfCharge** and **TimeDependentValues:Time**, respectively (see page 67).

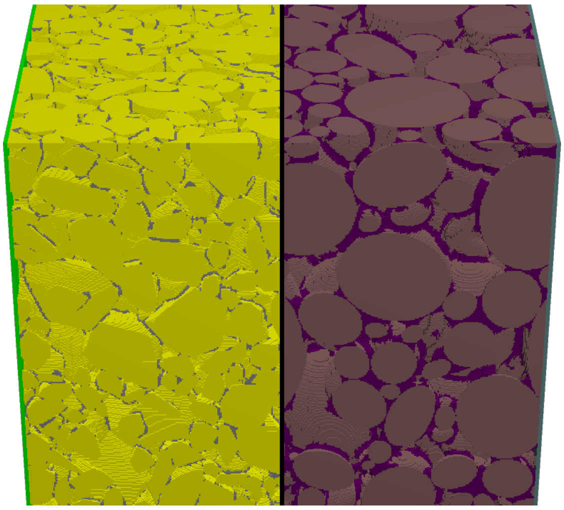
For simple simulations (charge rate <= 1, physical domain size < = 5 µm, only one active material per electrode, diffusivities >= 1e-12 m²/s, conductivities >= 1 S/m and no warnings during the simulation), the time step size is usually the maximum time step size set. Then, also the Cell-SOC step is a constant value.

However, for more complex simulations (charge rate >= 10, physical domain size >= 50 µm, two active materials in an electrode with different parameters, low diffusivities in the active materials and small conductivities), it might happen that the time step size may be smaller than the maximum time step size defined and not constant over the whole simulation.

## PARALLELIZATION BENCHMARK RESULTS

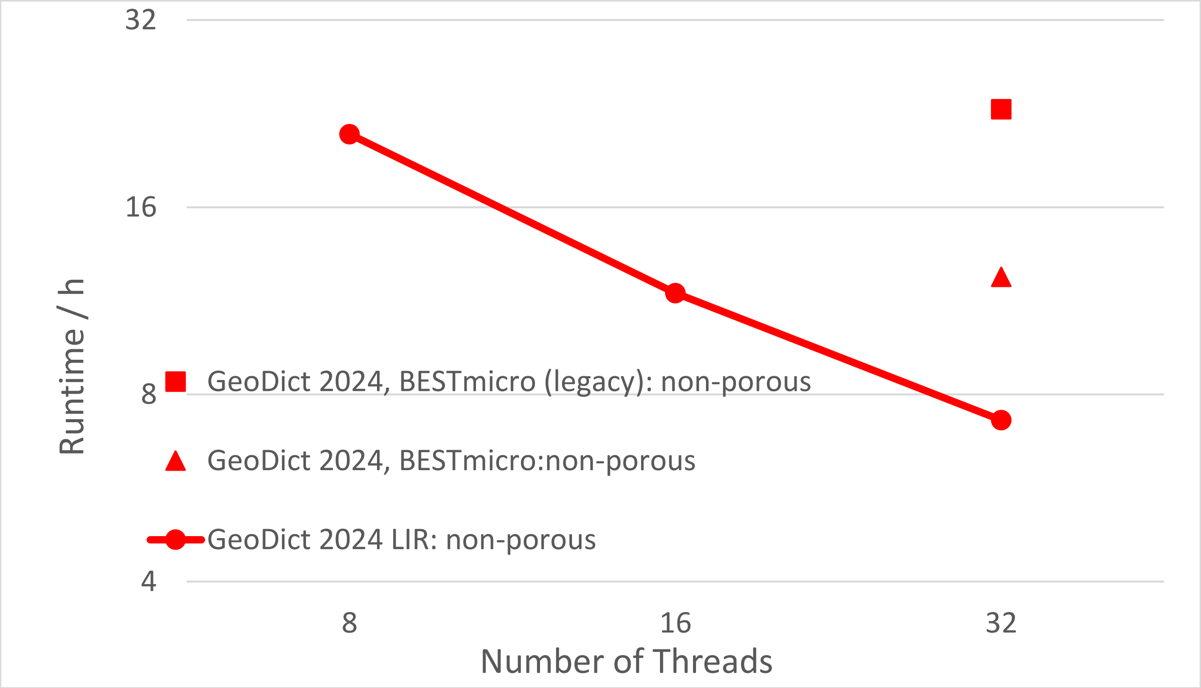
As an example for the parallelization, a full battery structure of size 409 x 400 x 400 voxels with 200 nm voxel length is used to simulate the charging from the cell state of charge 20% till 70%. The computation is run on a server with 2 x Intel E5-2697A v4 processors with 16 cores each, running with a maximum of 3.60 GHz, and 1 TB RAM.

The simulations are computed with GeoDict 2024, r71884.

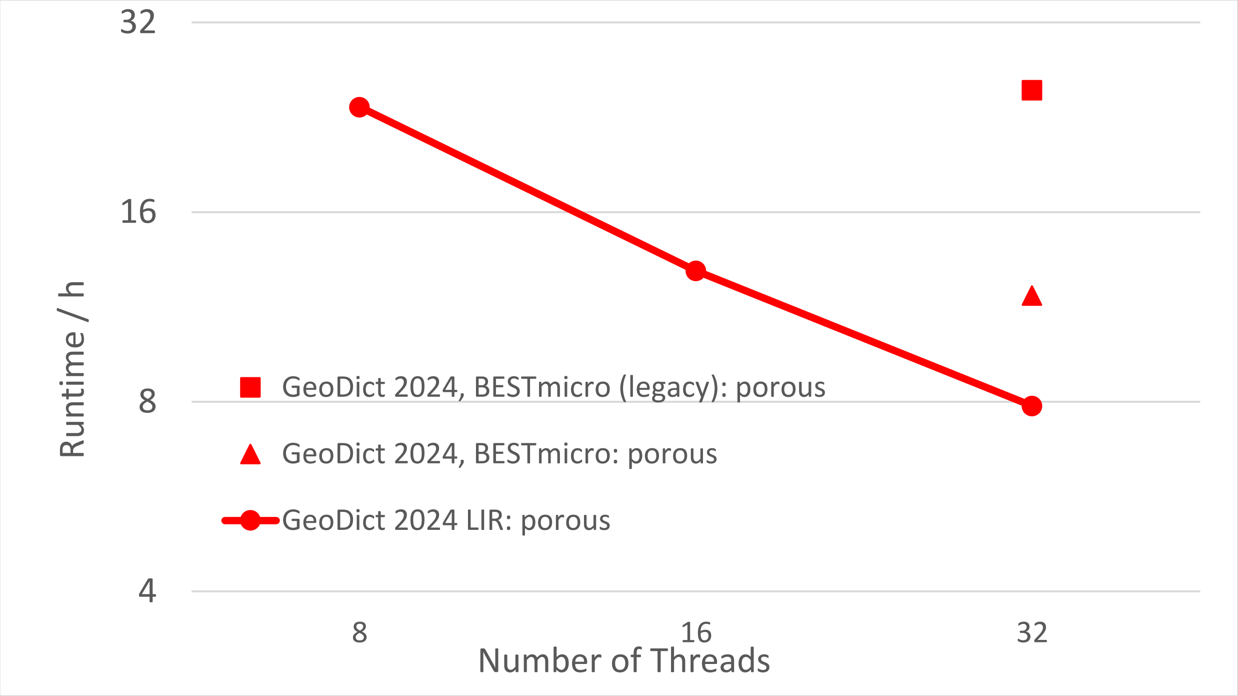


When the binder is considered as solid, the LIR solver needs only 1/3 of the runtime compared to BESTmicro (legacy) with GeoDict 2024. In GeoDict 2024, with the LIR solver, the runtime is almost the same with in GeoDict 2023. In GeoDict 2024 the BESTmicro solver takes only 54% of runtime of BESTmicro (legacy).

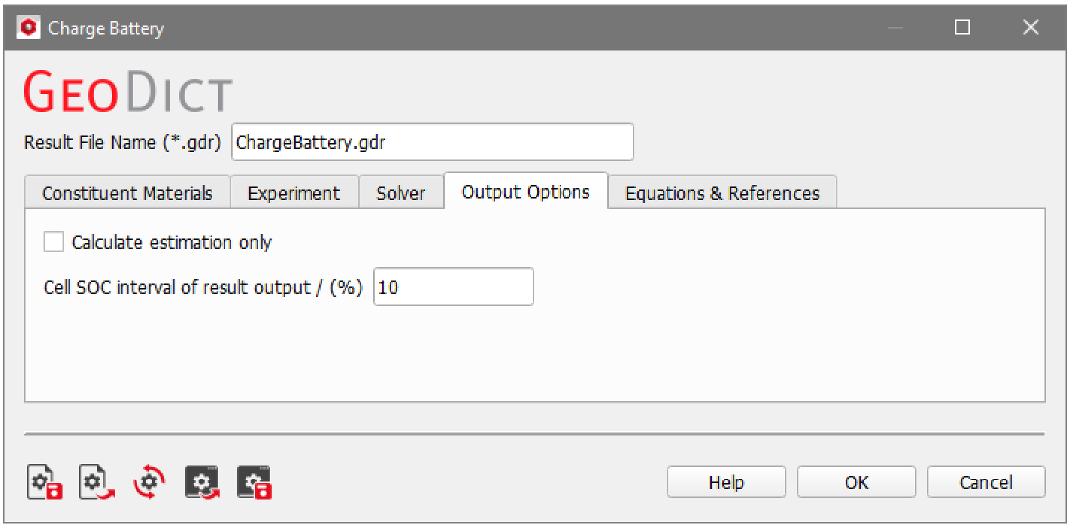
The LIR solver needs only 7.8 GB of RAM which is 3% of the memory required by BESTmicro (legacy) and 5.5% of the memory required by BESTmicro. The speedup for LIR solver is nearly optimal.



When the binder is considered as porous, since GeoDict 2022, LIR can also solve the porous case. The LIR solver needs 9 GB of RAM, only 2.6% of the memory required by BESTmicro (legacy), 347 GB and 6.2% of the memory required by BESTmicro. The runtimes of LIR, BESTmicro and BESTmicro (legacy) with 32 threads are 8 h, 12 h, and 25 h.



## OUTPUT OPTIONS



Result File Name (*.gdr) ChargeBattery.gdr

☐ Calculate estimation only

Cell SOC interval of result output / (%) 10

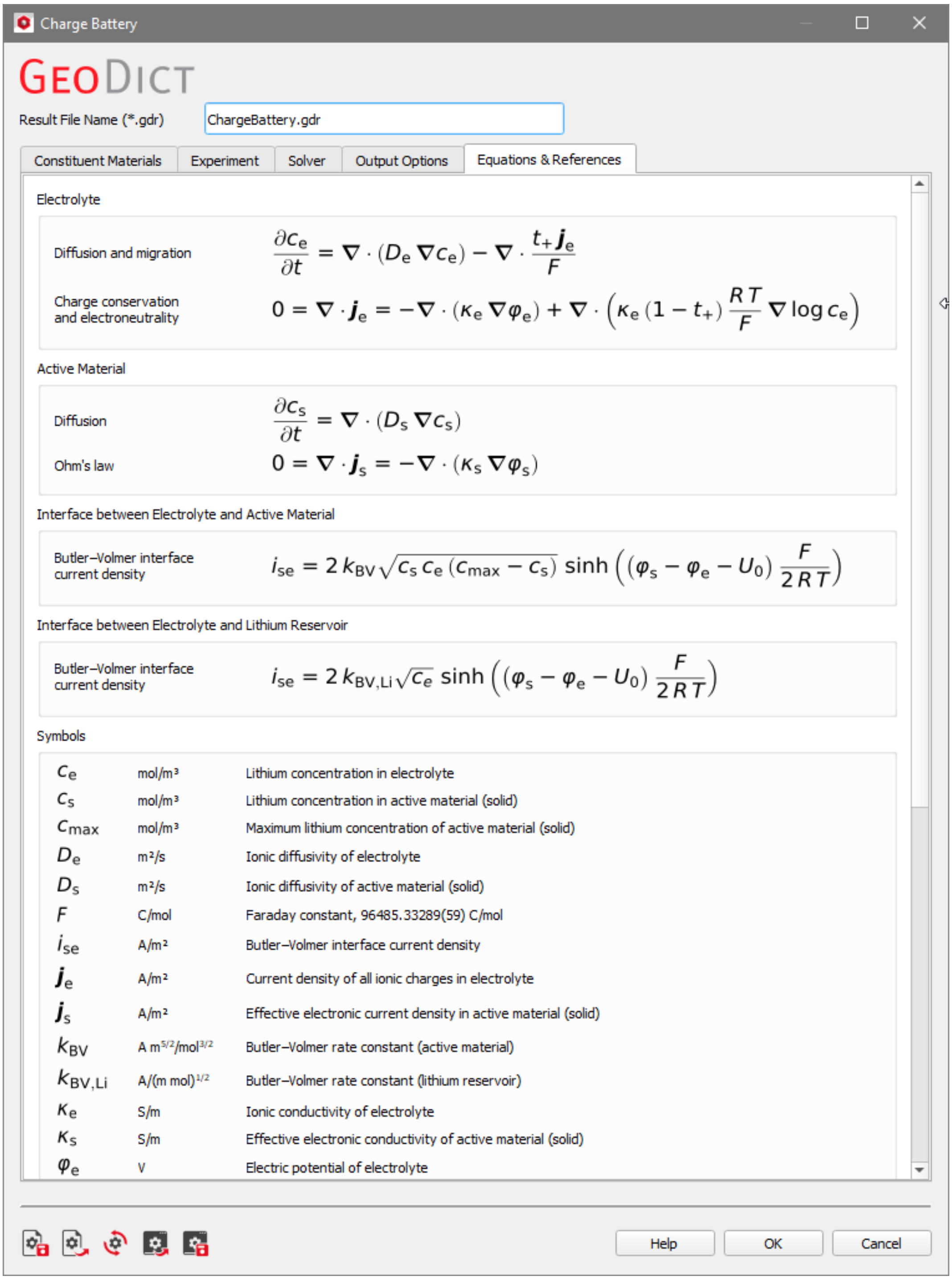
In the **Output Options** tab, **Calculate estimation only** can be checked, and then, the full simulation is not performed, but only the cell potential is estimated. This estimation is much faster than the full simulation. It considers the cell potential in equilibrium as well as the charge rate and part of the structure information, like the solid volume percentages of the different materials of the battery. From this information, Ohmic losses and overpotentials at the surfaces, but no overpotentials due to diffusion are considered in the estimation. In this case, no solver options need to be defined, and the **Solver** tab is inactive.

The **Cell SOC interval of result output** defines the interval for the export of intermediate result files in percent of the cell state of charge.

## EQUATIONS & REFERENCES

The differential equations solved in the fully resolved charging simulation are listed under the **Equations & References** tab and are described above in Theoretical Basis.

The references for the methods used are listed on this tab and can be found on page 109 n this BatteryDict handbook.



Result File Name (*.gdr) ChargeBattery.gdr

Electrolyte

Diffusion and migration
$$\frac{\partial c_e}{\partial t} = \nabla \cdot (D_e \nabla c_e) - \nabla \cdot \frac{t_+ \boldsymbol{j}_e}{F}$$

Charge conservation and electroneutrality
$$0 = \nabla \cdot \boldsymbol{j}_e = -\nabla \cdot (\kappa_e \nabla \varphi_e) + \nabla \cdot \left(\kappa_e (1 - t_+) \frac{RT}{F} \nabla \log c_e\right)$$

Active Material

Diffusion
$$\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s)$$

Ohm's law
$$0 = \nabla \cdot \boldsymbol{j}_s = -\nabla \cdot (\kappa_s \nabla \varphi_s)$$

Interface between Electrolyte and Active Material

Butler–Volmer interface current density
$$i_{se} = 2\, k_{BV} \sqrt{c_s\, c_e\, (c_{max} - c_s)}\, \sinh\left((\varphi_s - \varphi_e - U_0)\, \frac{F}{2RT}\right)$$

Interface between Electrolyte and Lithium Reservoir

Butler–Volmer interface current density
$$i_{se} = 2\, k_{BV,Li} \sqrt{c_e}\, \sinh\left((\varphi_s - \varphi_e - U_0)\, \frac{F}{2RT}\right)$$

Symbols

| | | |
|---|---|---|
| $c_e$ | $\mathrm{mol/m^3}$ | Lithium concentration in electrolyte |
| $c_s$ | $\mathrm{mol/m^3}$ | Lithium concentration in active material (solid) |
| $c_{max}$ | $\mathrm{mol/m^3}$ | Maximum lithium concentration of active material (solid) |
| $D_e$ | $\mathrm{m^2/s}$ | Ionic diffusivity of electrolyte |
| $D_s$ | $\mathrm{m^2/s}$ | Ionic diffusivity of active material (solid) |
| $F$ | C/mol | Faraday constant, 96485.33289(59) C/mol |
| $i_{se}$ | $\mathrm{A/m^2}$ | Butler–Volmer interface current density |
| $\boldsymbol{j}_e$ | $\mathrm{A/m^2}$ | Current density of all ionic charges in electrolyte |
| $\boldsymbol{j}_s$ | $\mathrm{A/m^2}$ | Effective electronic current density in active material (solid) |
| $k_{BV}$ | $\mathrm{A\,m^{5/2}/mol^{3/2}}$ | Butler–Volmer rate constant (active material) |
| $k_{BV,Li}$ | $\mathrm{A/(m\,mol)^{1/2}}$ | Butler–Volmer rate constant (lithium reservoir) |
| $\kappa_e$ | S/m | Ionic conductivity of electrolyte |
| $\kappa_s$ | S/m | Effective electronic conductivity of active material (solid) |
| $\varphi_e$ | V | Electric potential of electrolyte |

## RESULTS OF CHARGE BATTERY

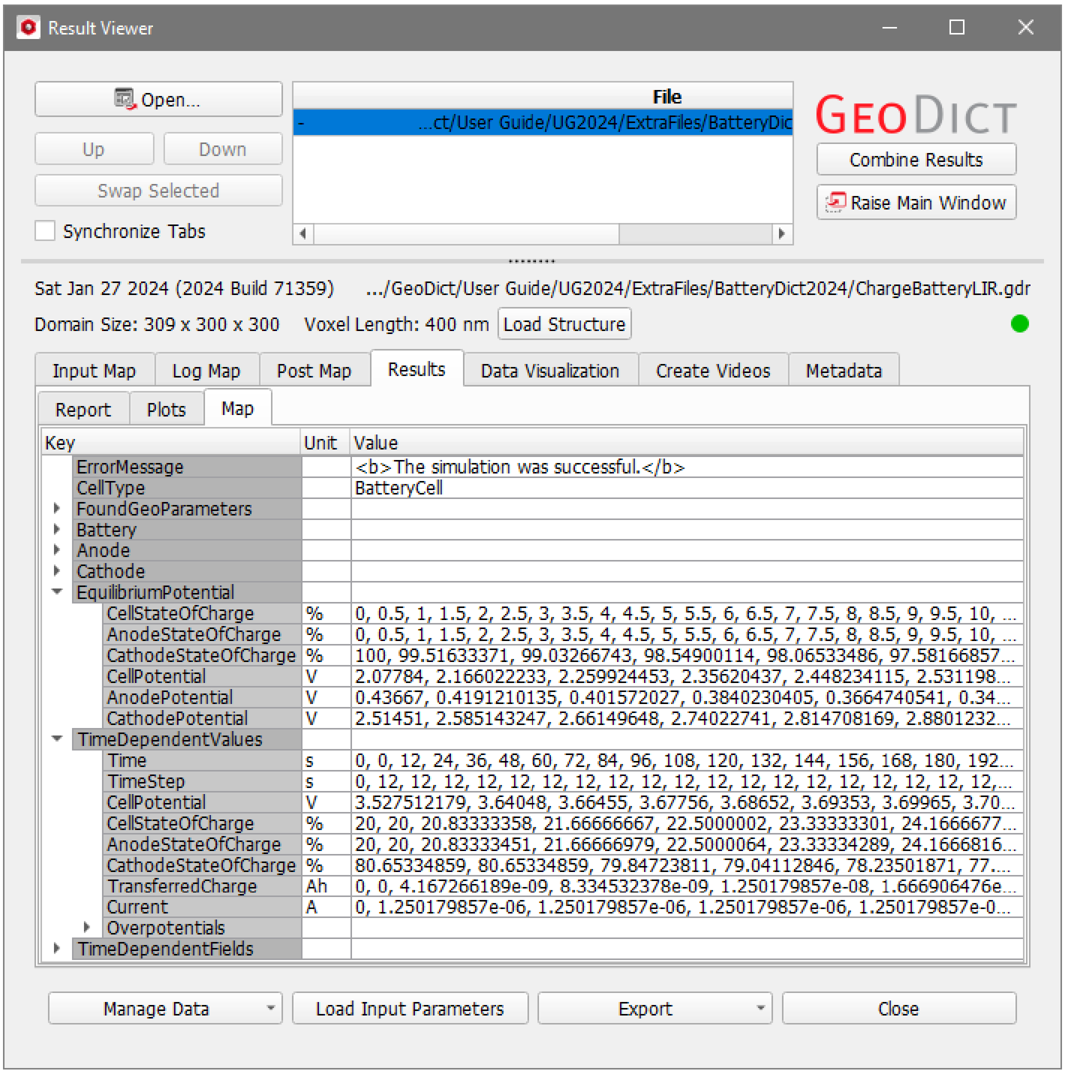
After a charging simulation has finished, a GeoDict result file (.gdr) is written and the **Result Viewer** of this result file automatically opens. The information of simulation result is shown, can be visualized, or further processed.

These results are accessible at any time by loading the .gdr file from the menu bar (**File** → **Open Results (*.gdr) ...**). The **Load Structure** button and the buttons available at the bottom of the **Result Viewer** are the same as for other result files and are explained on page 36.

In the following, results of a simulation with the battery designed above are shown.

The **Results** tab shows the computational results in several ways, through subtabs.

The **Results - Map** subtab lists all values available in the **Results - Report** subtab of the Result Viewer of the GeoDict result file and other information about the computation results.

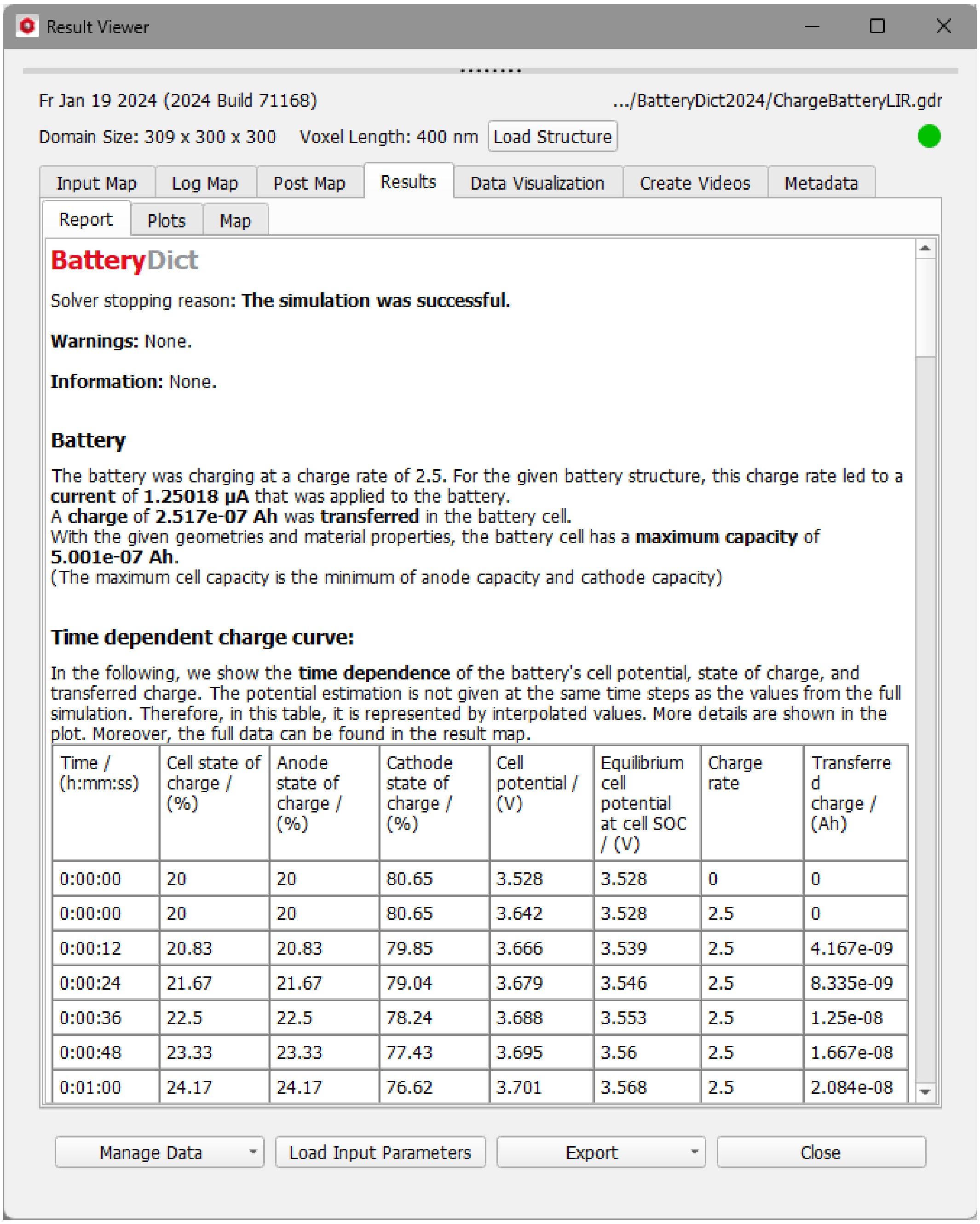


Sat Jan 27 2024 (2024 Build 71359) .../GeoDict/User Guide/UG2024/ExtraFiles/BatteryDict2024/ChargeBatteryLIR.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

| Key | Unit | Value |
|---|---|---|
| ErrorMessage | | <b>The simulation was successful.</b> |
| CellType | | BatteryCell |
| FoundGeoParameters | | |
| Battery | | |
| Anode | | |
| Cathode | | |
| EquilibriumPotential | | |
| CellStateOfCharge | % | 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, ... |
| AnodeStateOfCharge | % | 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, ... |
| CathodeStateOfCharge | % | 100, 99.51633371, 99.03266743, 98.54900114, 98.06533486, 97.58166857... |
| CellPotential | V | 2.07784, 2.166022233, 2.259924453, 2.35620437, 2.448234115, 2.531198... |
| AnodePotential | V | 0.43667, 0.4191210135, 0.401572027, 0.3840230405, 0.3664740541, 0.34... |
| CathodePotential | V | 2.51451, 2.585143247, 2.66149648, 2.74022741, 2.814708169, 2.8801232... |
| TimeDependentValues | | |
| Time | s | 0, 0, 12, 24, 36, 48, 60, 72, 84, 96, 108, 120, 132, 144, 156, 168, 180, 192... |
| TimeStep | s | 0, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12,... |
| CellPotential | V | 3.527512179, 3.64048, 3.66455, 3.67756, 3.68652, 3.69353, 3.69965, 3.70... |
| CellStateOfCharge | % | 20, 20, 20.83333358, 21.66666667, 22.5000002, 23.33333301, 24.1666677... |
| AnodeStateOfCharge | % | 20, 20, 20.83333451, 21.66666979, 22.5000064, 23.33334289, 24.1666816... |
| CathodeStateOfCharge | % | 80.65334859, 80.65334859, 79.84723811, 79.04112846, 78.23501871, 77.... |
| TransferredCharge | Ah | 0, 0, 4.167266189e-09, 8.334532378e-09, 1.250179857e-08, 1.666906476e... |
| Current | A | 0, 1.250179857e-06, 1.250179857e-06, 1.250179857e-06, 1.250179857e-0... |
| Overpotentials | | |
| TimeDependentFields | | |

In the **Results - Report** subtab, part of this information is shown, with explanations about the computation results. The table **Time dependent charge curve** shows part of the time dependent values in a clearly arranged way.



Fr Jan 19 2024 (2024 Build 71168) .../BatteryDict2024/ChargeBatteryLIR.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

**BatteryDict**

Solver stopping reason: **The simulation was successful.**

**Warnings:** None.

**Information:** None.

**Battery**

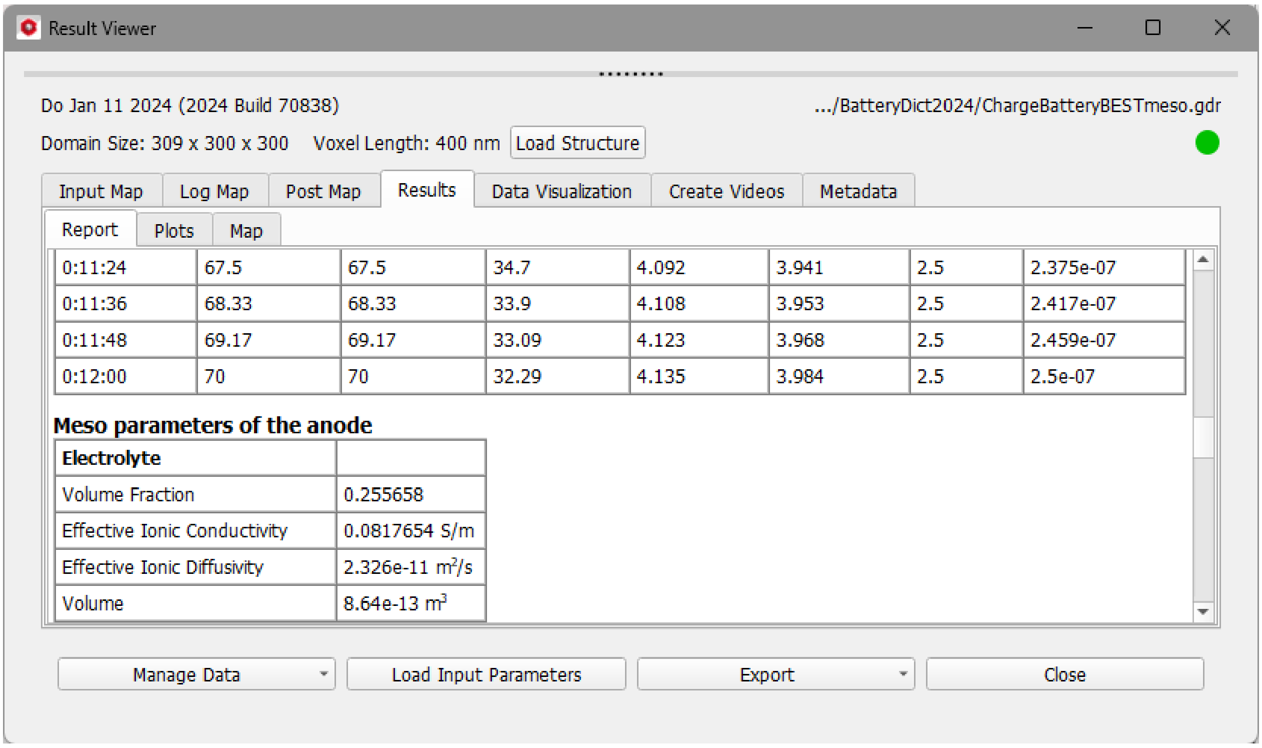
The battery was charging at a charge rate of 2.5. For the given battery structure, this charge rate led to a **current** of **1.25018 µA** that was applied to the battery.
A **charge** of **2.517e-07 Ah** was **transferred** in the battery cell.
With the given geometries and material properties, the battery cell has a **maximum capacity** of **5.001e-07 Ah**.
(The maximum cell capacity is the minimum of anode capacity and cathode capacity)

**Time dependent charge curve:**

In the following, we show the **time dependence** of the battery's cell potential, state of charge, and transferred charge. The potential estimation is not given at the same time steps as the values from the full simulation. Therefore, in this table, it is represented by interpolated values. More details are shown in the plot. Moreover, the full data can be found in the result map.

| Time / (h:mm:ss) | Cell state of charge / (%) | Anode state of charge / (%) | Cathode state of charge / (%) | Cell potential / (V) | Equilibrium cell potential at cell SOC / (V) | Charge rate | Transferred charge / (Ah) |
|---|---|---|---|---|---|---|---|
| 0:00:00 | 20 | 20 | 80.65 | 3.528 | 3.528 | 0 | 0 |
| 0:00:00 | 20 | 20 | 80.65 | 3.642 | 3.528 | 2.5 | 0 |
| 0:00:12 | 20.83 | 20.83 | 79.85 | 3.666 | 3.539 | 2.5 | 4.167e-09 |
| 0:00:24 | 21.67 | 21.67 | 79.04 | 3.679 | 3.546 | 2.5 | 8.335e-09 |
| 0:00:36 | 22.5 | 22.5 | 78.24 | 3.688 | 3.553 | 2.5 | 1.25e-08 |
| 0:00:48 | 23.33 | 23.33 | 77.43 | 3.695 | 3.56 | 2.5 | 1.667e-08 |
| 0:01:00 | 24.17 | 24.17 | 76.62 | 3.701 | 3.568 | 2.5 | 2.084e-08 |

**Meso parameters** computed for both electrodes are shown below the **Time dependent charge curve**, for the homogenized simulation with BESTmeso



Do Jan 11 2024 (2024 Build 70838)

.../BatteryDict2024/ChargeBatteryBESTmeso.gdr

Domain Size: 309 x 300 x 300   Voxel Length: 400 nm

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 0:11:24 | 67.5 | 67.5 | 34.7 | 4.092 | 3.941 | 2.5 | 2.375e-07 |
| 0:11:36 | 68.33 | 68.33 | 33.9 | 4.108 | 3.953 | 2.5 | 2.417e-07 |
| 0:11:48 | 69.17 | 69.17 | 33.09 | 4.123 | 3.968 | 2.5 | 2.459e-07 |
| 0:12:00 | 70 | 70 | 32.29 | 4.135 | 3.984 | 2.5 | 2.5e-07 |

**Meso parameters of the anode**

| **Electrolyte** | |
|---|---|
| Volume Fraction | 0.255658 |
| Effective Ionic Conductivity | 0.0817654 S/m |
| Effective Ionic Diffusivity | 2.326e-11 m²/s |
| Volume | 8.64e-13 m³ |

If the solver stopped unexpectedly before one of the stopping criteria defined was reached, the reason for this is shown on top of the report.

In the same way, warnings shown before starting the simulation (e.g., due to the parameters selected) and information about the simulation steps for a charging profile are shown there.

Under **Battery**, the charge rate applied, the applied current, the charge transferred, and the maximum capacity of the battery cell are listed.

The maximum capacity of the battery cell, $C_{B,max}$, is the minimum of the maximum anode capacity, $C_{A,max}$, and the cathode capacity, $C_{C,max}$

$$C_{B,max} = \min\left(C_{A,max}, C_{C,max}\right),$$

with

$$C_{A,max} = l_V^3 * F * \sum_{V \in \{Anode\ Active\ Material\ Voxels\}} c_{max}(V)$$

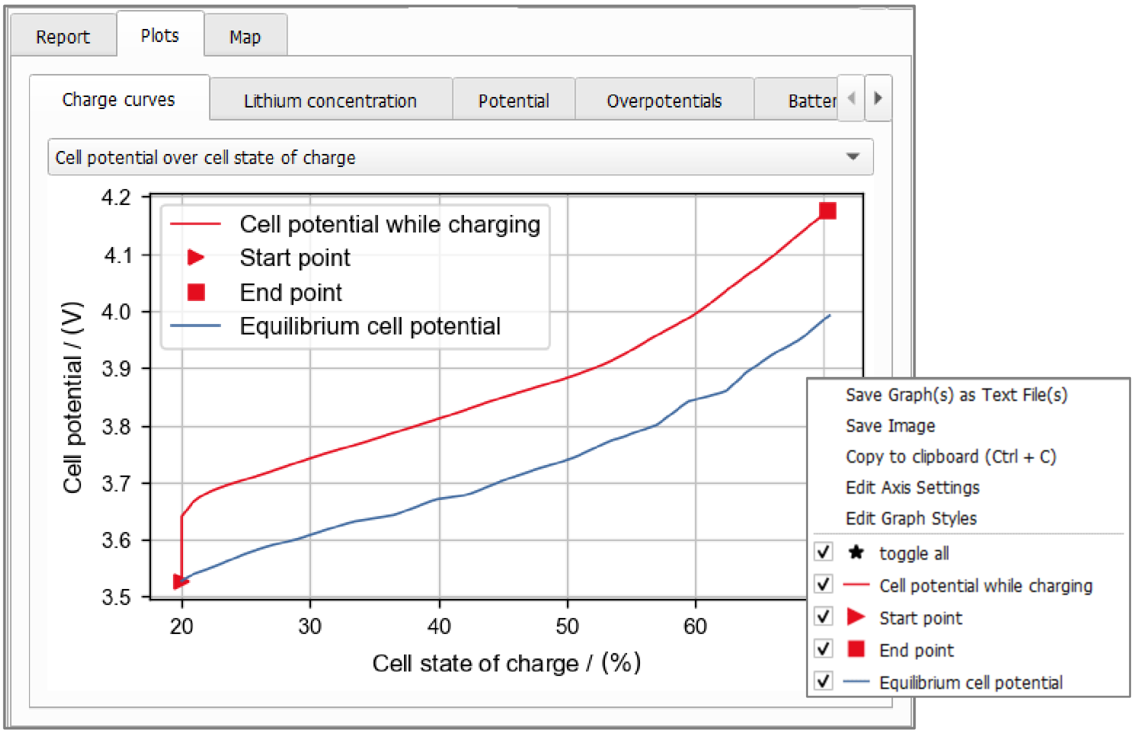
and

$$C_{C,max} = l_V^3 * F * \sum_{V \in \{Cathode\ Active\ Material\ Voxels\}} c_{max}(V)$$

$l_V$ denotes hereby the voxel length of the structure, $F$ the Faraday constant, and $c_{max}(V)$ the maximum removable lithium concentration of each active material voxel.

Under the **Results - Plots** subtab, several standard plots for the visualization of the BatteryDict simulation results are available: On the tab **Charge Curves**, **Cell potential**, **Cell state of charge, Cell capacity density, Charge rate, Current**

**density, Current**, and **Transferred charge** are plotted over **Time**. Additionally, the **Cell potential** and the **Electrode state of charge** can be plotted over the **Cell state of charge** and the **Cell potential** over the **Cell capacity density**.



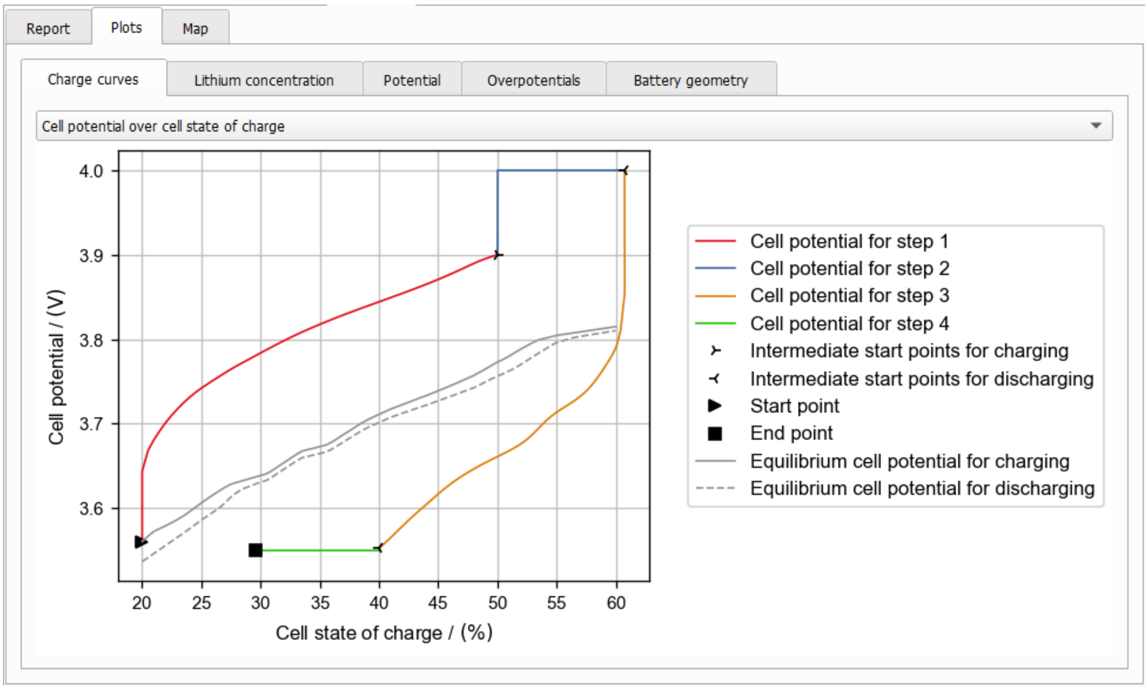
Clicking the right mouse button allows to change properties of each plot shown, to save the image, or to copy the values to the clipboard. In the same Context Menu, Graphs shown can be switched on and off as well.

In the **Cell potential over Cell state of charge** plot (above), the cell potential while charging or discharging is compared to the cell potential in equilibrium, i.e., while loading in infinite time. When the battery is charged or discharged slowly over an infinite amount of time, it remains in a state of equilibrium. However, when the process is done in a finite amount of time, the battery deviates from this equilibrium state.

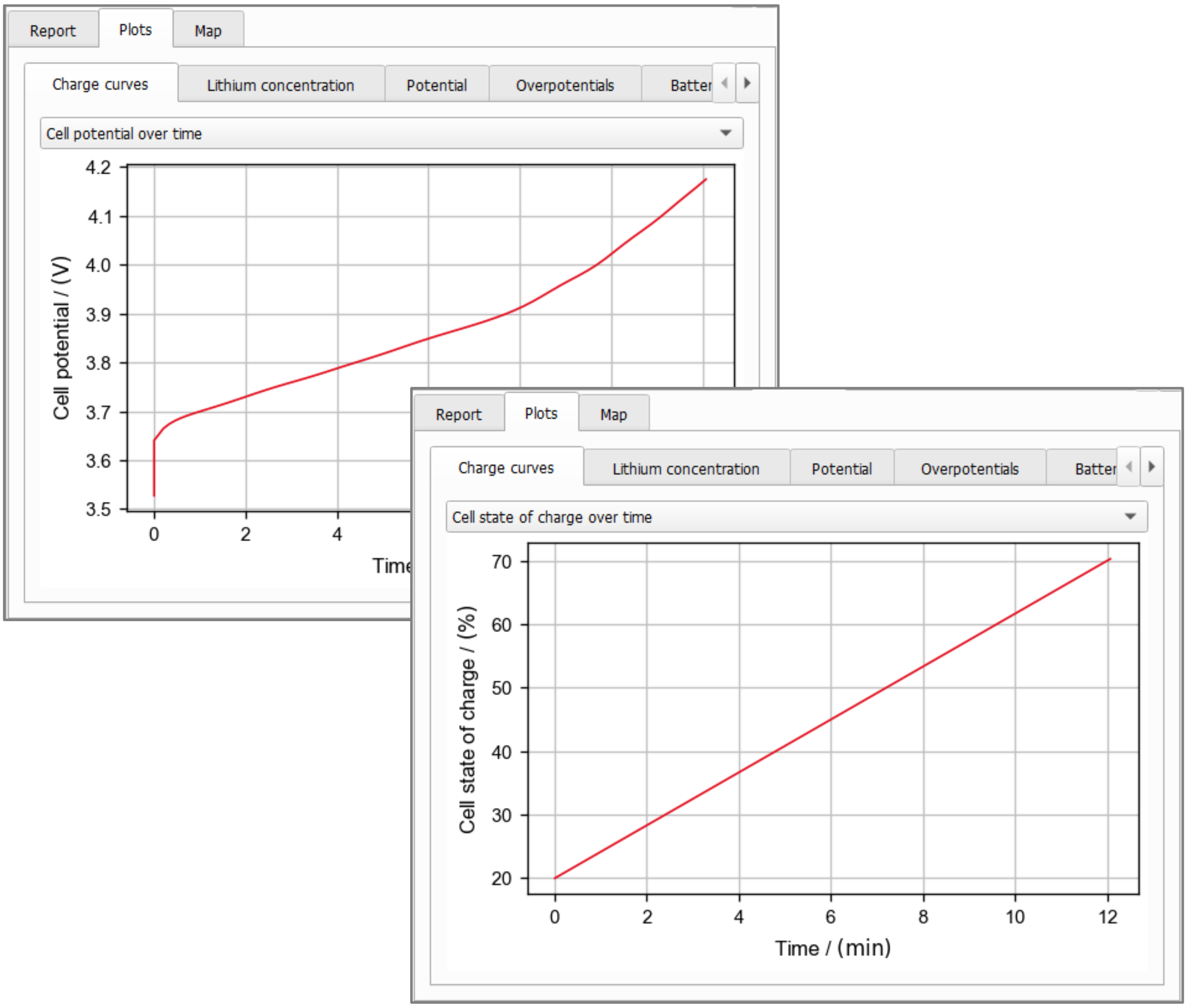
During charging, the curves always show higher values than the equilibrium curve, indicating that charging the battery requires a higher potential than what is observed in equilibrium. On the other hand, during discharging, the curves are always below the equilibrium curve. If Calculate estimation only was chosen as option, the estimation of the cell potential is shown instead of the computed time evolution of the potential.

In case a charging profile was selected for the simulation (see page 57), the cell potential is shown for each simulation step in the profile in a different color. If the charging profile consists of charging and discharging steps, the equilibrium cell potential is shown both for charging and discharging.

Start and end point of the whole simulation as well as intermediate start points for the steps are shown in the graph.



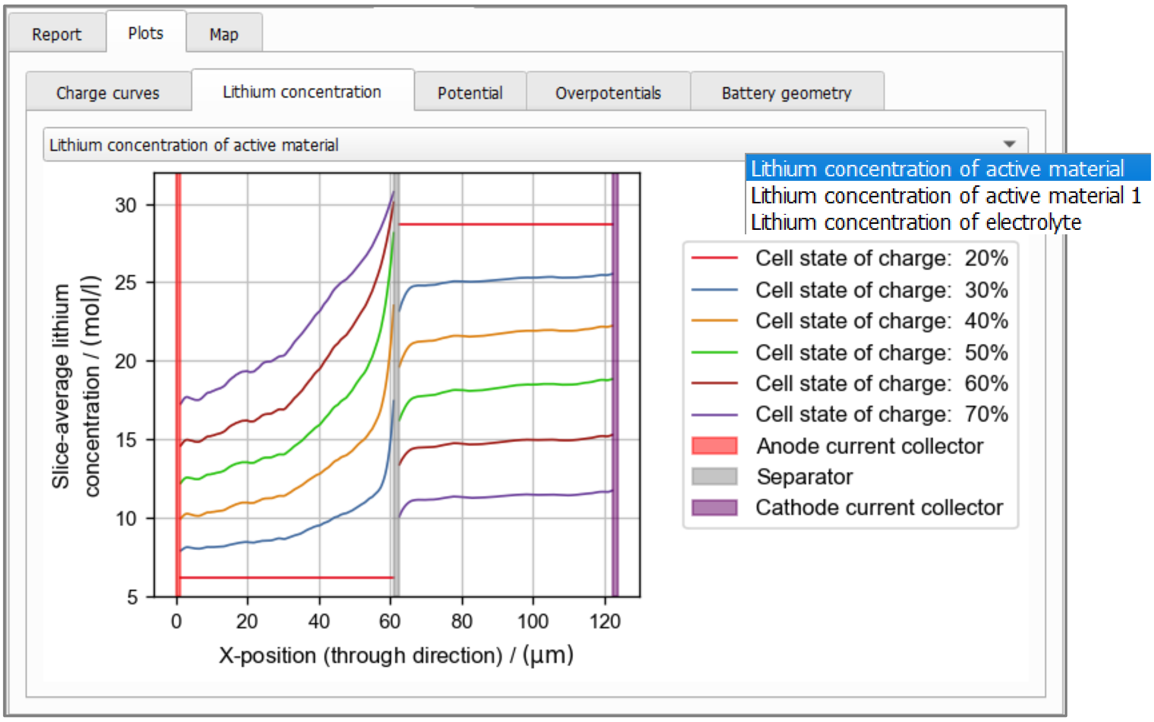
Due to simulation with a constant charge rate and without the selection of an upper cut-off voltage in the example shown, the state of charge increases linearly with the simulated time. The trend of the **Cell potential over time** is therefore the same as for the **Cell potential** over **Cell state of charge** and the **Cell state of charge** over **Time** is a straight line.



The **Current over time**, as well as the **Current density over time**, and the **Charge rate over time** are constant for the example shown.

The **Lithium concentration** tab shows the mean concentration of lithium ions for each slice in y-z-direction for a constant x value. It can be displayed as **Lithium concentration of electrolyte**, **Lithium concentration of active material** (for all active materials together), or of each active material separately (**Lithium Concentration of active material 1, Lithium concentration of active material 2, etc.**).

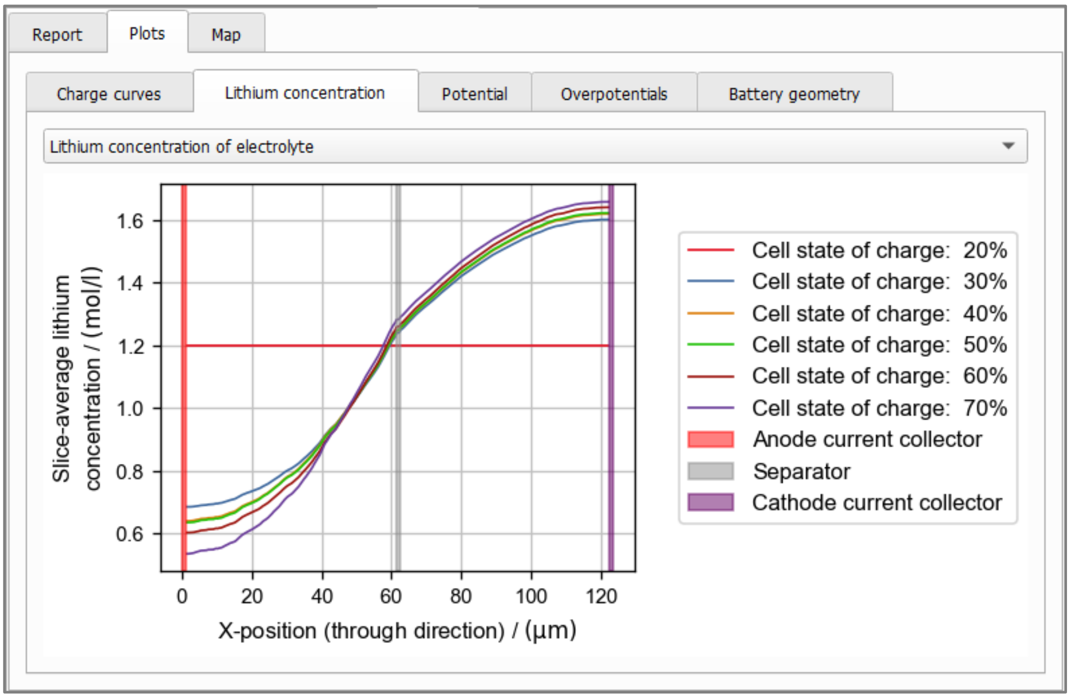
A separate curve is shown in these plots for each state of charge with an intermediate result available. As can be seen in the following plot, the concentration of lithium ions in the cathode (right-part of the plot) is decreasing during charging of the battery, while the concentration in the anode is increasing.



At the beginning of the simulation, the Li-ion concentration of the electrochemically connected part of the electrolyte is constant throughout the battery. Its value is the equilibrium Lithium concentration specified in the settings.

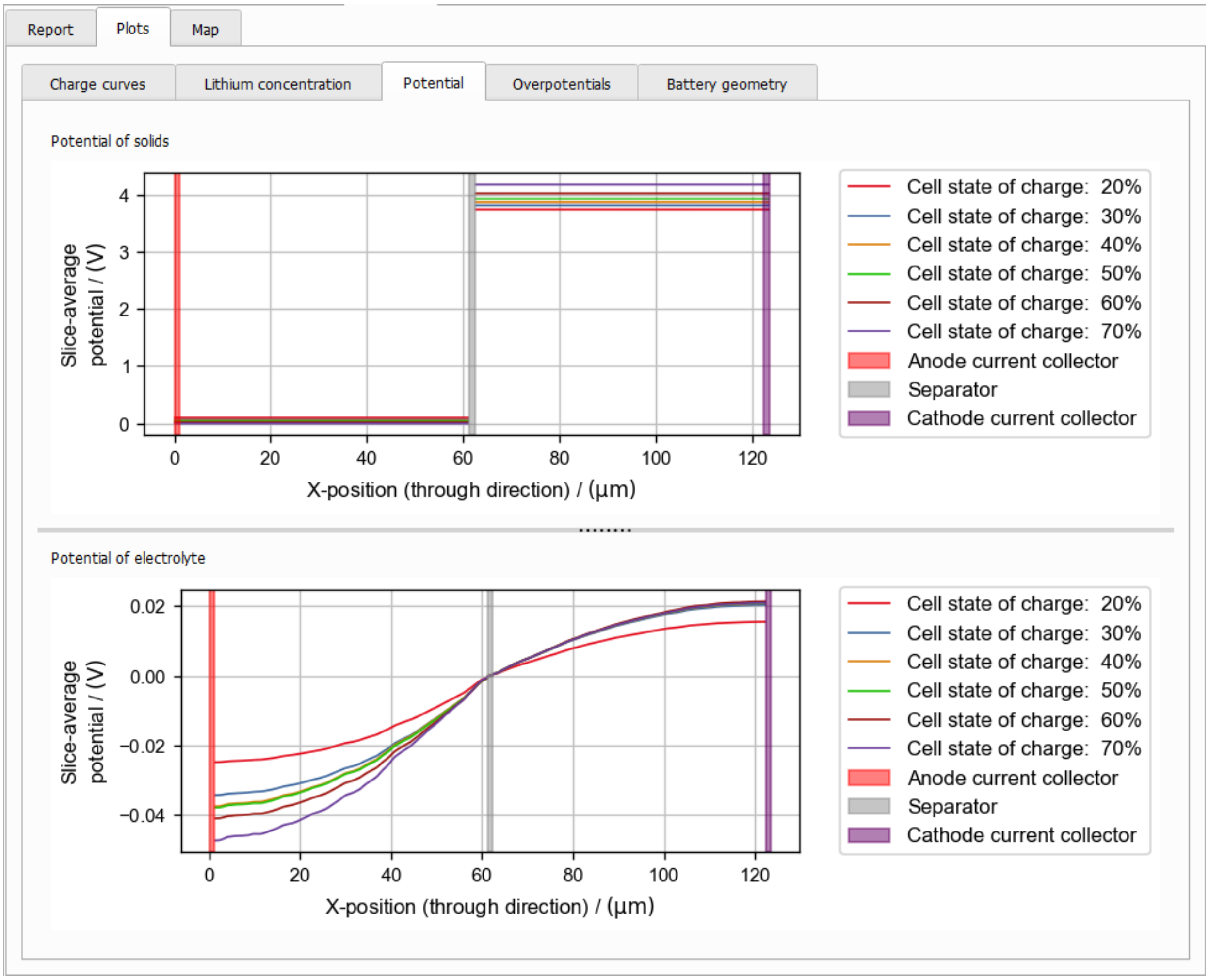
While charging, the cathode releases Li-ions into the electrolyte, causing the Li-ion concentration to increase on the cathode side. Simultaneously, the Li-ions intercalate into the anode.

Since the diffusion of the Li-ions takes some time, the gradient of the Li-ion concentration in the electrolyte is visible in the example.



The **Potential** tab shows the mean potential for each slice in y- and z-direction for the solid part of the battery, as well as for the electrolyte. All potentials are calculated with respect to an imagined lithium reference electrode in the center of the separator.

Again, for each state of charge with an intermediate result available, a separate curve is shown in the plot. Click the right mouse button in the plot to change view settings.



In the example shown here, for each time step, the potential in the solid is constant within each electrode. This indicates that the conductivity is high enough. If the conductivity were much smaller, the potential would exhibit a drop within one electrode.

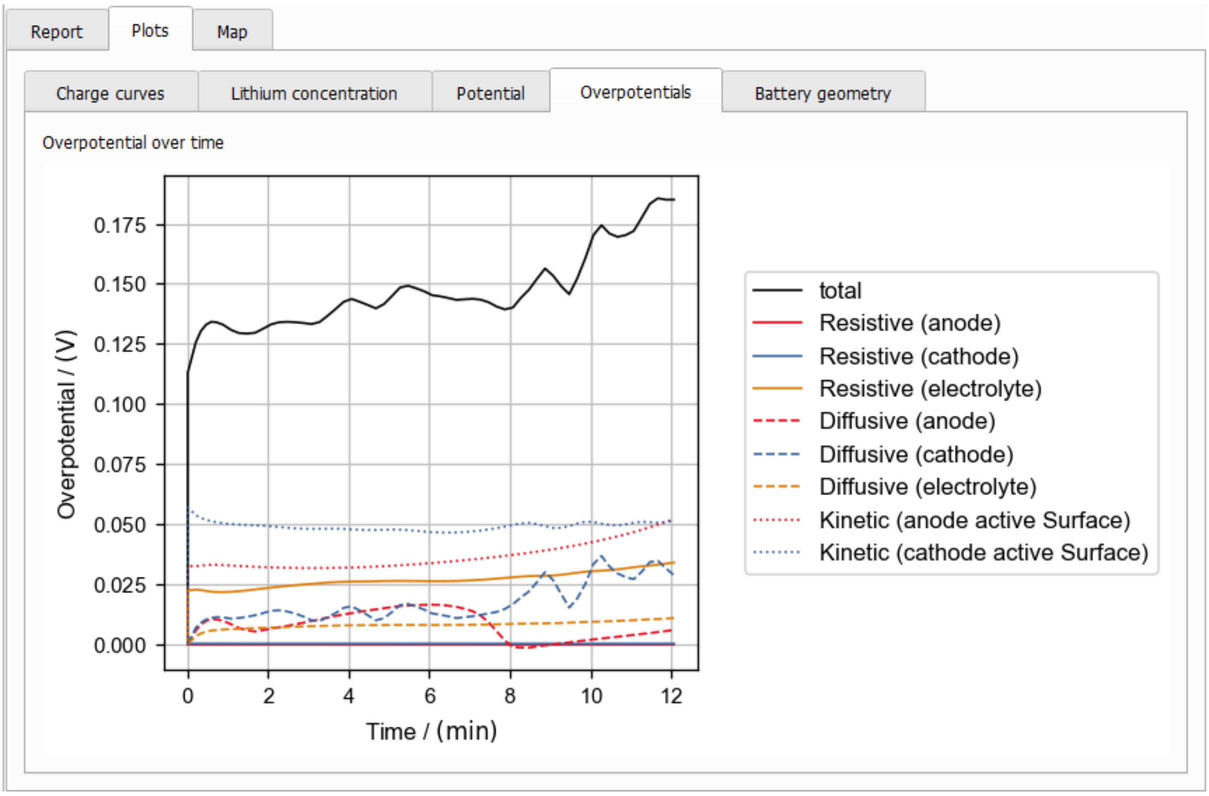
In this example, the solver calculates the battery charging by applying a constant electric current. The necessary potential difference for keeping up the current is determined from the electric current in the solids, the ionic current in the electrolyte, and the overpotentials on the boundary of electrolyte and active material.

The current is only dependent on the potential difference and not on the total potential offset. The latter can be chosen freely.

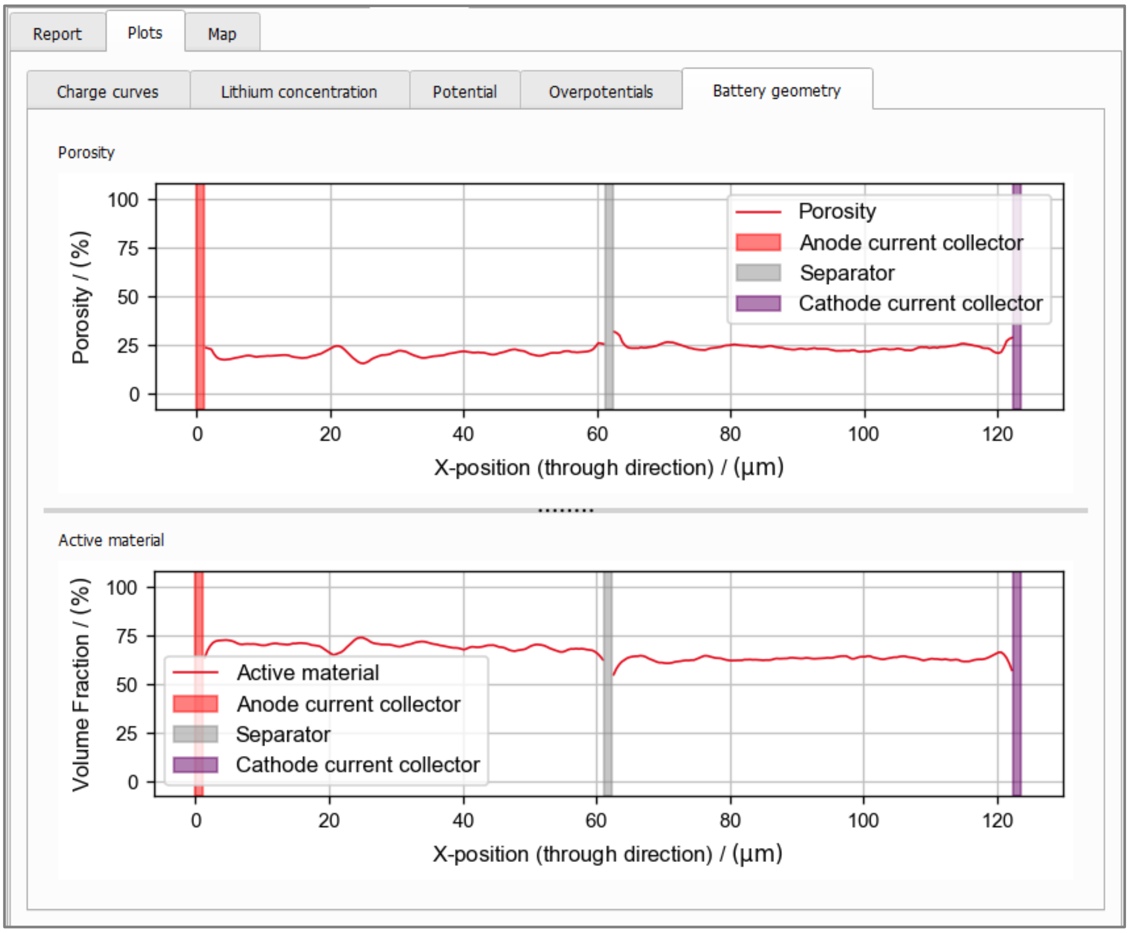
For the potential of the electrolyte, a gradient is visible between the anode current collector and the cathode current collector. This gradient increases for higher charge rates and the potential grows from left to right. This is caused by the charge current that is driven by the ions resolved in the electrolyte. The charge current leads to a growing potential in flow direction because the ionic conductivity is not zero. The lower the ionic conductivity, the stronger the growth of the electrolyte potential in flow direction.

Note that the **Lithium concentration** and the **potential** subtabs of the **Plots** tab do not exist for simulation results computed with BESTmeso. For the homogenized simulation, the voxel and slice-based information shown on these two tabs is not available.

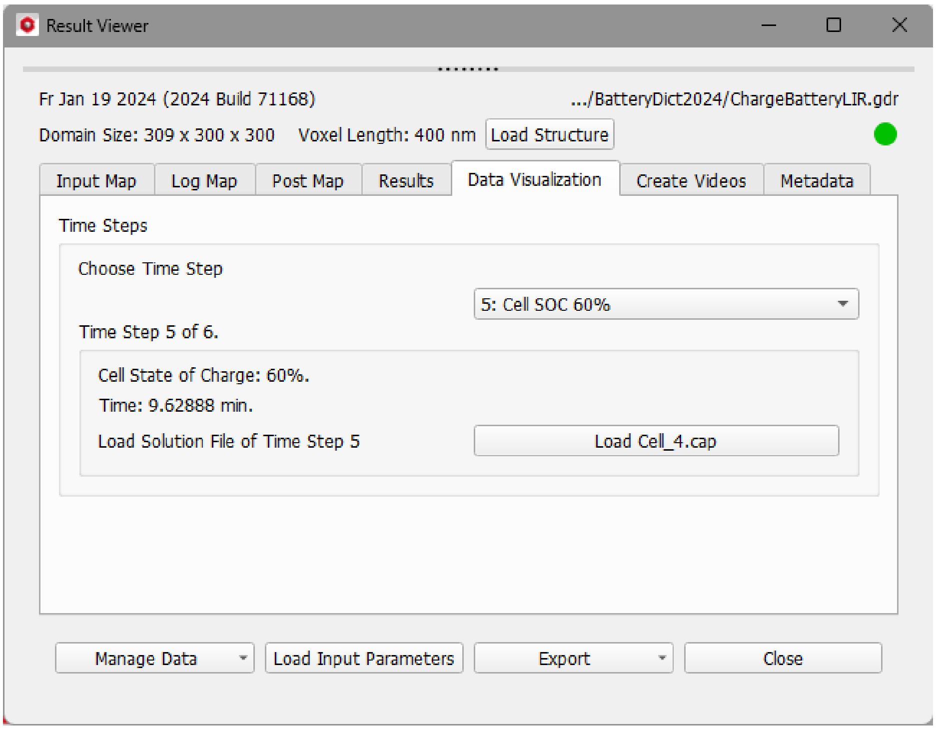
On the **Overpotentials** tab, the evolution of the different overpotentials over time is visualized. For an explanation of the overpotentials see page 16.



The **Battery geometry** tab shows the mean of porosity and the volume fraction of active material for each slice in y- and z-direction.



Solution files can be accessed via the **Data Visualization** tab. The number of available solution files depends on the length of the interval selected for output of intermediate results in [Output Options](#) (see above).



Fr Jan 19 2024 (2024 Build 71168) .../BatteryDict2024/ChargeBatteryLIR.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

Time Steps

Choose Time Step 5: Cell SOC 60%

Time Step 5 of 6.

Cell State of Charge: 60%.

Time: 9.62888 min.

Load Solution File of Time Step 5 Load Cell_4.cap

For instance, let us select the solution file at a state of charge of 60%. For the example shown here, we just need to select step 5. By clicking **Load Cell_4.cap**, the available volume fields (tab Select Volume Fields) of the file can be selected. Additionally, the user may have a look at the file header of the result file (View File Header).

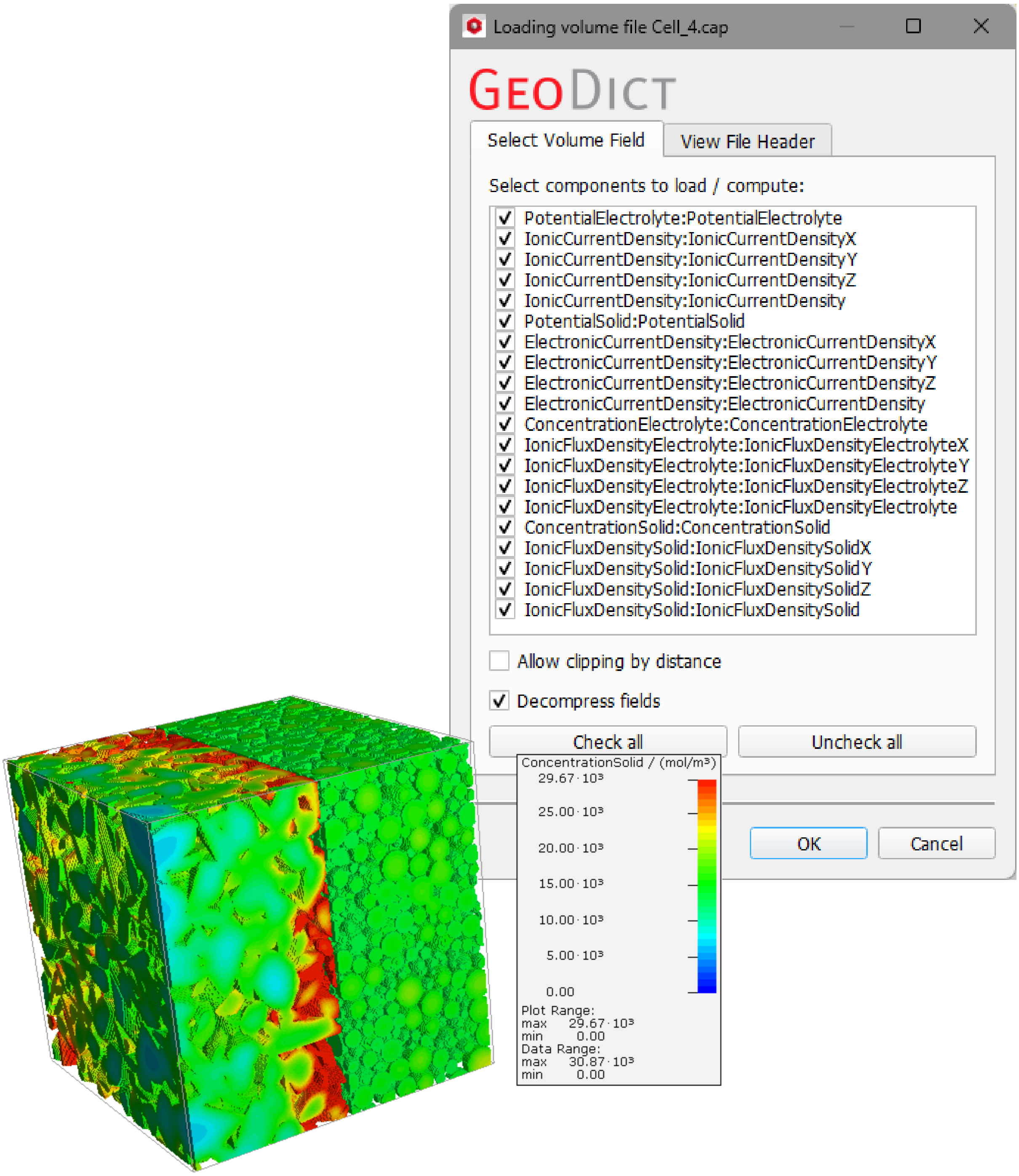
Volume Fields available depend on the solver used for the computation (LIR or BESTmicro) and on the fact whether porous binder is used or not.

Load, for example, only the concentration in the solid part of the battery.

In this case, first click **Uncheck all**.

Select **ConcentrationSolid:ConcentrationSolid**. After clicking **OK**, the selected field is loaded into the GeoDict main window.

The concentration field of lithium ions for the active materials is visualized here. More information on visualization of results is available in the Visualization handbook.



Loading volume file Cell_4.cap

Select components to load / compute:

☑ PotentialElectrolyte:PotentialElectrolyte
☑ IonicCurrentDensity:IonicCurrentDensityX
☑ IonicCurrentDensity:IonicCurrentDensityY
☑ IonicCurrentDensity:IonicCurrentDensityZ
☑ IonicCurrentDensity:IonicCurrentDensity
☑ PotentialSolid:PotentialSolid
☑ ElectronicCurrentDensity:ElectronicCurrentDensityX
☑ ElectronicCurrentDensity:ElectronicCurrentDensityY
☑ ElectronicCurrentDensity:ElectronicCurrentDensityZ
☑ ElectronicCurrentDensity:ElectronicCurrentDensity
☑ ConcentrationElectrolyte:ConcentrationElectrolyte
☑ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyteX
☑ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyteY
☑ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyteZ
☑ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyte
☑ ConcentrationSolid:ConcentrationSolid
☑ IonicFluxDensitySolid:IonicFluxDensitySolidX
☑ IonicFluxDensitySolid:IonicFluxDensitySolidY
☑ IonicFluxDensitySolid:IonicFluxDensitySolidZ
☑ IonicFluxDensitySolid:IonicFluxDensitySolid

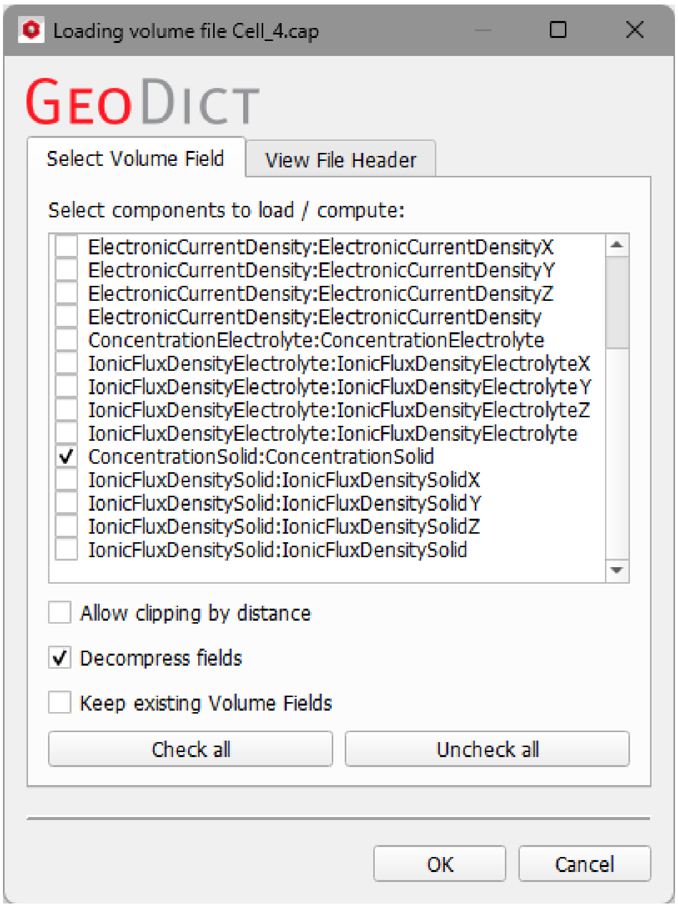
☐ Allow clipping by distance
☑ Decompress fields

The concentration gradient in the anode (left part of the battery) is in the example shown higher as in the cathode (right part of the battery).

Check **Allow clipping by distance** to create a distance map regarding the solid material. Its value is zero on the surface of the solid material, inside the material the values are negative and outside positive. This allows clipping any result field by its distance to the surface of the solid material.

Check **Keep existing Volume Fields** if you repeat loading result fields for another time step or have other previously loaded volume fields in memory that you want to keep. If this box is not checked, previously loaded volume fields are discarded.

If the simulation was run with LIR solver, volume fields are stored in a compressed way. Check **Decompress fields**, to be able to use all visualization features.



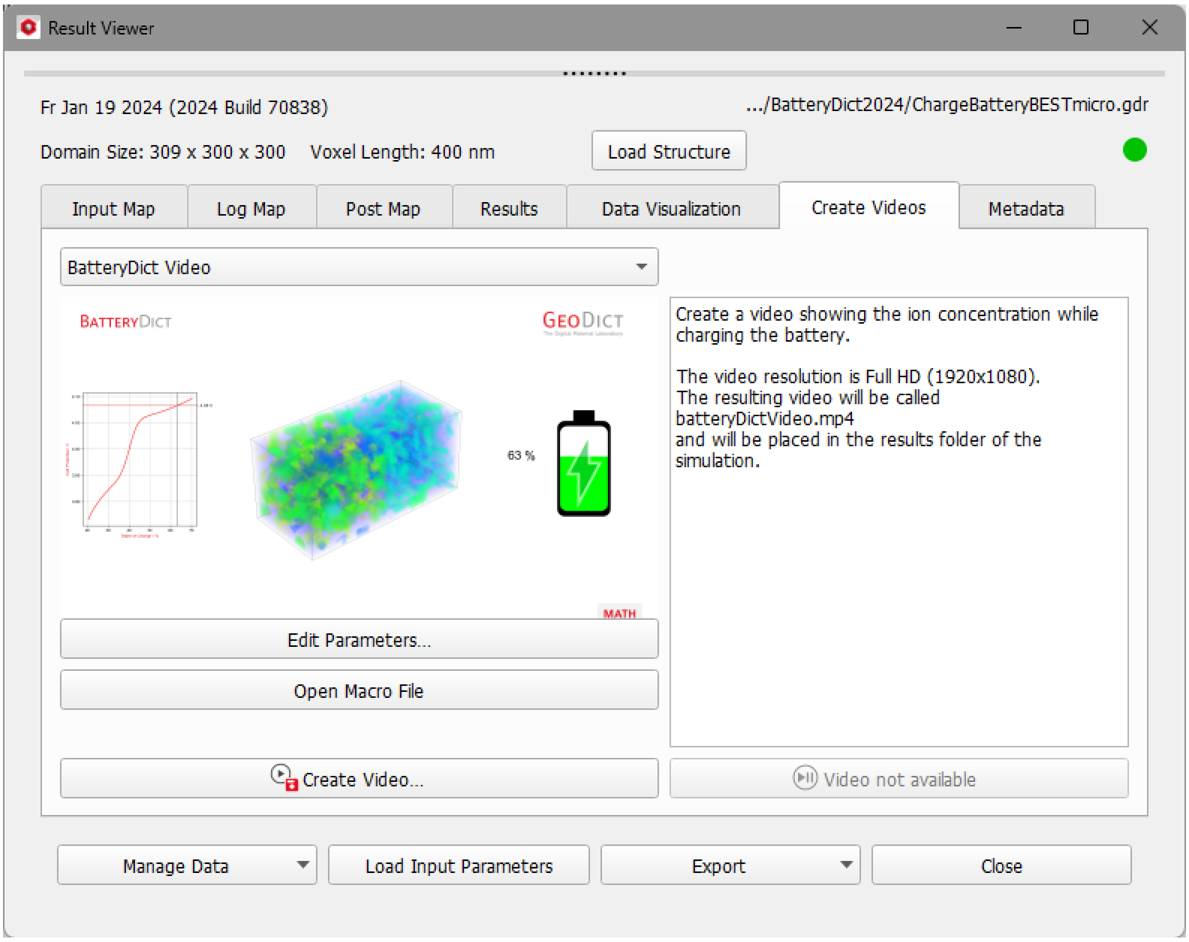
Select components to load / compute:

☐ ElectronicCurrentDensity:ElectronicCurrentDensityX
☐ ElectronicCurrentDensity:ElectronicCurrentDensityY
☐ ElectronicCurrentDensity:ElectronicCurrentDensityZ
☐ ElectronicCurrentDensity:ElectronicCurrentDensity
☐ ConcentrationElectrolyte:ConcentrationElectrolyte
☐ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyteX
☐ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyteY
☐ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyteZ
☐ IonicFluxDensityElectrolyte:IonicFluxDensityElectrolyte
☑ ConcentrationSolid:ConcentrationSolid
☐ IonicFluxDensitySolid:IonicFluxDensitySolidX
☐ IonicFluxDensitySolid:IonicFluxDensitySolidY
☐ IonicFluxDensitySolid:IonicFluxDensitySolidZ
☐ IonicFluxDensitySolid:IonicFluxDensitySolid

☐ Allow clipping by distance
☑ Decompress fields
☐ Keep existing Volume Fields

Uncheck the box to visualize the adaptive grid structure used for the computation. In this case, not all visualization features can be used.

Through the **Create Videos** tab, a video showing the ion concentration while charging or discharging of the battery can be created. The first part of the video shows the cropping of the battery structure together with the ion concentration at the start of the simulation.



Fr Jan 19 2024 (2024 Build 70838)

.../BatteryDict2024/ChargeBatteryBESTmicro.gdr

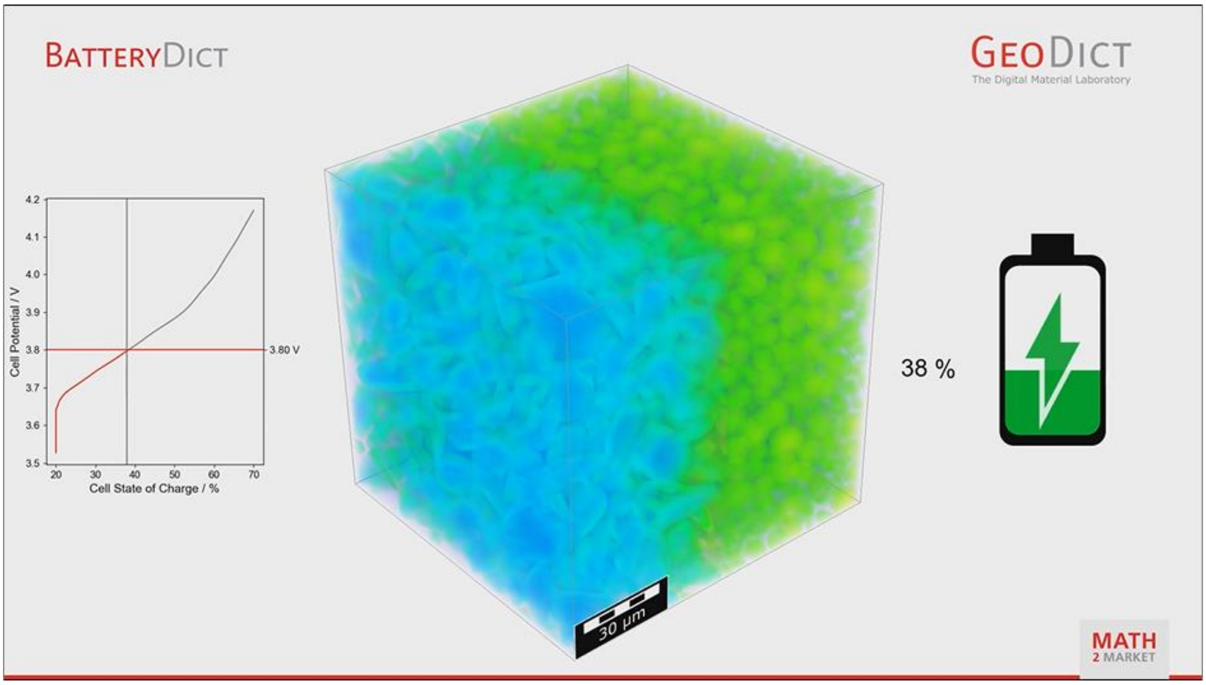
Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

Create a video showing the ion concentration while charging the battery.

The video resolution is Full HD (1920x1080).
The resulting video will be called
batteryDictVideo.mp4
and will be placed in the results folder of the simulation.

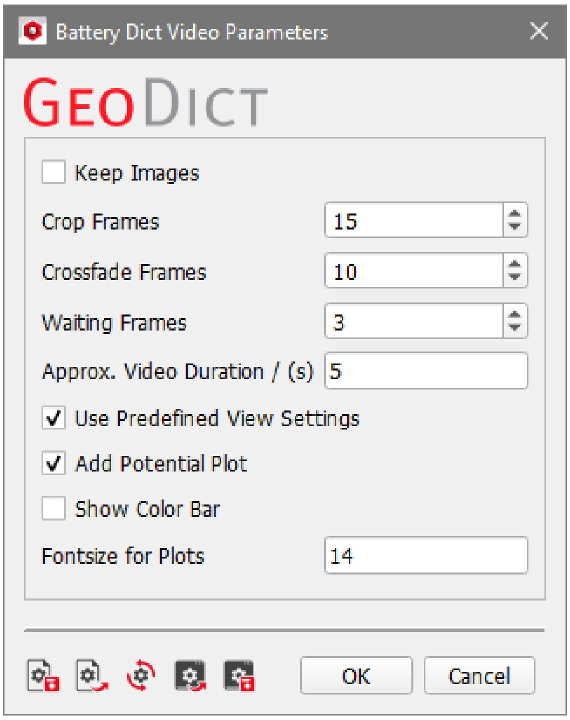
Click **Create Video** to generate the video with the default settings.

A screenshot of such a video is shown here. On the left side, you can see a graph displaying the cell potential over state of charge, with the current state of charge value indicated. In the middle, the ion concentration within the battery structure is illustrated. On the right side, a schematic representation of the current state of charge of the battery is provided.



Click **Open Macro File**, under the **Create Videos** tab, to open the GeoDict Python macro used to create the video, if you are interested in modifying it with a text editor.

Click **Edit Parameters...** to modify the default settings of the video creation.



☐ Keep Images
Crop Frames: 15
Crossfade Frames: 10
Waiting Frames: 3
Approx. Video Duration / (s): 5
☑ Use Predefined View Settings
☑ Add Potential Plot
☐ Show Color Bar
Fontsize for Plots: 14

Check **Keep Images** to save not only the video, but also the created images for the ion concentration in a separate folder.

The number defined in **Crop Frames** defines the time for the cropping of the structure at the start of the video.

**Crossfade Frames** defines the time for the visualization of the ion concentration field. The shorter the time defined here, the faster the charging is shown in the video.

**Waiting Frames**: A higher number indicates a longer pause before and after charging.

Check **Use Predefined View Settings** to use the predefined orientation of the structure for the video creation as shown in the example above. Uncheck this box to use the orientation of the structure as shown in the GeoDict Visualization Area.

Check **Add Potential Plot** to keep the graph with the potential curve at the left of the video.

Check **Show Color Bar** to add an additional color bar for the ion concentration below the structure.

The font size for the potential curve graph can be set with **Fontsize for Plots**.

If the video is created, the **Play Video** button is activated on the **Create Videos** tab.

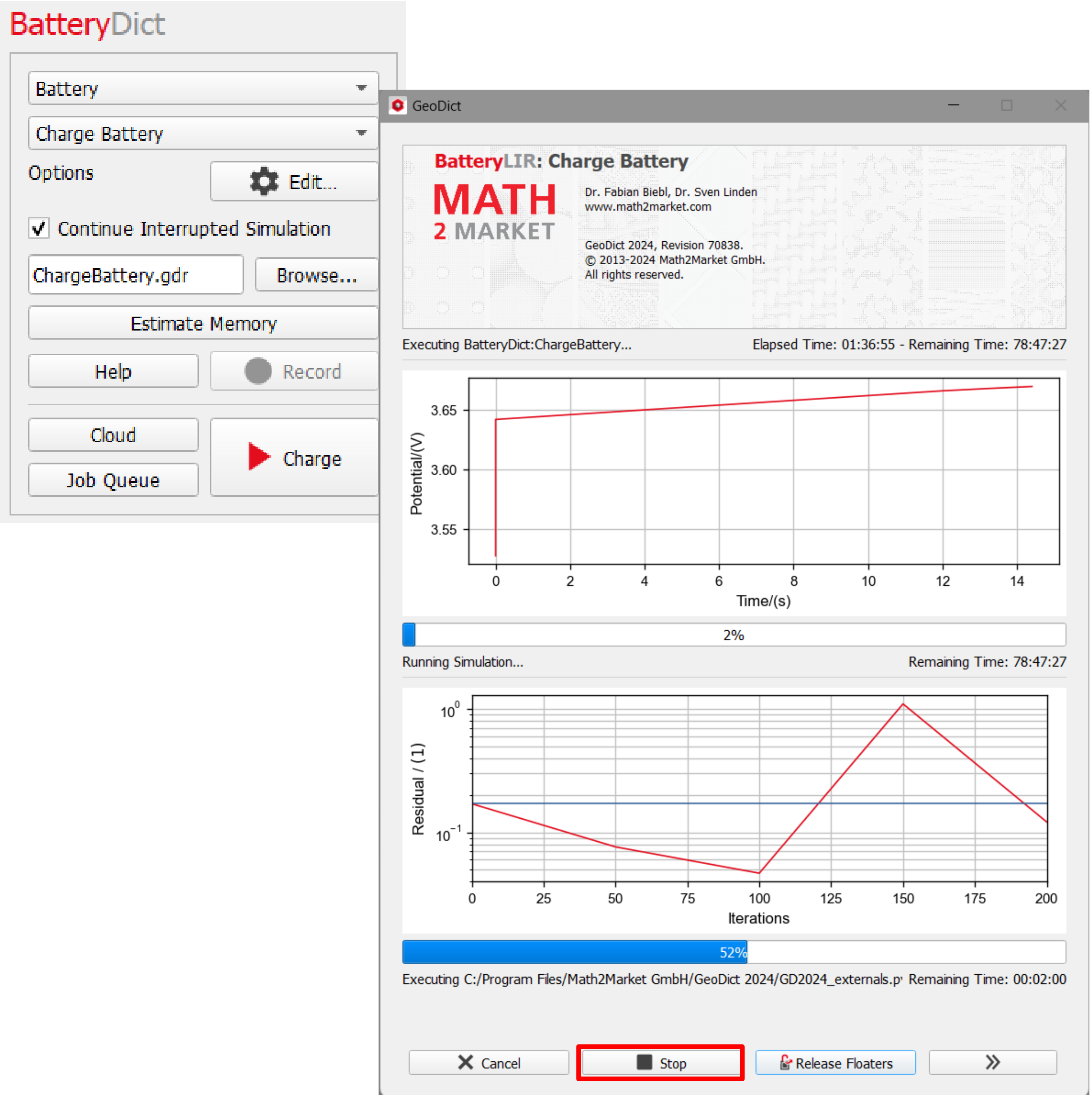
## CONTINUE INTERRUPTED SIMULATION

It is possible to continue a previously interrupted charging simulation.

If **Battery** and **Charge Battery** are selected from the BatteryDict pull-down menu, check **Continue Interrupted Simulation**.

Browse for a GeoDict result file, created earlier with the command **Battery – Charge Battery**, and continue an unfinished simulation by selecting **Charge**.

Continuing an interrupted simulation is possible, if a previously run charging simulation was stopped and GeoDict could create a result file.



Battery

Charge Battery

☑ Continue Interrupted Simulation

ChargeBattery.gdr

Executing BatteryDict:ChargeBattery... Elapsed Time: 01:36:55 - Remaining Time: 78:47:27

Running Simulation... Remaining Time: 78:47:27

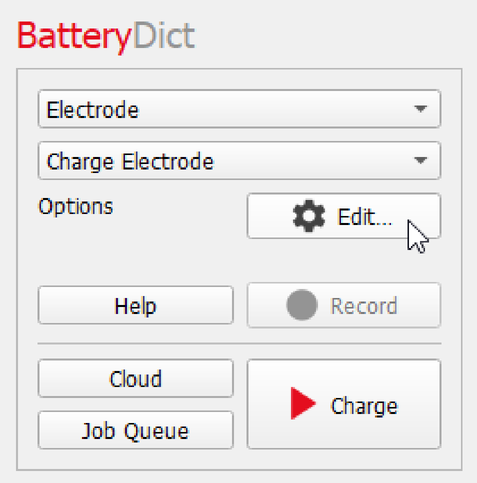
Executing C:/Program Files/Math2Market GmbH/GeoDict 2024/GD2024_externals.p Remaining Time: 00:02:00

If the simulation was canceled, it is not possible to continue the simulation later.

## ELECTRODE - CHARGE ELECTRODE

In GeoDict 2024, the command to simulate charging of a single electrode is called **Charge Electrode**. It can be used for charging simulations of arbitrary structures loaded in GeoDict, consisting of a single electrode or an electrode together with a separator and/or a current collector. Input parameters and results are adapted here, to fit for the simulation of an electrode. The electrode can consist of any active material. Electrochemically, the lithium reservoir is always considered as the anode in the computation and the investigated electrode is considered as the cathode. As the electrochemical potential of the lithium reservoir is by definition 0, the cell potential of the half cell is the electrochemical potential of the investigated electrode.

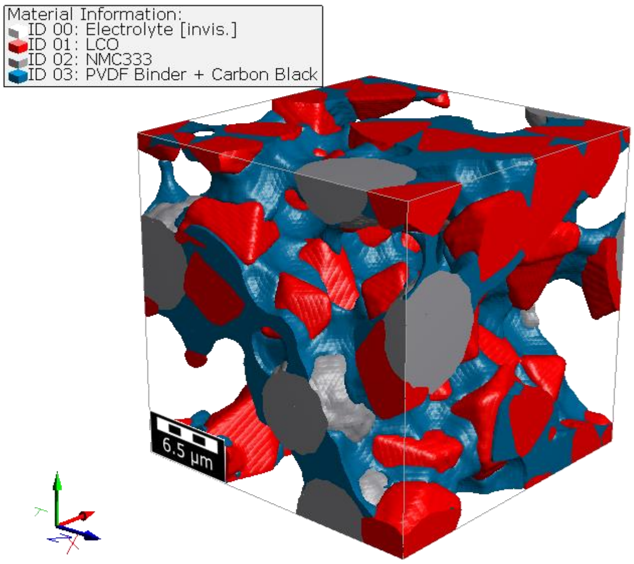
Click the options' **Edit** button to define the parameters for the simulation.

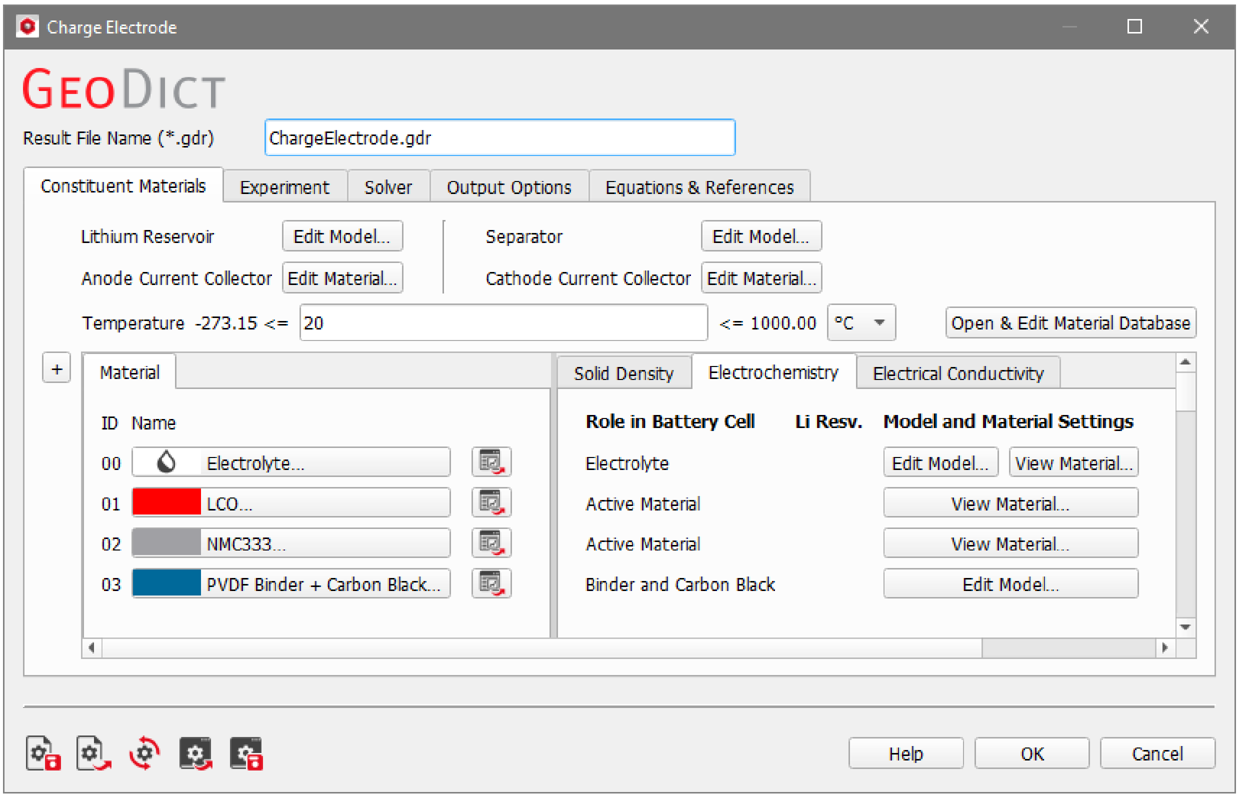


## CONSTITUENT MATERIALS

If the structure of a single electrode is loaded in GeoDict, this structure is considered as the cathode for the half cell simulation. The half cell is created by attaching the electrode in X+ direction to the separator. The lithium reservoir will be attached in X- direction to the separator.

If a Material ID for the separator is provided, it must adhere to the rule that the half cell is assembled in the X-direction.





Result File Name (*.gdr) ChargeElectrode.gdr

Lithium Reservoir — Edit Model...
Anode Current Collector — Edit Material...
Separator — Edit Model...
Cathode Current Collector — Edit Material...

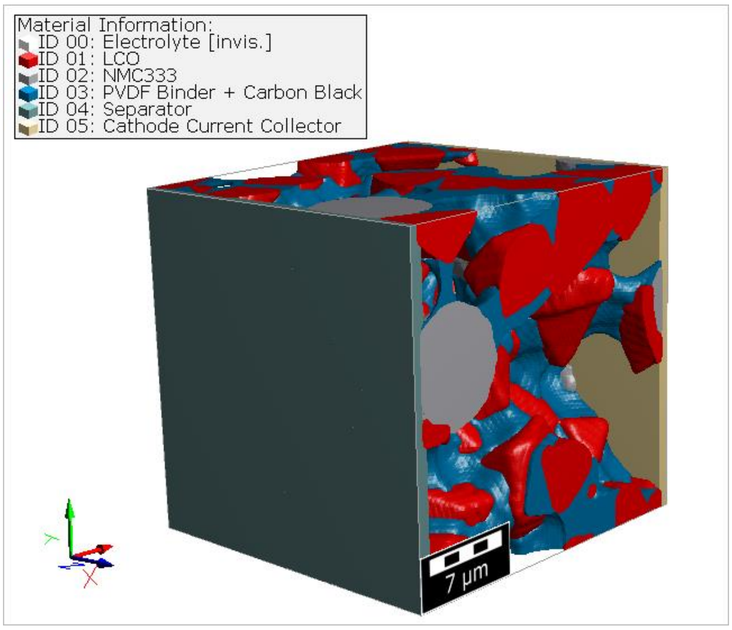
Temperature -273.15 <= 20 <= 1000.00 °C

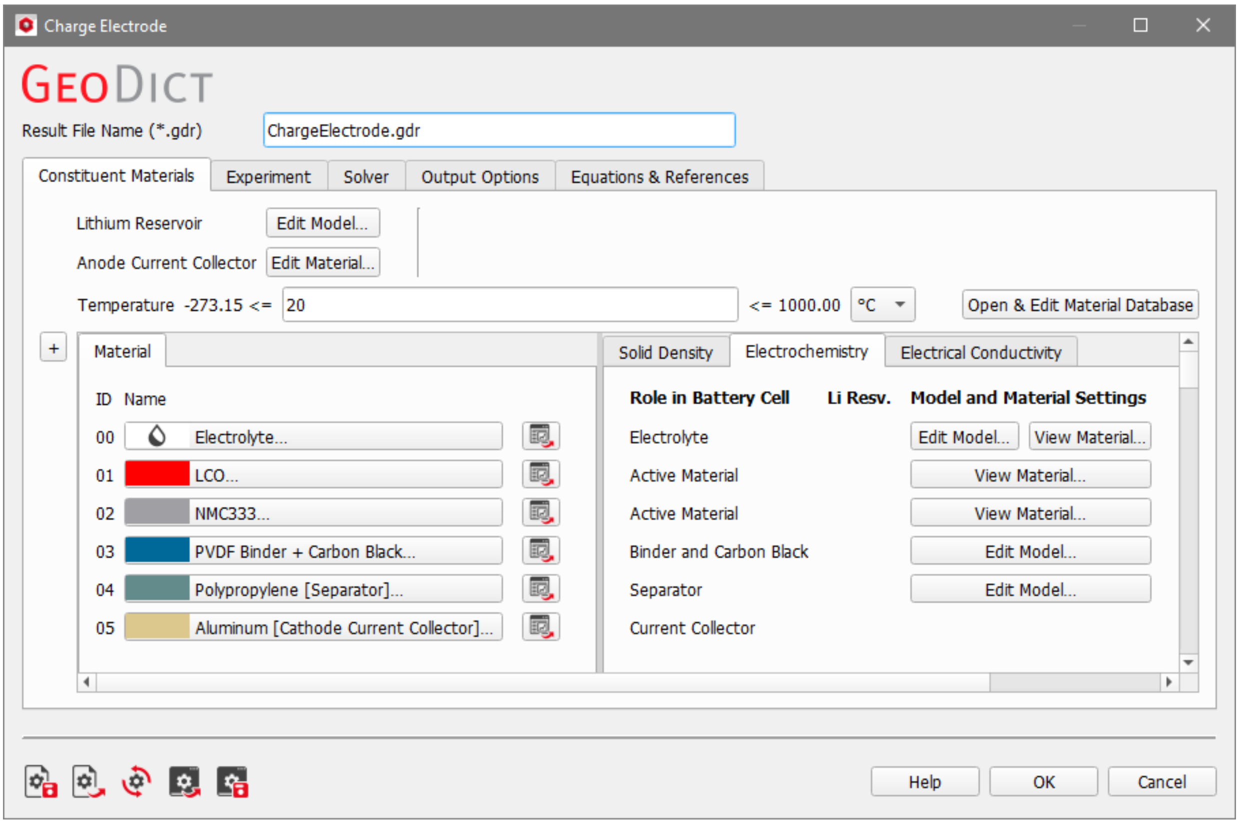
| ID | Name | Role in Battery Cell | Li Resv. | Model and Material Settings |
|---|---|---|---|---|
| 00 | Electrolyte... | Electrolyte | | Edit Model... View Material... |
| 01 | LCO... | Active Material | | View Material... |
| 02 | NMC333... | Active Material | | View Material... |
| 03 | PVDF Binder + Carbon Black... | Binder and Carbon Black | | Edit Model... |

In the Charge Electrode dialog, materials available for the electrode are shown. In the same way as for battery charging, the parameters of the materials can be shown or modified. See page 43ff for a more detailed description.

On top of the dialog, the parameters for anode current collector and lithium reservoir can be modified. If not specified by a separate Material ID in the structure, the parameters for the separator and the cathode current collector can also be defined.

If the structure is created with separate Material IDs for cathode current collector and separator, these roles can be defined for the materials on the **Electrochemistry** subtab. In this case, the buttons for modifying the corresponding properties disappear from the top of the dialog.





Charge Electrode

Result File Name (*.gdr): ChargeElectrode.gdr

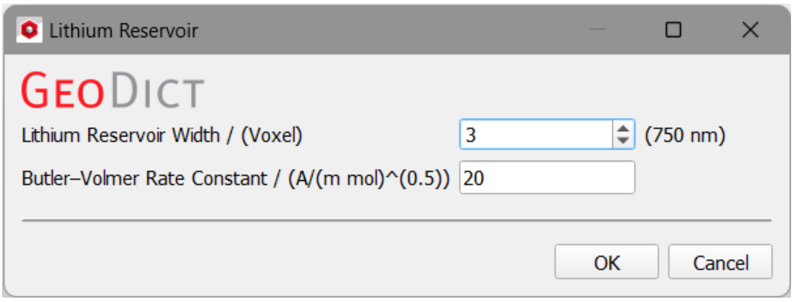
Lithium Reservoir: Edit Model...

Anode Current Collector: Edit Material...

Temperature -273.15 <= 20 <= 1000.00 °C

| ID | Name | Role in Battery Cell | Li Resv. | Model and Material Settings |
|---|---|---|---|---|
| 00 | Electrolyte... | Electrolyte | | Edit Model... View Material... |
| 01 | LCO... | Active Material | | View Material... |
| 02 | NMC333... | Active Material | | View Material... |
| 03 | PVDF Binder + Carbon Black... | Binder and Carbon Black | | Edit Model... |
| 04 | Polypropylene [Separator]... | Separator | | Edit Model... |
| 05 | Aluminum [Cathode Current Collector]... | Current Collector | | |

For the lithium reservoir, choose **Edit Model** to enter the width in number of voxels and the Butler-Volmer Rate Constant for the simulation.

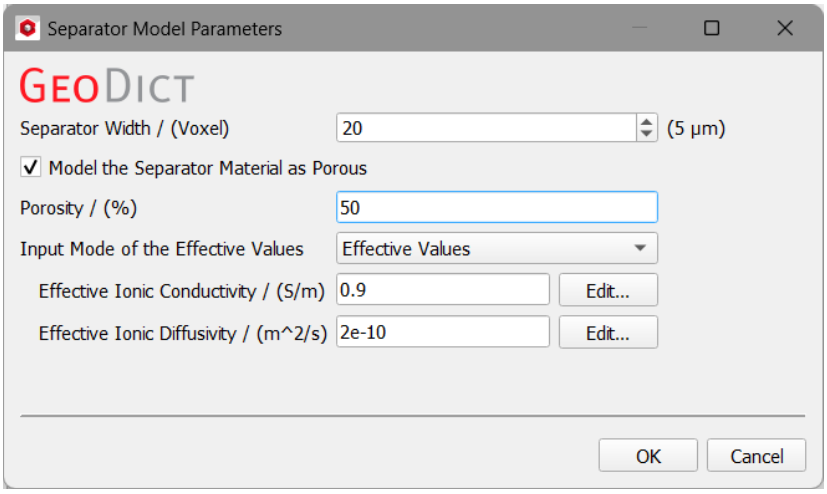


Lithium Reservoir

Lithium Reservoir Width / (Voxel): 3 (750 nm)

Butler–Volmer Rate Constant / (A/(m mol)^(0.5)): 20

For the separator, with **Edit Model** the ionic conductivity and ionic diffusivity of the electrolyte can be selected (uncheck **Model the Separator Material as Porous**), or effective values can be defined. See page 51 for more details. The width of the separator can be selected in number of voxels.



Separator Model Parameters

Separator Width / (Voxel): 20 (5 µm)

☑ Model the Separator Material as Porous

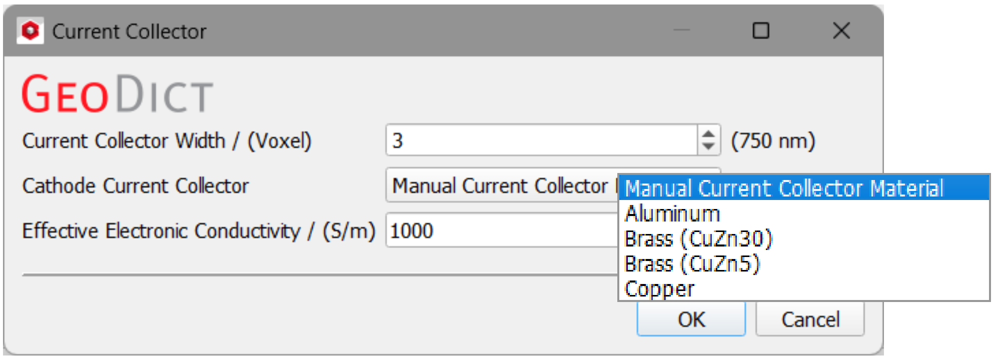
Porosity / (%): 50

Input Mode of the Effective Values: Effective Values

Effective Ionic Conductivity / (S/m): 0.9

Effective Ionic Diffusivity / (m^2/s): 2e-10

Width, material, and electronic conductivity of the current collectors can be defined with the **Edit Material** buttons.



Current Collector Width / (Voxel) 3 (750 nm)

Cathode Current Collector Manual Current Collector

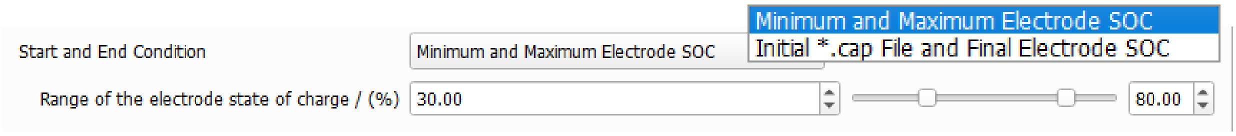
Effective Electronic Conductivity / (S/m) 1000

Note, that even for materials from the GeoDict Material Database, the effective electronic conductivity needs to be defined in the dialog. It is recommended that the value defined is not higher than 1000 S/m to avoid numerical problems of the solver (see page 46 for more details).

## EXPERIMENT

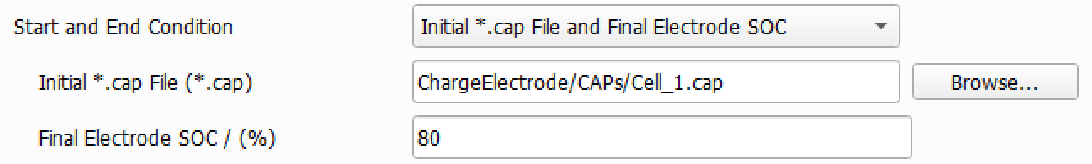
For the charging simulation of an electrode, the parameters that need to be selected on the **Experiment** tab, are nearly the same as for the simulation of a whole battery, see page 55.

Differences arise because, in a half cell simulation, only the state of charge (SOC) of the electrode being studied needs to be taken into account. The other electrode is modelled as a never-ending lithium reservoir. Therefore, as **Experiment Type Lithiate Electrode** and **Delithiate Electrode** are available that simulate lithiation or delithiation of the investigated electrode vs the lithium reservoir. The **Start and End Condition** for the simulation are defined by selecting **Minimum and Maximum Electrode SOC**.


Start and End Condition: Minimum and Maximum Electrode SOC

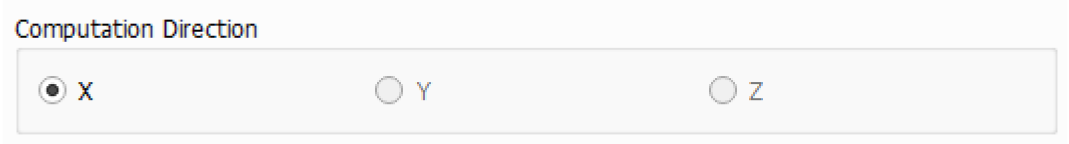
Range of the electrode state of charge / (%): 30.00 – 80.00

To start the simulation from a lithium concentration in the electrode, resulting from a previous simulation, select **Initial *.cap File and Final Electrode SOC**. Choose a .cap file as starting point of the simulation, and define the final SOC of the electrode that is not modelled as the lithium reservoir.


Start and End Condition: Initial *.cap File and Final Electrode SOC

Initial *.cap File (*.cap): ChargeElectrode/CAPs/Cell_1.cap

Final Electrode SOC / (%): 80


Computation Direction

● X ○ Y ○ Z

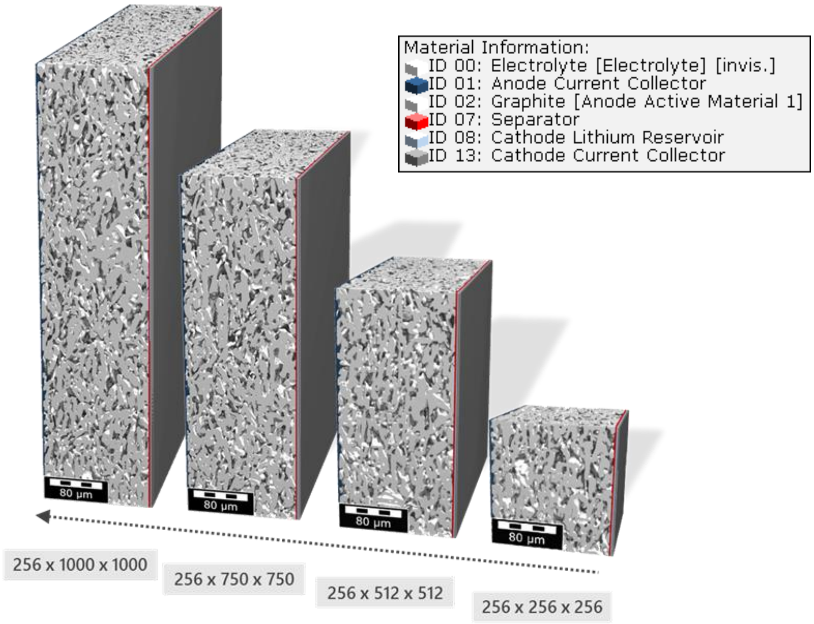
The **Computation Direction** is fixed in X direction in GeoDict 2024.

## SOLVER, OUTPUT OPTIONS, AND EQUATIONS & REFERENCES TAB

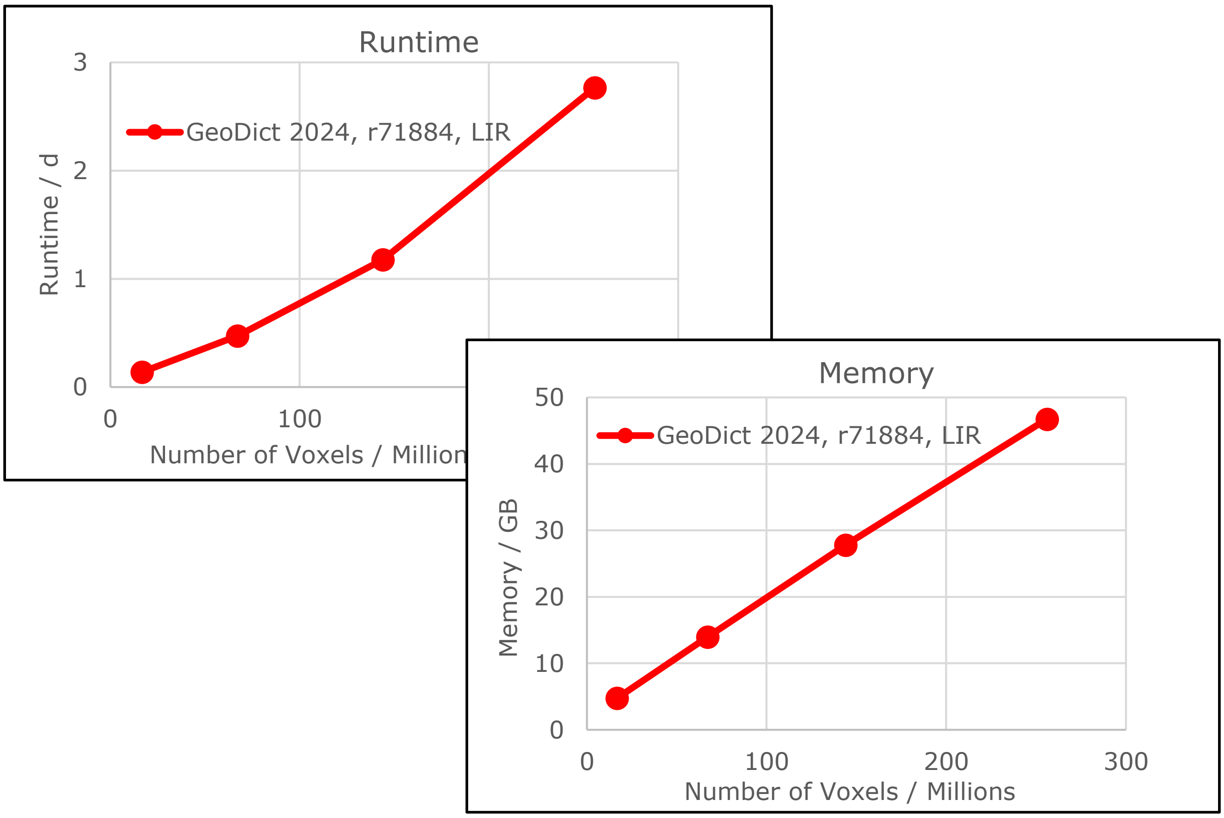
The options that can be selected on the **Solver** and the **Output Options** tab, as well as the equations on the **Equations & References** tab, are the same as for the charging of a whole battery. A description can be found on page 59ff.

## PARALLELIZATION BENCHMARK RESULTS

A half cell consisting of a graphite electrode and a lithium reservoir is simulated. The graphite electrode is charged from 5% to 91%. The simulation is run for increasing structure size to account for inhomogeneities or for battery ageing simulations.



The simulation is run with LIR solver. The necessary memory for the computation is increasing linearly with the number of voxels simulated. Even a simulation with 250 million voxels can be run in less than 3 days, with only 50 GB RAM required.

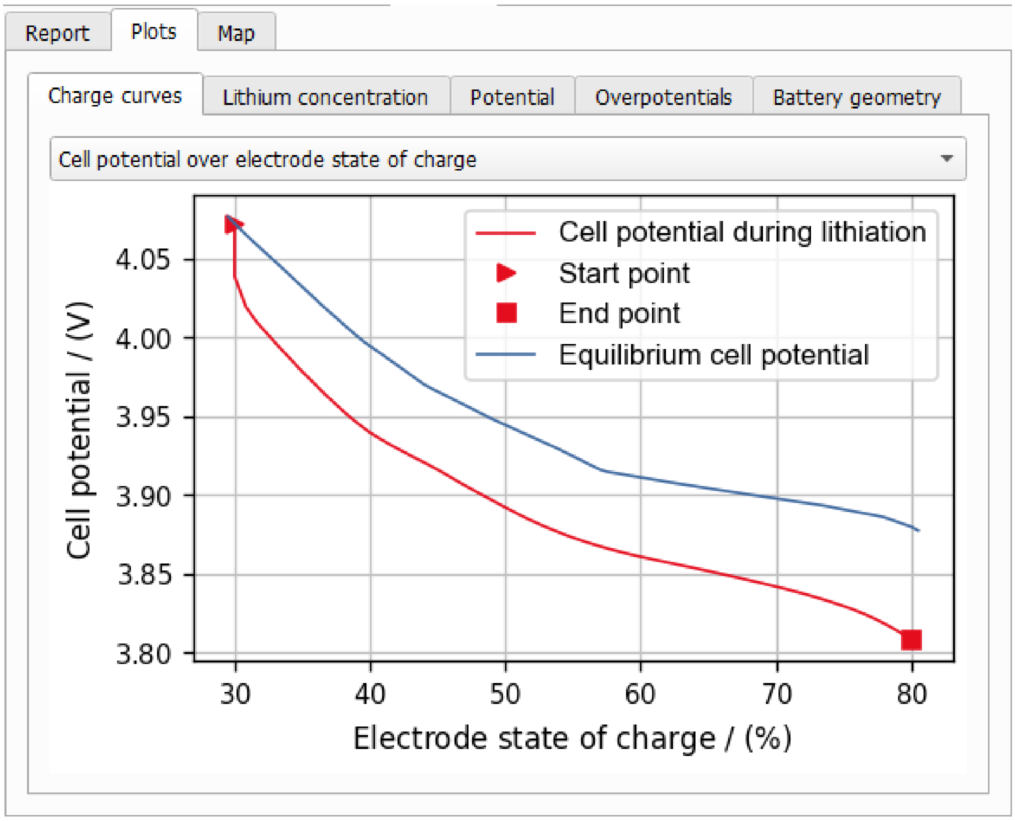


## RESULTS OF CHARGE ELECTRODE

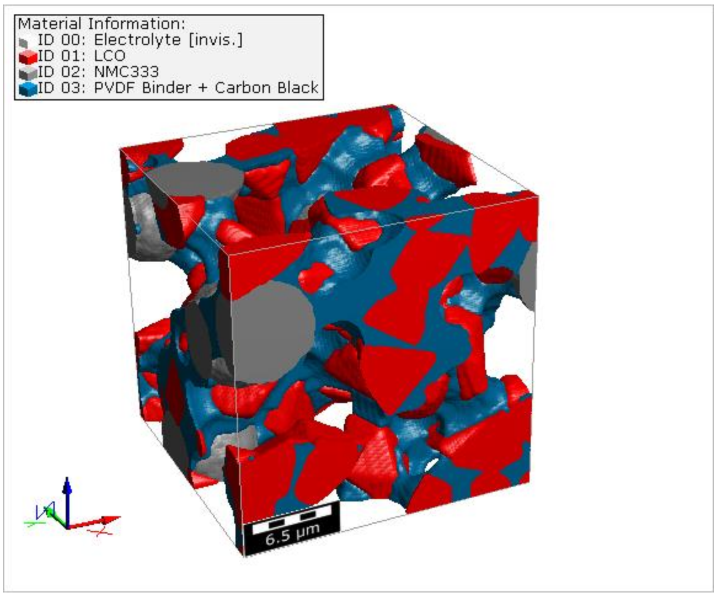
When the simulation of charging the electrode has finished, a GeoDict result file (.gdr) is available in the project folder and the Result Viewer of this result file automatically opens.

For the charging simulation of a single electrode, the same information as for charging a whole battery is available in this result file. It is shown, can be visualized, or further processed in the same way, see page 67ff.

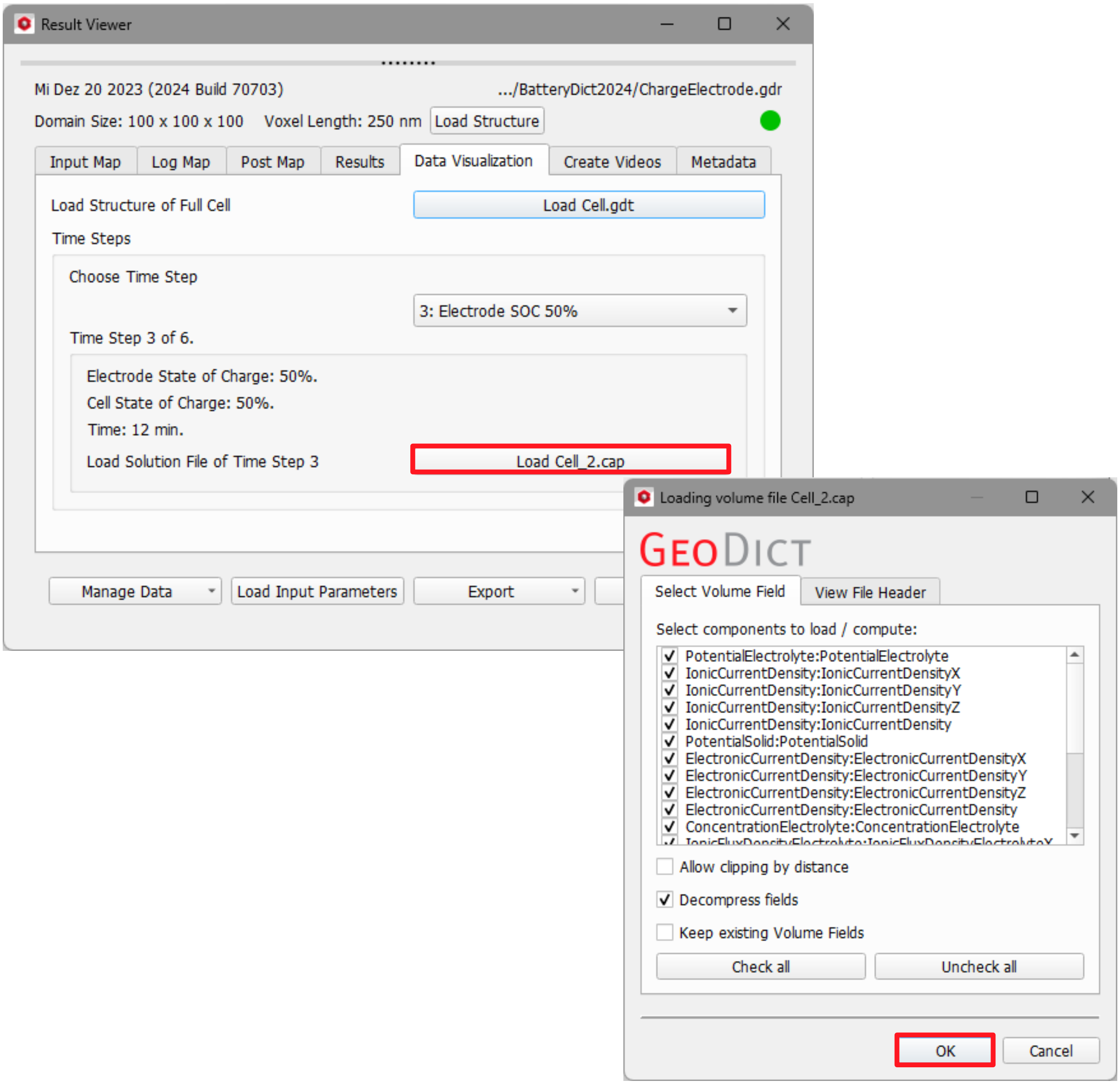
Note that for the charging simulation of a half cell, the modelled electrode is electrochemically always considered as the cathode (see page 81). Lithiating the cathode, i.e. increasing the electrode state of charge, means discharging the half cell. On the **Results -Plots – Charge Curves** subtab the cell potential is shown over the electrode state of charge and is therefore decreasing during the charging simulation of the half cell.



It is important to note that in the volume files of simulation (*.cap files), the result fields are stored for the entire half cell structure (including the electrode, both current collectors, separator, and lithium reservoir), rather than just the electrode alone. If the structure used as input for the simulation (and shown in the Visualization area of the main GUI) does not contain all components of the half cell, the size of the volume fields therefore does not fit to the structure size.



If one or more volume field(s) are loaded on the **Data Visualization** tab, the structure shown in the Visualization area is therefore extended to contain the missing half cell components as well.



Mi Dez 20 2023 (2024 Build 70703) .../BatteryDict2024/ChargeElectrode.gdr

Domain Size: 100 x 100 x 100 Voxel Length: 250 nm

Load Structure of Full Cell

Time Steps

Choose Time Step: 3: Electrode SOC 50%

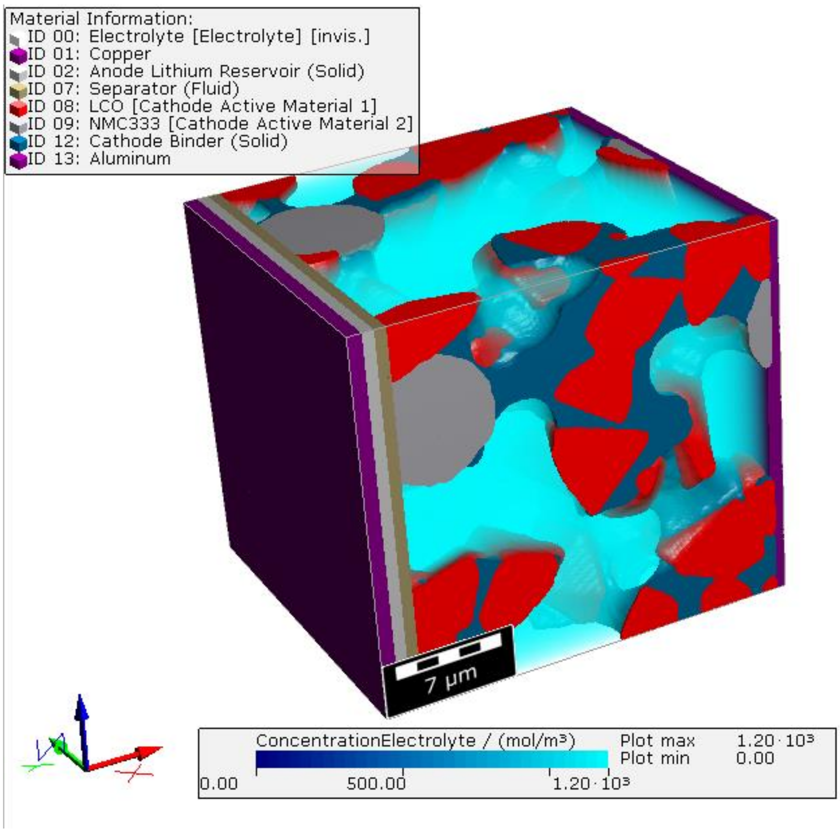
Time Step 3 of 6.

Electrode State of Charge: 50%.
Cell State of Charge: 50%.
Time: 12 min.
Load Solution File of Time Step 3

Select components to load / compute:

☑ PotentialElectrolyte:PotentialElectrolyte
☑ IonicCurrentDensity:IonicCurrentDensityX
☑ IonicCurrentDensity:IonicCurrentDensityY
☑ IonicCurrentDensity:IonicCurrentDensityZ
☑ IonicCurrentDensity:IonicCurrentDensity
☑ PotentialSolid:PotentialSolid
☑ ElectronicCurrentDensity:ElectronicCurrentDensityX
☑ ElectronicCurrentDensity:ElectronicCurrentDensityY
☑ ElectronicCurrentDensity:ElectronicCurrentDensityZ
☑ ElectronicCurrentDensity:ElectronicCurrentDensity
☑ ConcentrationElectrolyte:ConcentrationElectrolyte

☐ Allow clipping by distance
☑ Decompress fields
☐ Keep existing Volume Fields

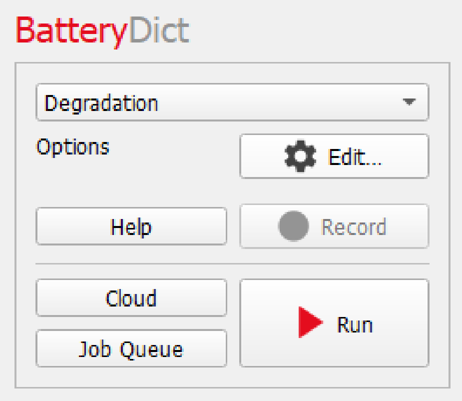


Choose **Load Cell.gdt** on the **Data Visualization** tab to load only the structure of the whole half cell without additional volume fields.

## DEGRADATION

Since GeoDict 2023, the functionality to compute mechanical deformations of a battery cell due to lithium intercalation is available as a command in BatteryDict. If the lithium concentration fields have been calculated with Charge Electrode, it is required to load the automatically built complete battery cell for the half cell simulation, see page 89.

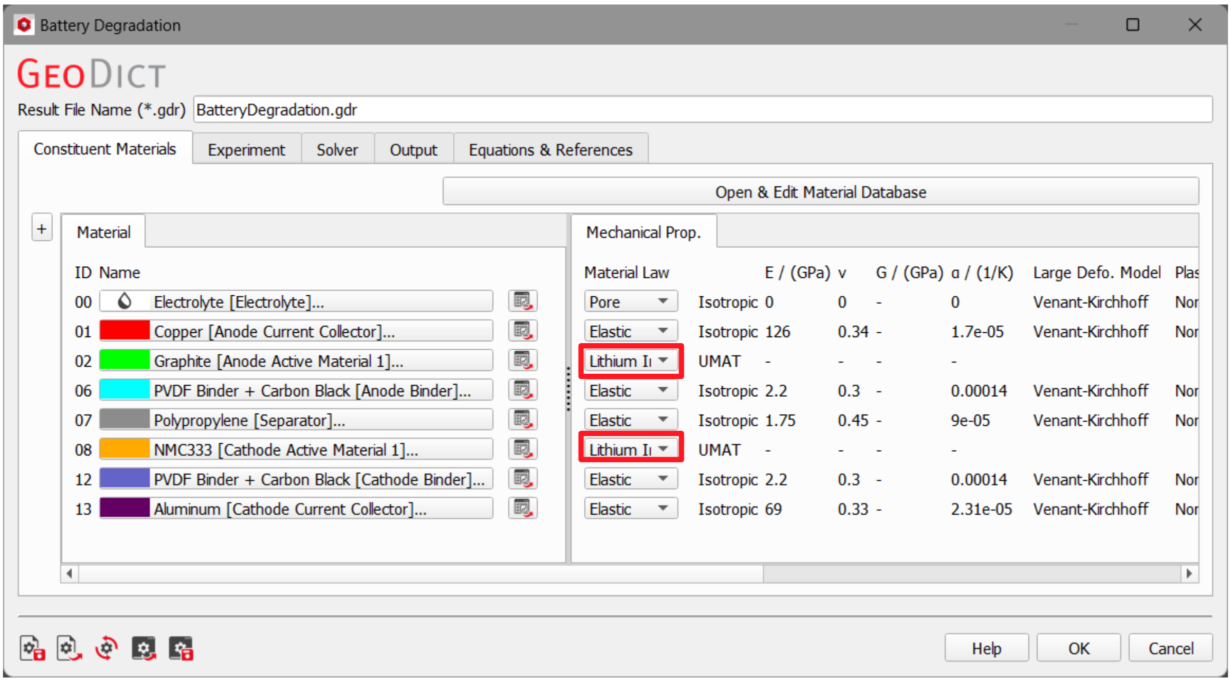
Select **Degradation** in the BatteryDict section and click **Edit ...** to open the options dialog for the simulation.



### CONSTITUENT MATERIALS

On the Constituent Materials tab, the mechanical properties of all materials are defined for the deformation simulation. Select the appropriate materials.

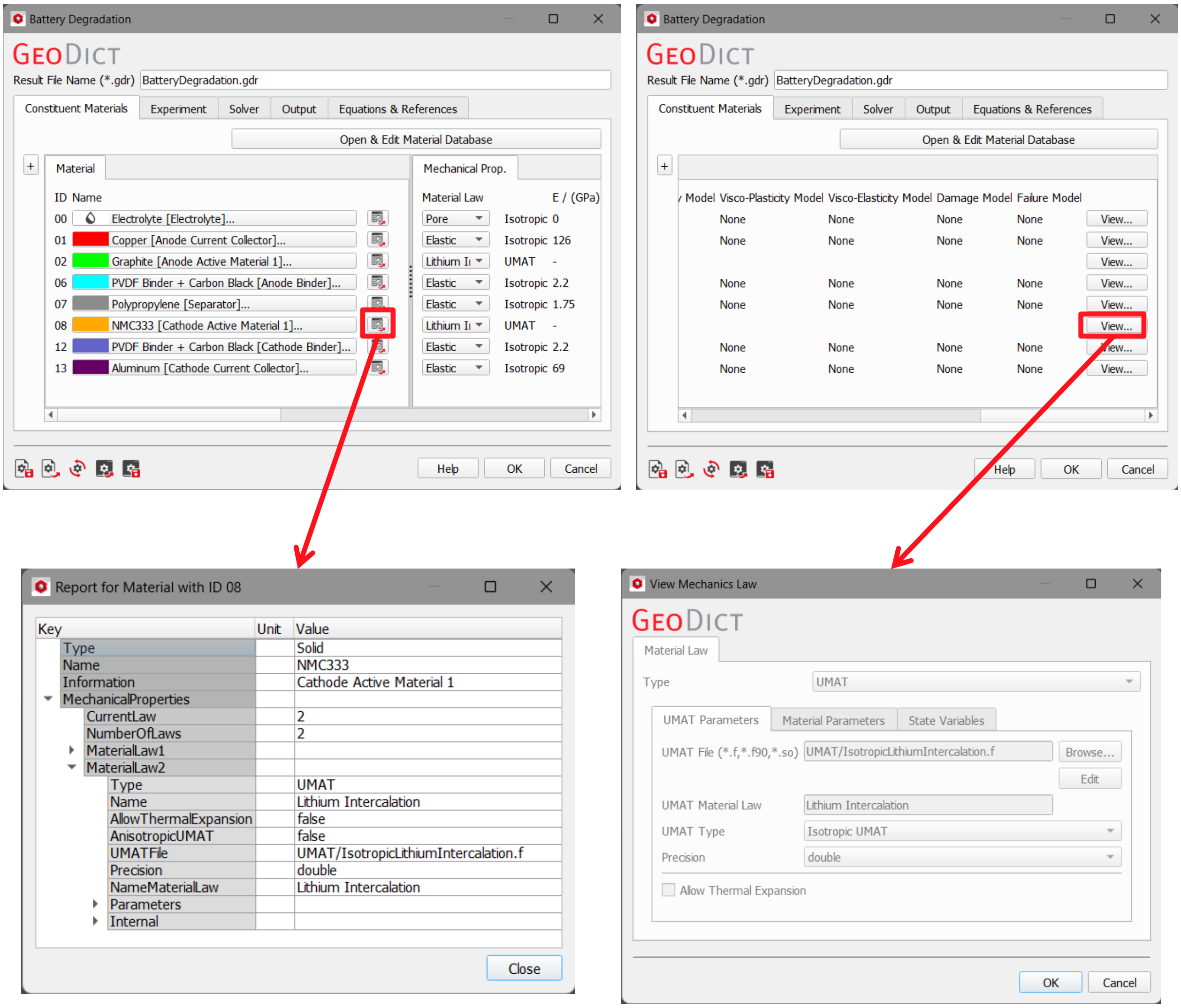
For all active materials of the battery cell, choose the **Material Law Lithium Intercalation** to account for expansion of the material due to changes in the local lithium concentration. The GeoDict Material Database currently provides the materials Graphite, NMC333, NMC532, NMC622, and Silicon with the Material Law Lithium Intercalation.



Result File Name (*.gdr) BatteryDegradation.gdr

| ID | Name | Material Law | | E / (GPa) | ν | G / (GPa) | α / (1/K) | Large Defo. Model | Plas |
|---|---|---|---|---|---|---|---|---|---|
| 00 | Electrolyte [Electrolyte]... | Pore | Isotropic | 0 | 0 | - | 0 | Venant-Kirchhoff | Nor |
| 01 | 🟥 Copper [Anode Current Collector]... | Elastic | Isotropic | 126 | 0.34 | - | 1.7e-05 | Venant-Kirchhoff | Nor |
| 02 | 🟩 Graphite [Anode Active Material 1]... | Lithium I | UMAT | - | - | - | - | | |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... | Elastic | Isotropic | 2.2 | 0.3 | - | 0.00014 | Venant-Kirchhoff | Nor |
| 07 | Polypropylene [Separator]... | Elastic | Isotropic | 1.75 | 0.45 | - | 9e-05 | Venant-Kirchhoff | Nor |
| 08 | 🟧 NMC333 [Cathode Active Material 1]... | Lithium I | UMAT | - | - | - | - | | |
| 12 | 🟦 PVDF Binder + Carbon Black [Cathode Binder]... | Elastic | Isotropic | 2.2 | 0.3 | - | 0.00014 | Venant-Kirchhoff | Nor |
| 13 | 🟪 Aluminum [Cathode Current Collector]... | Elastic | Isotropic | 69 | 0.33 | - | 2.31e-05 | Venant-Kirchhoff | Nor |

For all other solid materials, mechanical properties (Young's modulus and Poisson ratio) need to be defined for the simulation. All Material Laws that are available in ElastoDict, can be used in a degradation simulation as well (refer to the ElastoDict handbook for details). Click **View**, on the right of the mechanical properties shown, to see the parameters defined in the layout of the GeoDict Material Database or click the icon to see the parameters as a report.



Result File Name (*.gdr) BatteryDegradation.gdr

| ID | Name | Material Law | E / (GPa) |
|---|---|---|---|
| 00 | Electrolyte [Electrolyte]... | Pore | Isotropic 0 |
| 01 | Copper [Anode Current Collector]... | Elastic | Isotropic 126 |
| 02 | Graphite [Anode Active Material 1]... | Lithium I | UMAT - |
| 06 | PVDF Binder + Carbon Black [Anode Binder]... | Elastic | Isotropic 2.2 |
| 07 | Polypropylene [Separator]... | Elastic | Isotropic 1.75 |
| 08 | NMC333 [Cathode Active Material 1]... | Lithium I | UMAT - |
| 12 | PVDF Binder + Carbon Black [Cathode Binder]... | Elastic | Isotropic 2.2 |
| 13 | Aluminum [Cathode Current Collector]... | Elastic | Isotropic 69 |

| Model | Visco-Plasticity Model | Visco-Elasticity Model | Damage Model | Failure Model | |
|---|---|---|---|---|---|
| | None | None | None | None | View... |
| | None | None | None | None | View... |
| | | | | | View... |
| | None | None | None | None | View... |
| | None | None | None | None | View... |
| | | | | | View... |
| | None | None | None | None | View... |
| | None | None | None | None | View... |

| Key | Unit | Value |
|---|---|---|
| Type | | Solid |
| Name | | NMC333 |
| Information | | Cathode Active Material 1 |
| MechanicalProperties | | |
| CurrentLaw | | 2 |
| NumberOfLaws | | 2 |
| MaterialLaw1 | | |
| MaterialLaw2 | | |
| Type | | UMAT |
| Name | | Lithium Intercalation |
| AllowThermalExpansion | | false |
| AnisotropicUMAT | | false |
| UMATFile | | UMAT/IsotropicLithiumIntercalation.f |
| Precision | | double |
| NameMaterialLaw | | Lithium Intercalation |
| Parameters | | |
| Internal | | |

Type: UMAT

UMAT File (*.f,*.f90,*.so): UMAT/IsotropicLithiumIntercalation.f

UMAT Material Law: Lithium Intercalation

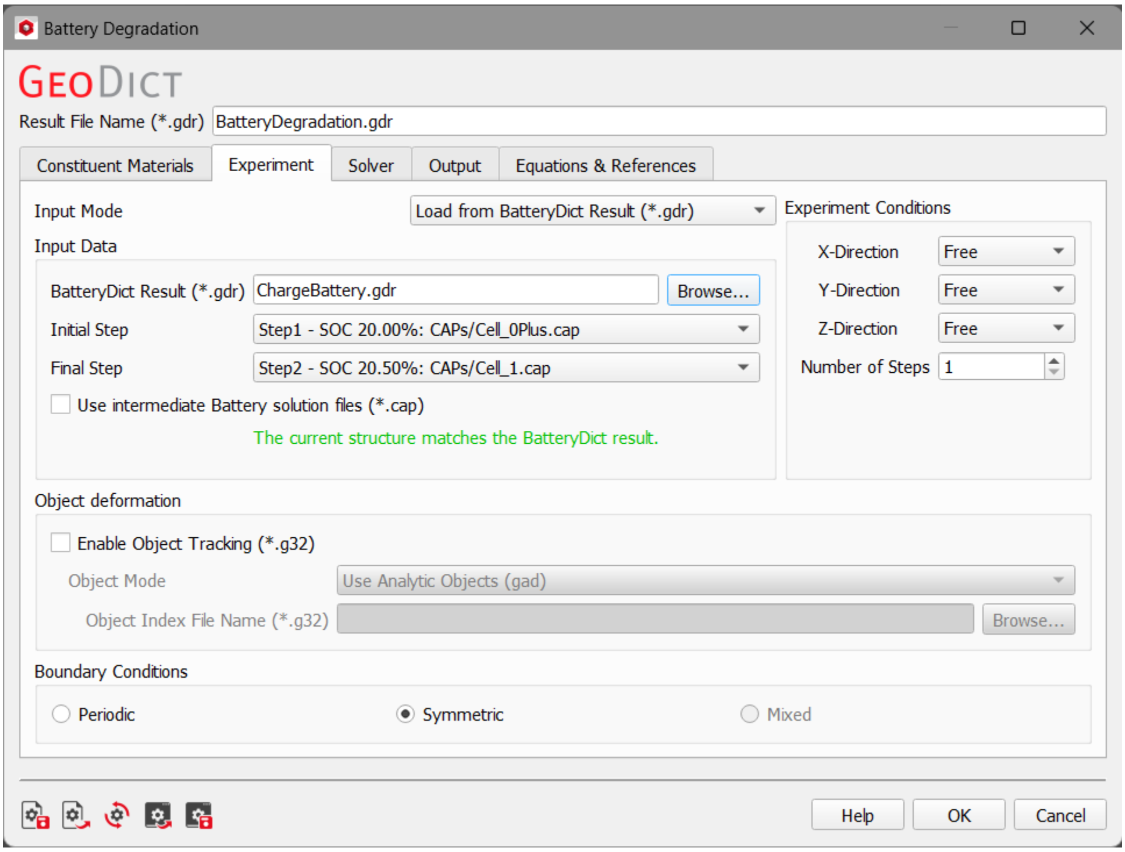
UMAT Type: Isotropic UMAT

Precision: double

☐ Allow Thermal Expansion

## EXPERIMENT

On the Experiment tab, define the parameters for the simulation itself.



Result File Name (*.gdr) BatteryDegradation.gdr

Input Mode: Load from BatteryDict Result (*.gdr)

Input Data

BatteryDict Result (*.gdr): ChargeBattery.gdr

Initial Step: Step1 - SOC 20.00%: CAPs/Cell_0Plus.cap

Final Step: Step2 - SOC 20.50%: CAPs/Cell_1.cap

☐ Use intermediate Battery solution files (*.cap)

The current structure matches the BatteryDict result.

Experiment Conditions

X-Direction: Free

Y-Direction: Free

Z-Direction: Free

Number of Steps: 1

Object deformation

☐ Enable Object Tracking (*.g32)

Object Mode: Use Analytic Objects (gad)

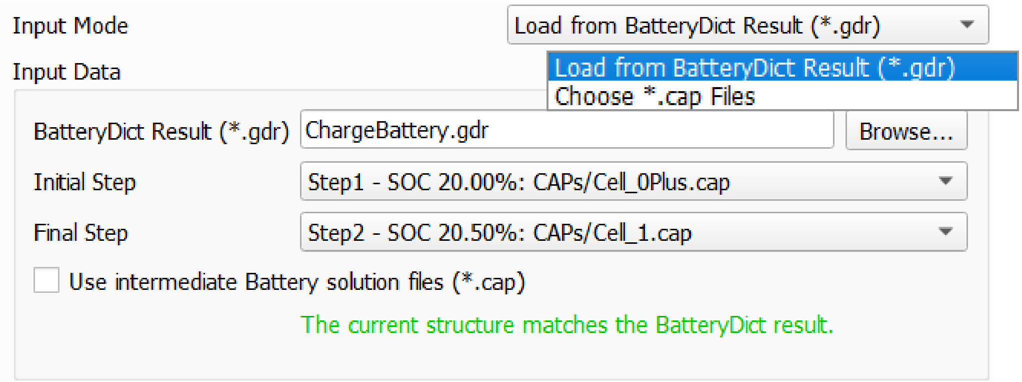
Object Index File Name (*.g32)

Boundary Conditions

○ Periodic ● Symmetric ○ Mixed

The input for a degradation simulation is the lithium concentration at the start and the end of a charging simulation. A previously run charging simulation with **Charge Battery** (see page 43) or **Charge Electrode** (see page 81) is therefore required before a degradation simulation can be run. With the **Input Mode**, define how the results of the charging simulation are provided for the expansion simulation.

Select **Load from BatteryDict Results (*.gdr)** to choose a charging simulation result file. Browse to the result file and choose the simulation step that you want to use as initial and final step for the degradation simulation.



Input Mode: Load from BatteryDict Result (*.gdr)

Input Data

BatteryDict Result (*.gdr): ChargeBattery.gdr

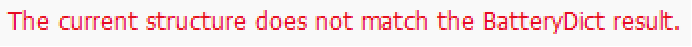
Initial Step: Step1 - SOC 20.00%: CAPs/Cell_0Plus.cap

Final Step: Step2 - SOC 20.50%: CAPs/Cell_1.cap

☐ Use intermediate Battery solution files (*.cap)

The current structure matches the BatteryDict result.

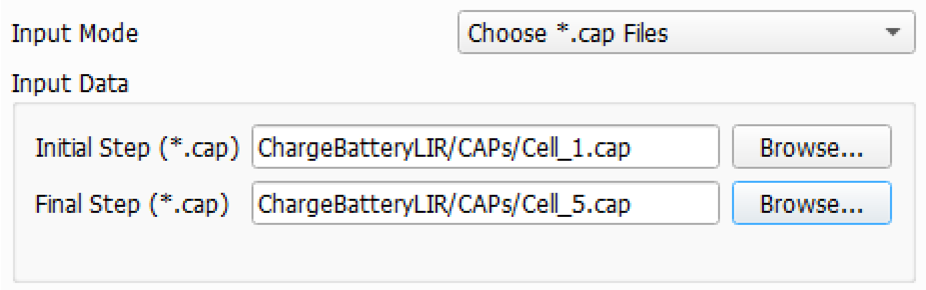
GeoDict verifies if the battery currently in memory matches the selected result file. If a match is found, it will be displayed in green below the .cap files chosen as the initial and final steps. If a different structure is currently loaded, a warning is displayed in red.



The current structure does not match the BatteryDict result.

Check **Use intermediate Battery solution files (*.cap)** to use all intermediate *.cap files between initial step and final step in the simulation.

Select **Choose *.cap Files** as **Input Mode** to define the .cap file directly. Browse to the .cap file with the lithium concentration for initial and final step of the expansion simulation. Make sure that the structure currently in memory fits to the selected .cap files.



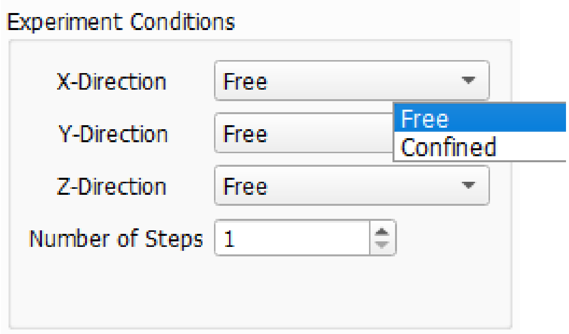
Input Mode: Choose *.cap Files

Input Data

Initial Step (*.cap): ChargeBatteryLIR/CAPs/Cell_1.cap

Final Step (*.cap): ChargeBatteryLIR/CAPs/Cell_5.cap

In the upper right part of the dialog, choose the **Experiment Conditions**. In each coordinate direction, define if the cell can expand **Free** in this coordinate direction, or if it cannot expand at all (**Confined**).



Experiment Conditions

X-Direction: Free

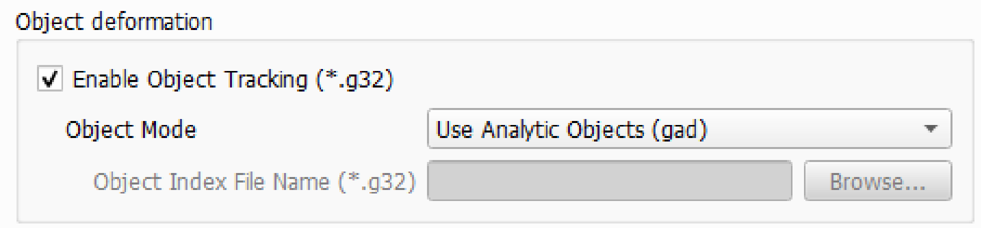
Y-Direction: Free

Z-Direction: Free

Number of Steps: 1

Additionally, define the **Number of Steps** for the simulation. The number of steps defines the number of intermediate steps in the computation of the expansion. Either the whole concentration difference between initial and final step is applied in one step, or it is divided linearly and applied in several steps. If **Use intermediate Battery solution files (*.cap)** is checked, the number of steps defined is applied between all intermediate .cap files available.

**Enable Object Tracking** in the Object deformation part of the dialog to keep object indices in the deformation simulation. This allows for the identification of the deformation of each individual object in the simulation. If the structure considered contains analytic object information, the .g32 file with object indices can be created from this analytic information,



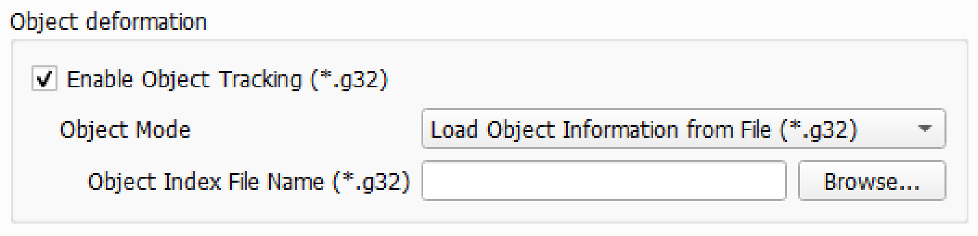
Object deformation

☑ Enable Object Tracking (*.g32)

Object Mode: Use Analytic Objects (gad)

Object Index File Name (*.g32):

or a previously created .g32 file can be selected.



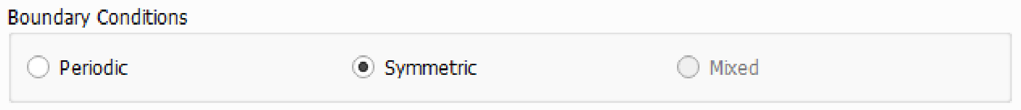
Object deformation

☑ Enable Object Tracking (*.g32)

Object Mode: Load Object Information from File (*.g32)

Object Index File Name (*.g32):

Finally, select the boundary conditions for the structure in the simulation. Use **Periodic** if the structure is periodic in all coordinate directions, **Symmetric** if it is not. Mixed boundary conditions are not available so far in BatteryDict-Degradation.

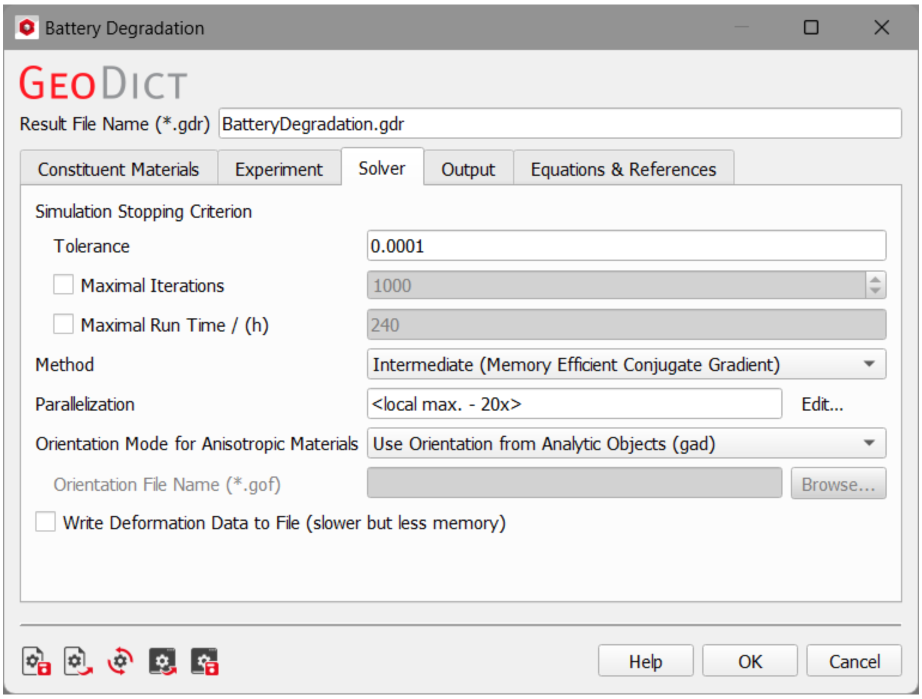


Boundary Conditions

○ Periodic ● Symmetric ○ Mixed

## SOLVER

On the Solver tab, specify the settings for the FeelMath solver. The settings are part of the FeelMath solver settings explained in more detail in the ElastoDict handbook.



Result File Name (*.gdr) BatteryDegradation.gdr

Simulation Stopping Criterion

Tolerance 0.0001

☐ Maximal Iterations 1000

☐ Maximal Run Time / (h) 240

Method Intermediate (Memory Efficient Conjugate Gradient)

Parallelization <local max. - 20x>

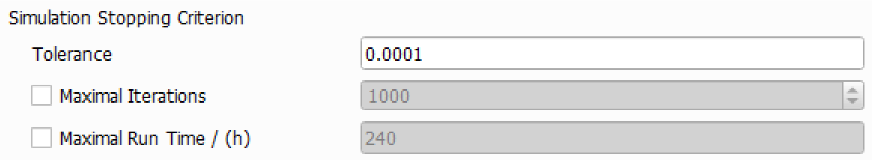
Orientation Mode for Anisotropic Materials Use Orientation from Analytic Objects (gad)

Orientation File Name (*.gof)

☐ Write Deformation Data to File (slower but less memory)

Under **Simulation Stopping Criterion** define the **Tolerance**, the **Maximal Iterations**, and **Maximal Run Time** to control the iterative process of the solver. Only the tolerance must be set, the other two parameters are optional.

For each iteration step, the relative error of the current solution is computed. If this relative error is smaller than the given tolerance for ten subsequent steps, the computation is finished. When there is doubt about the quality of the solution, decrease the tolerance value by a factor of ten for that solver. In general, it is recommended to keep the default setting for tolerance.



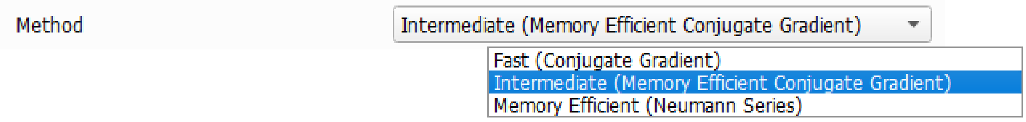
Simulation Stopping Criterion

Tolerance 0.0001

☐ Maximal Iterations 1000

☐ Maximal Run Time / (h) 240

When the solver stops because the **Maximal Iterations** or the **Maximal Run Time** are reached, the quality of the solution might be doubtful since the requested accuracy is not reached. Therefore, those two options are disabled by default and should only be selected if there are strong constraints on the allowed runtime.



Method Intermediate (Memory Efficient Conjugate Gradient)

For the **FeelMath-Deformations** solver, three different iterative methods are available: **Fast (Conjugate Gradient)**, **Intermediate (Memory Efficient Conjugate Gradient),** and **Memory Efficient (Neumann Series)**.

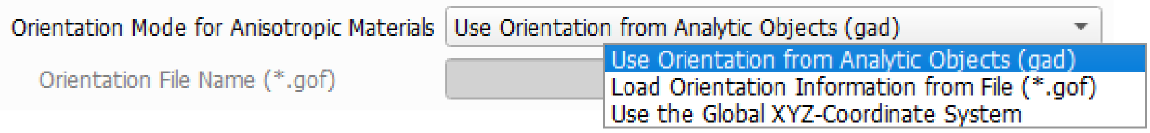
The **Fast** method converges faster, especially for strongly varying material parameters and nonlinear material laws (as e.g. plasticity or damage), but needs about four times as much memory as the **Memory Efficient** method.

The **Intermediate Method** needs approximately 40 % less memory than the **Fast** method but is slower. The **Estimate Memory** button in the **ElastoDict** section, can be used to decide which method is applicable for the current structure on the available computer.

In general, it is recommended to use the default (**Memory Efficient Conjugate Gradient**) or the **Conjugate Gradient** method. The **Neumann Series** method should only be used if the memory is not enough for the other methods.

The degradation simulation, like the charging simulation, can be accelerated by running the computation on multiple CPU cores, as explained on page 62. The maximum number of processes licensed for the degradation simulation is the number of licensed ElastoDict processes.

For information on how to set up and use BatteryDict-Degradation in a **Cluster** configuration, contact Math2Market.



Orientation Mode for Anisotropic Materials: Use Orientation from Analytic Objects (gad)

BatteryDict-Degradation can handle non-isotropic constituent materials. For these materials, an orientation must be additionally specified. If the analyzed structure consists of analytical objects (gad data), the orientation of these objects is used when **Use Orientation from Analytic Objects (gad)** is selected.

Alternatively, with **Load Orientation Information from File (*.gof)**, orientation information can be loaded from a file. Such a file can be generated for example with GrainFind for granular structures. The third option, **Use the Global XYZ-Coordinate System**, allows to use anisotropic materials even if no orientation information for the structure is available. This makes sense only if the grains are all oriented directly according to the coordinate axis, which is usually not the case.

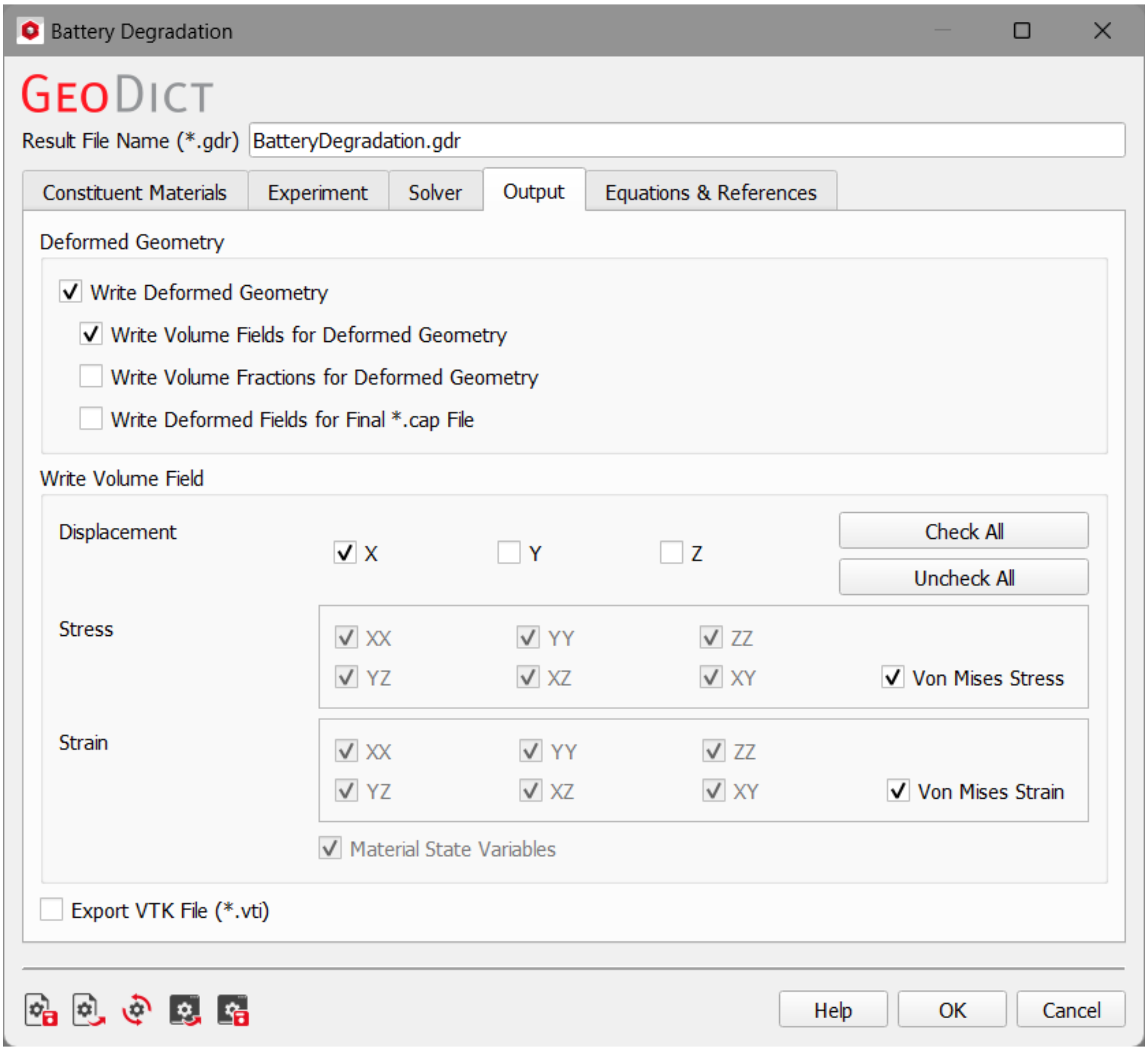
☐ Write Deformation Data to File (slower but less memory)

For the computation of the deformed structures, intermediate data is computed which describes the displacement for each voxel. Before this computation, it is not clear how large this data will be, since a voxel in the original structure might be partially moved in multiple voxels in the deformed structure. Therefore, this data might not fit in the main memory of the computer. Due to this, it is possible to write the deformation data to a file on the hard disk. Nevertheless, there is an issue with this approach: Writing and loading data from the hard drive is many times slower than writing and loading data in the main memory (even if the drive is an SSD). This causes a bottleneck, which can slow down the simulation.

Therefore, the default is to keep the deformation data in memory. In most cases, the data fits into the main memory, and this option is many times faster. See the benchmark results in the ElastoDict handbook. We recommend keeping this setting, and to select **Write Deformation Data to File** only if the simulation fails because the data does not fit into the RAM.

## OUTPUT

The options available in the Output tab define which information is written to the hard disk during the computation.



Result File Name (*.gdr) BatteryDegradation.gdr

Deformed Geometry

☑ Write Deformed Geometry
  ☑ Write Volume Fields for Deformed Geometry
  ☐ Write Volume Fractions for Deformed Geometry
  ☐ Write Deformed Fields for Final *.cap File

Write Volume Field

Displacement ☑ X ☐ Y ☐ Z

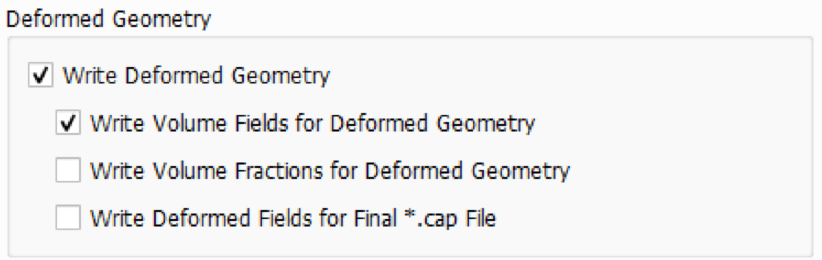
Stress ☑ XX ☑ YY ☑ ZZ ☑ YZ ☑ XZ ☑ XY ☑ Von Mises Stress

Strain ☑ XX ☑ YY ☑ ZZ ☑ YZ ☑ XZ ☑ XY ☑ Von Mises Strain

☑ Material State Variables

☐ Export VTK File (*.vti)

In the **Deformed Geometry** section of the tab, select which information is exported for the deformed geometry.



Deformed Geometry

☑ Write Deformed Geometry
  ☑ Write Volume Fields for Deformed Geometry
  ☐ Write Volume Fractions for Deformed Geometry
  ☐ Write Deformed Fields for Final *.cap File

When **Write Deformed Geometry** is chosen, a geometry with the current displacements is resampled and saved after each step.

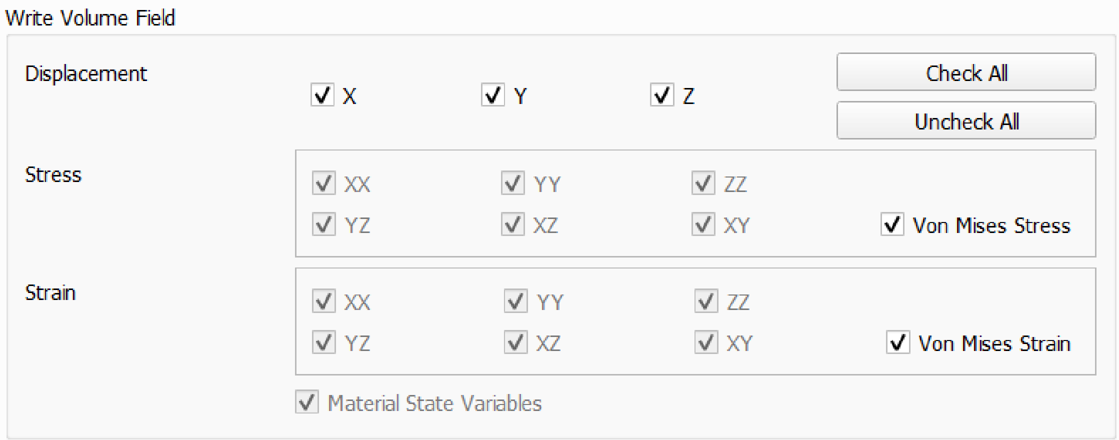
With **Write Volume Fields for Deformed Geometry**, also the result fields are resampled with the current displacements so that they match the deformed geometries. A GeoDict *.das file is created for this volume fields.

With **Write Volume Fractions for Deformed Geometry**, the volume fractions for each material ID in each voxel after the deformation are additionally written to the

*.das files. This information is used for the computation of the deformed geometries. In general, it is not necessary to save this information. However, it is required for the export of the deformed fields for the final .cap file.

If **Write Deformed Fields for Final *.cap File** is checked, the fields of the final .cap file are resampled to match the final geometry and exported to the .das file as well. This is necessary if the deformed geometry of the degradation simulation should be used as starting point for a new charging or discharging simulation.

Under **Write Volume Field**, checking or un-checking the boxes for **Displacement**, **Stress**, and **Strain** determines whether these result outputs are available for visualization and post-processing after the run of the FeelMath solver.


Write Volume Field

Displacement ☑ X ☑ Y ☑ Z

Stress ☑ XX ☑ YY ☑ ZZ ☑ YZ ☑ XZ ☑ XY ☑ Von Mises Stress

Strain ☑ XX ☑ YY ☑ ZZ ☑ YZ ☑ XZ ☑ XY ☑ Von Mises Strain

☑ Material State Variables

Different from ElastoDict, the stress and strain tensor itself (XX, YY, …) is currently always exported in BatteryDict-Degradation, but Von Mises Stress and Strain can be checked or unchecked.

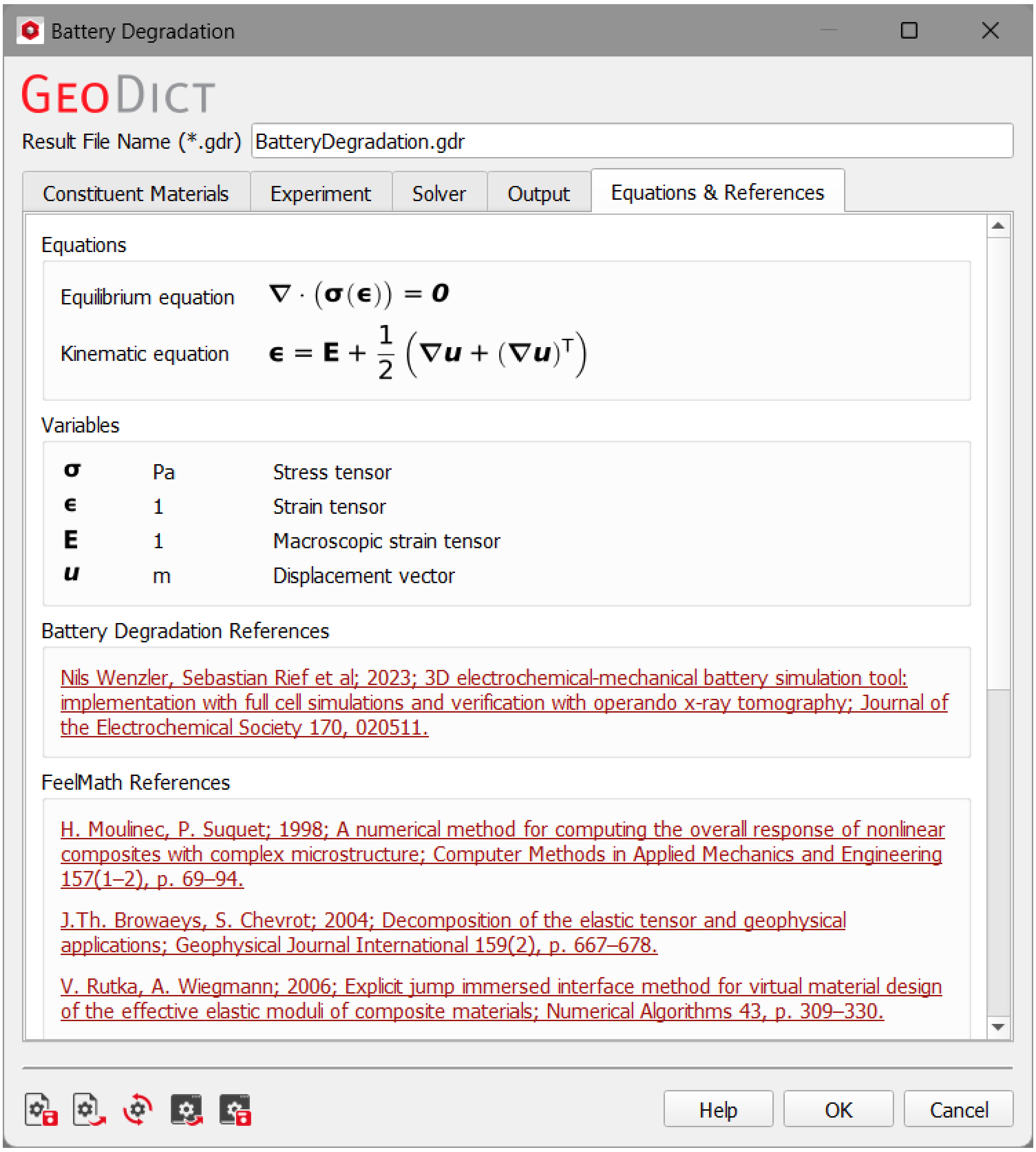
Besides using GeoDict's own visualization tools, it is possible to export the solution in the commonly used VTK (Visualization Toolkit) format (see: [https://vtk.org/](https://vtk.org/) and, [https://www.paraview.org/](https://www.paraview.org/)) by checking **Export VTK File (*.vti)**.


☐ Export VTK File (*.vti)

## EQUATIONS & REFERENCES

The differential equations solved in the simulation are listed under the **Equations & References** tab. Additionally, the references for the degradation simulation and the FeelMath solver are shown on this tab.

The degradation references can be found on page 109 of this BatteryDict handbook



Result File Name (*.gdr) BatteryDegradation.gdr

Equations

Equilibrium equation $\nabla \cdot (\boldsymbol{\sigma}(\boldsymbol{\epsilon})) = \boldsymbol{0}$

Kinematic equation $\boldsymbol{\epsilon} = \mathbf{E} + \frac{1}{2}\left(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^{\mathrm{T}}\right)$

Variables

| | | |
|---|---|---|
| $\boldsymbol{\sigma}$ | Pa | Stress tensor |
| $\boldsymbol{\epsilon}$ | 1 | Strain tensor |
| $\mathbf{E}$ | 1 | Macroscopic strain tensor |
| $\boldsymbol{u}$ | m | Displacement vector |

Battery Degradation References

Nils Wenzler, Sebastian Rief et al; 2023; 3D electrochemical-mechanical battery simulation tool: implementation with full cell simulations and verification with operando x-ray tomography; Journal of the Electrochemical Society 170, 020511.

FeelMath References

H. Moulinec, P. Suquet; 1998; A numerical method for computing the overall response of nonlinear composites with complex microstructure; Computer Methods in Applied Mechanics and Engineering 157(1–2), p. 69–94.

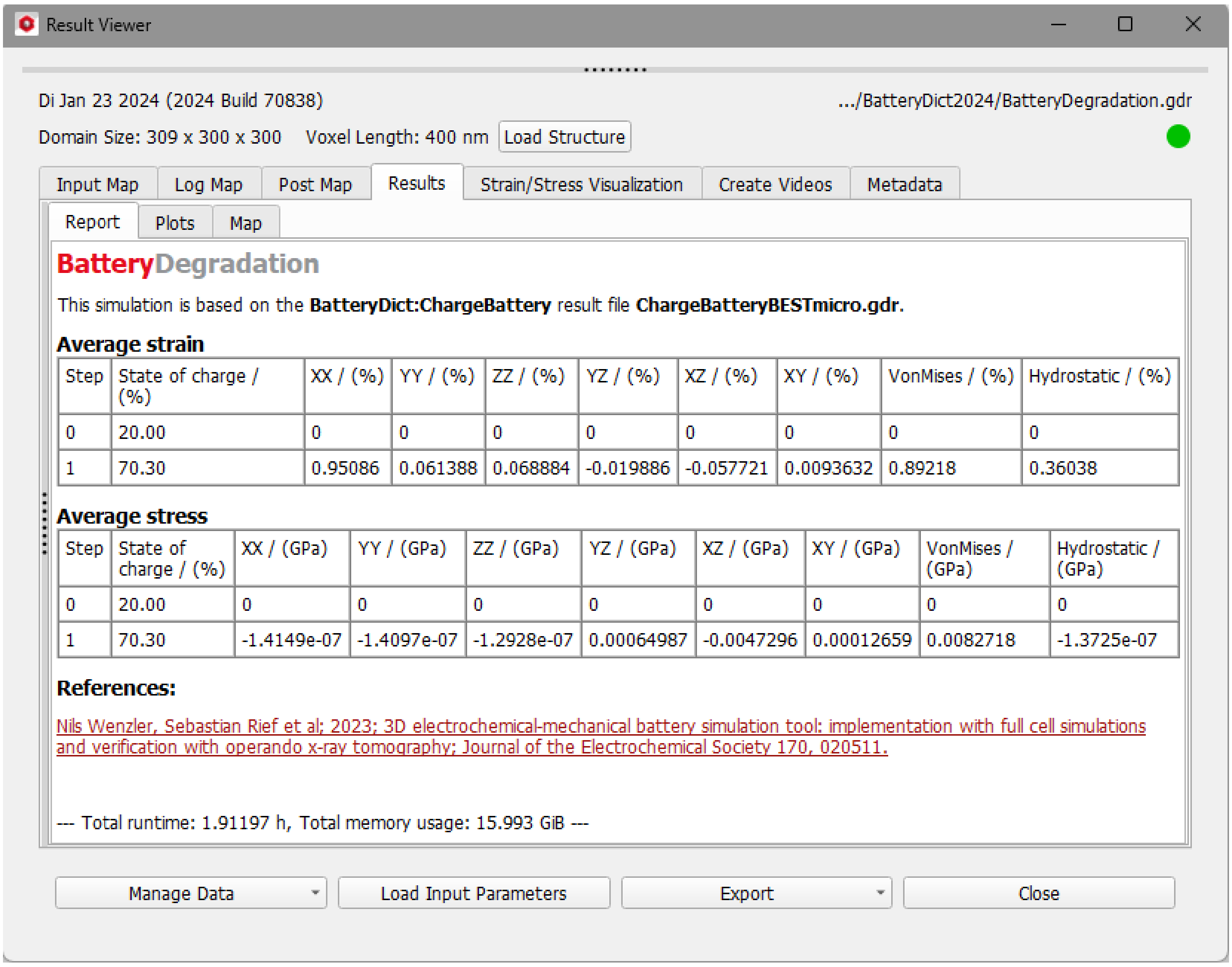
J.Th. Browaeys, S. Chevrot; 2004; Decomposition of the elastic tensor and geophysical applications; Geophysical Journal International 159(2), p. 667–678.

V. Rutka, A. Wiegmann; 2006; Explicit jump immersed interface method for virtual material design of the effective elastic moduli of composite materials; Numerical Algorithms 43, p. 309–330.

## RESULTS OF A DEGRADATION SIMULATION

If the degradation simulation finished successfully, the GeoDict Result Viewer opens for the result file (*.gdr file created).

The **Results - Report** subtab shows the average strain and stress tensor, as well as the average Von Mises and hydrostatic strain and stress for each computation step.



Di Jan 23 2024 (2024 Build 70838)

.../BatteryDict2024/BatteryDegradation.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

**BatteryDegradation**

This simulation is based on the **BatteryDict:ChargeBattery** result file **ChargeBatteryBESTmicro.gdr**.

**Average strain**

| Step | State of charge / (%) | XX / (%) | YY / (%) | ZZ / (%) | YZ / (%) | XZ / (%) | XY / (%) | VonMises / (%) | Hydrostatic / (%) |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 20.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 70.30 | 0.95086 | 0.061388 | 0.068884 | -0.019886 | -0.057721 | 0.0093632 | 0.89218 | 0.36038 |

**Average stress**

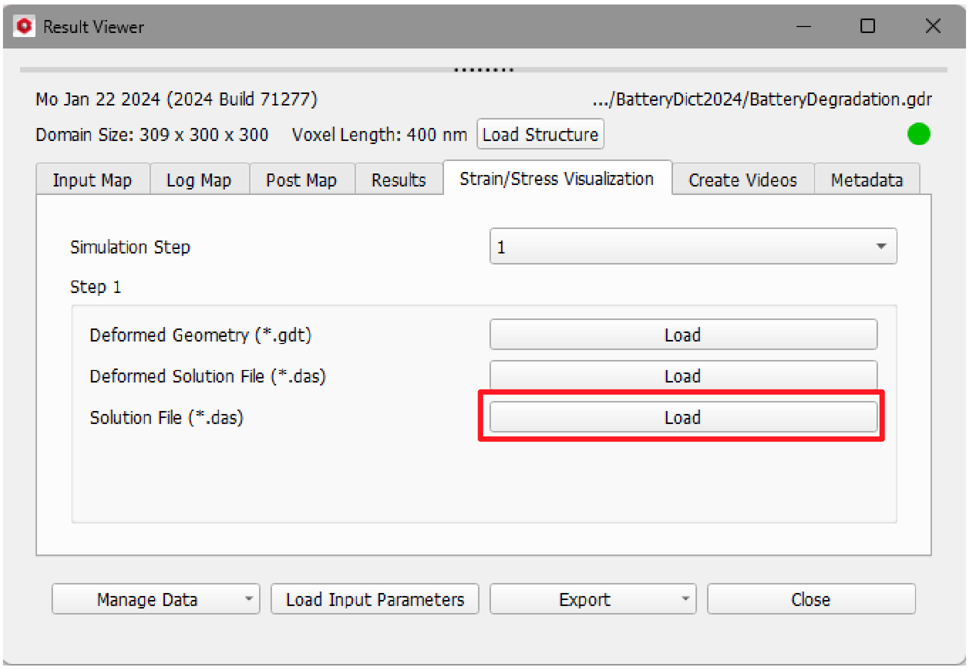
| Step | State of charge / (%) | XX / (GPa) | YY / (GPa) | ZZ / (GPa) | YZ / (GPa) | XZ / (GPa) | XY / (GPa) | VonMises / (GPa) | Hydrostatic / (GPa) |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 20.00 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 70.30 | -1.4149e-07 | -1.4097e-07 | -1.2928e-07 | 0.00064987 | -0.0047296 | 0.00012659 | 0.0082718 | -1.3725e-07 |

**References:**

Nils Wenzler, Sebastian Rief et al; 2023; 3D electrochemical-mechanical battery simulation tool: implementation with full cell simulations and verification with operando x-ray tomography; Journal of the Electrochemical Society 170, 020511.

--- Total runtime: 1.91197 h, Total memory usage: 15.993 GiB ---

On the **Strain/Stress Visualization** tab, the volume fields for each simulation step can be loaded by clicking on the **Load button** for Solution File (*.das). If the deformed geometry and the volume fields for the deformed geometry are written to the hard disk (see page 97), they can be loaded for visualization here as well. For details on the (deformed) solution files, we refer to the ElastoDict handbook.



Mo Jan 22 2024 (2024 Build 71277) .../BatteryDict2024/BatteryDegradation.gdr

Domain Size: 309 x 300 x 300 Voxel Length: 400 nm

Simulation Step: 1

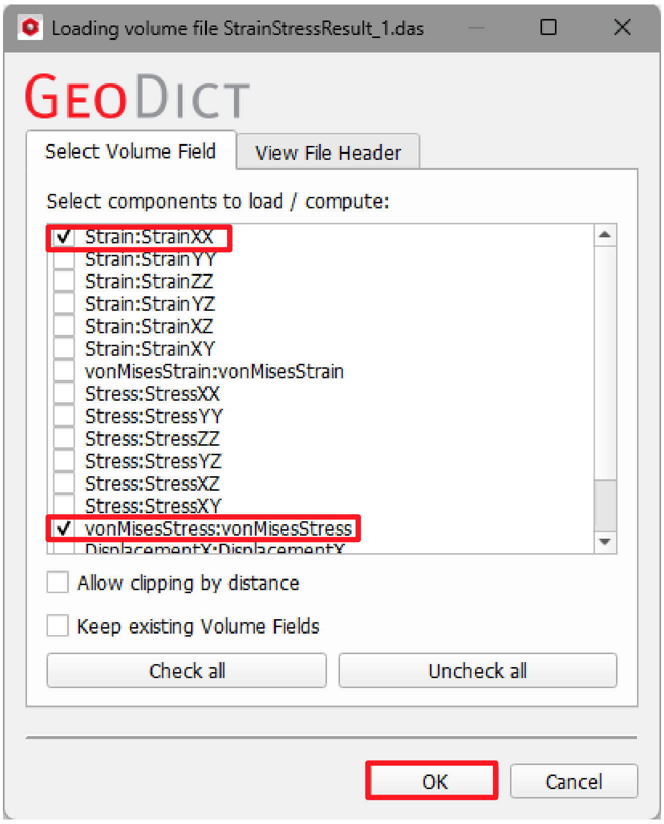
Step 1

Deformed Geometry (*.gdt)

Deformed Solution File (*.das)

Solution File (*.das)

Visualize e.g. the von Mises Stress and the strain component XX in the battery after expansion, by loading the Solution File (*.das), selecting the volume fields to load and clicking **OK**.



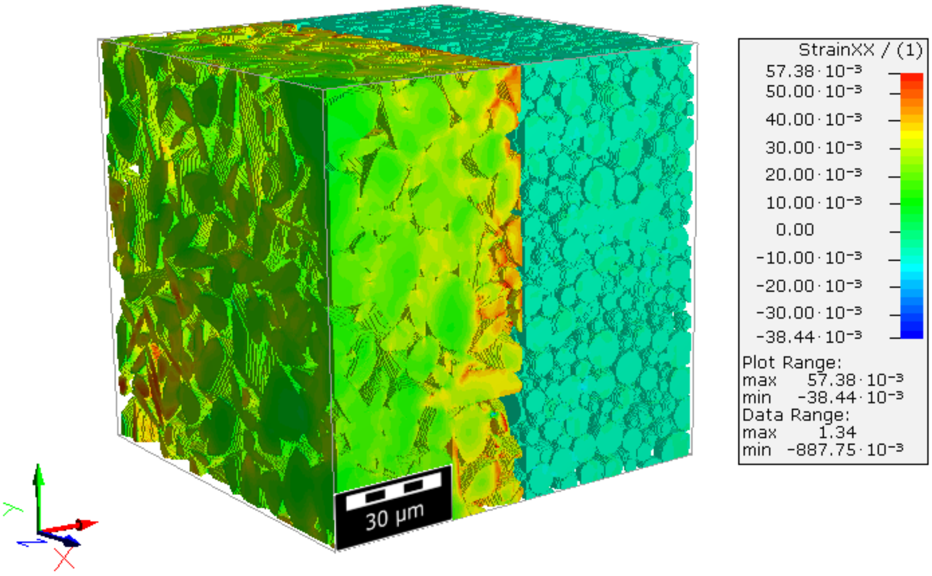
Select components to load / compute:

- ☑ Strain:StrainXX
- ☐ Strain:StrainYY
- ☐ Strain:StrainZZ
- ☐ Strain:StrainYZ
- ☐ Strain:StrainXZ
- ☐ Strain:StrainXY
- ☐ vonMisesStrain:vonMisesStrain
- ☐ Stress:StressXX
- ☐ Stress:StressYY
- ☐ Stress:StressZZ
- ☐ Stress:StressYZ
- ☐ Stress:StressXZ
- ☐ Stress:StressXY
- ☑ vonMisesStress:vonMisesStress
- ☐ DisplacementX:DisplacementX

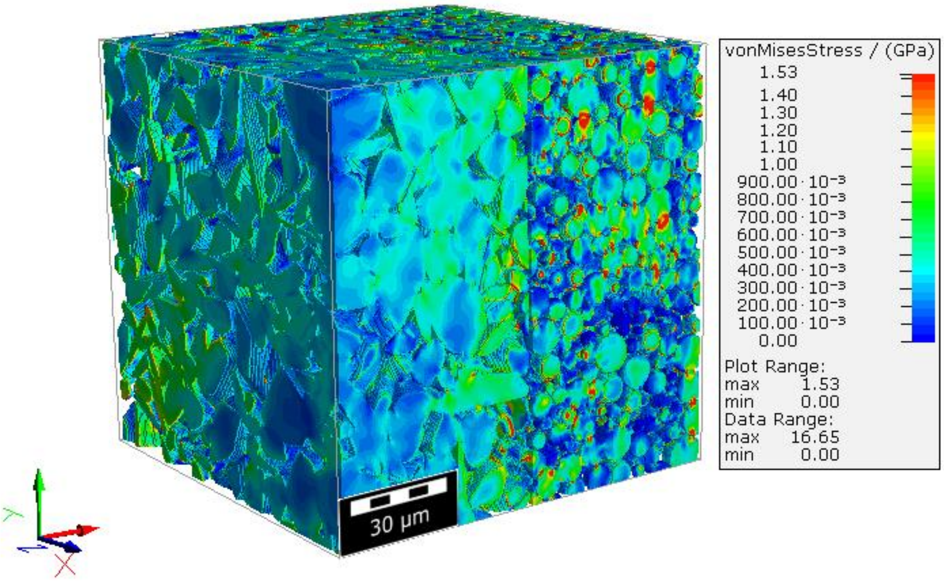
☐ Allow clipping by distance

☐ Keep existing Volume Fields

In the visualization of the strain component XX in the active materials, positive values are visible in the graphite particles. They are expanding due to lithium intercalation in the anode while charging the battery cell. In contrast to this, the NMC particles in the cathode show negative values. They are shrinking due to de-intercalation of lithium.



The von Mises Stress in the cathode shows its highest values at the boundary of the NMC grains where they are in contact to neighboring grains. This is reasonable since breaking contacts during shrinking of the active material is not yet possible in BatteryDict-Degradation.



On the **Create Videos** tab, a video visualizing the change of one of the volume fields during a BatteryDict-Degradation simulation can be visualized.

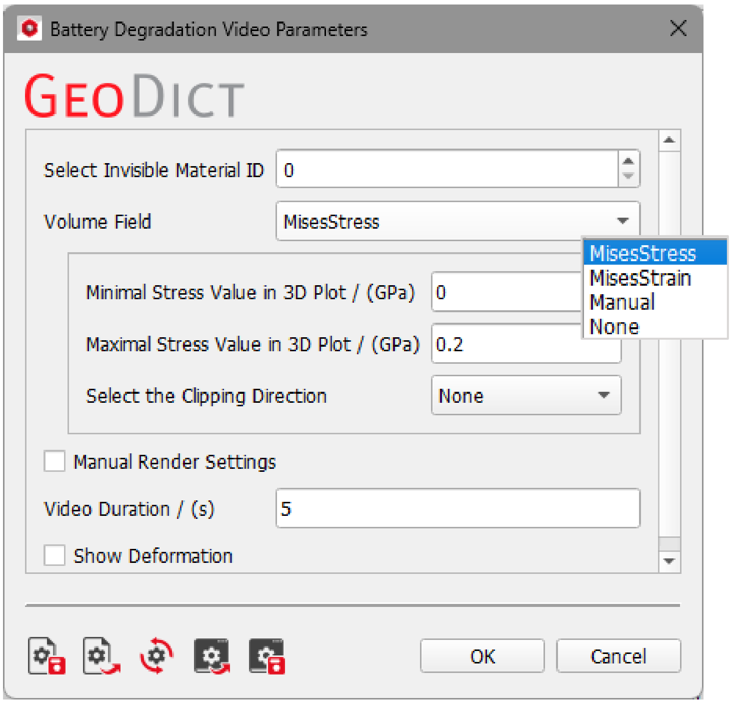
Click **Create Video** to generate the video with the default settings. Once the video is created successfully, the button **Play Video** gets active.

Select **Edit Parameters** to modify the settings for the video generation.

With **Select Invisible Material ID** one material can be selected to be invisible in the video. This can be e.g. the pore material.

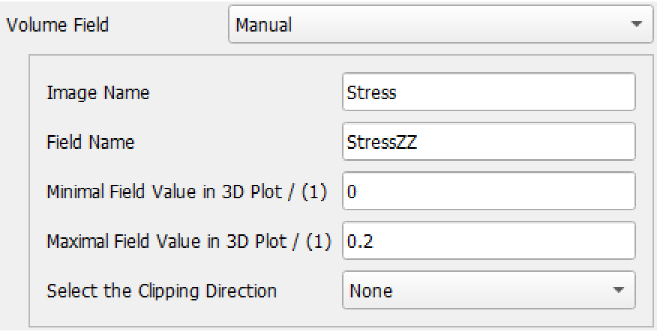
Choose the **Volume Field** to be shown in the plot. Dependent on the selection here, additional parameters need to be defined.

If **Mises Stress** or **Mises Strain** is selected, the minimal and maximal stress or strain values can be set for the color map.



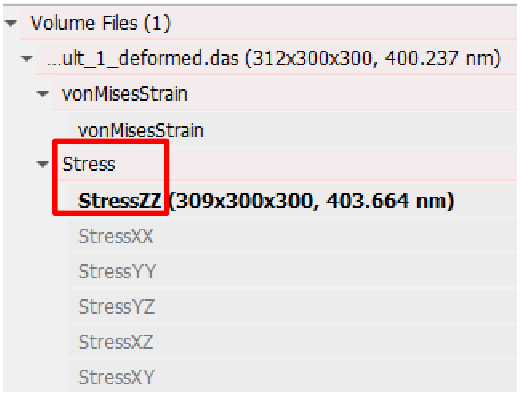
Select Invisible Material ID: 0
Volume Field: MisesStress
Minimal Stress Value in 3D Plot / (GPa): 0
Maximal Stress Value in 3D Plot / (GPa): 0.2
Select the Clipping Direction: None
☐ Manual Render Settings
Video Duration / (s): 5
☐ Show Deformation

Select **Manual** to choose another volume field available for the visualization. Additional to minimal and maximal value, the name of the image respectively field needs to be chosen as well.



Volume Field: Manual
Image Name: Stress
Field Name: StressZZ
Minimal Field Value in 3D Plot / (1): 0
Maximal Field Value in 3D Plot / (1): 0.2
Select the Clipping Direction: None

For scalar fields like von Mises Strain, image and field names are the same. For vector and tensor fields, the field name has the direction as suffix. In the example shown here, the image name is **Stress**, the field name **StressZZ**. If the volume field is loaded into the visualization area, image and field names are visible e.g. under Volume Files on the left of the Visualization area.



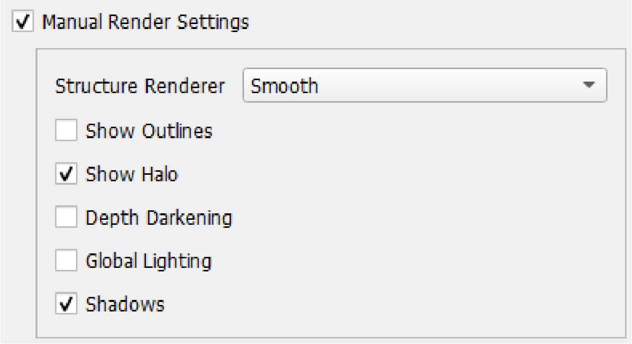
Volume Files (1)
...ult_1_deformed.das (312x300x300, 400.237 nm)
vonMisesStrain
vonMisesStrain
Stress
**StressZZ (309x300x300, 403.664 nm)**
StressXX
StressYY
StressYZ
StressXZ
StressXY

Choose **None**, if no volume field at all should be visualized.

The value in **Video Duration** defines the overall length of the video in seconds.

If **Show Deformation** is checked, the video is based on the deformed geometries and volume fields. Otherwise, the shows the values of the volume fields in the undeformed geometry.

Check **Manual Render Settings** to change the options of the structure renderer.



☑ Manual Render Settings

Structure Renderer: Smooth

☐ Show Outlines

☑ Show Halo

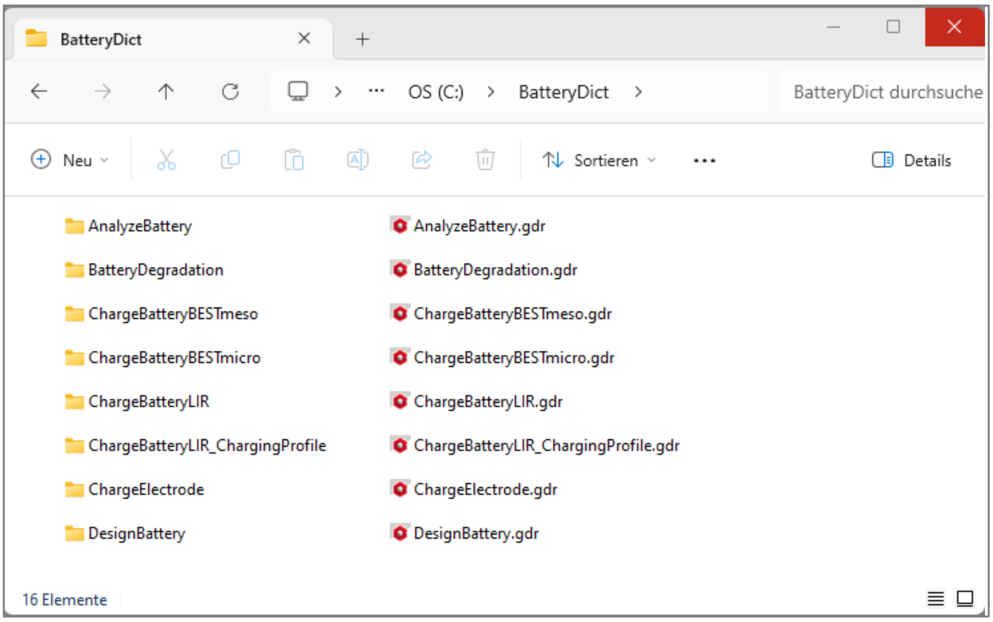
☐ Depth Darkening

☐ Global Lighting

☑ Shadows

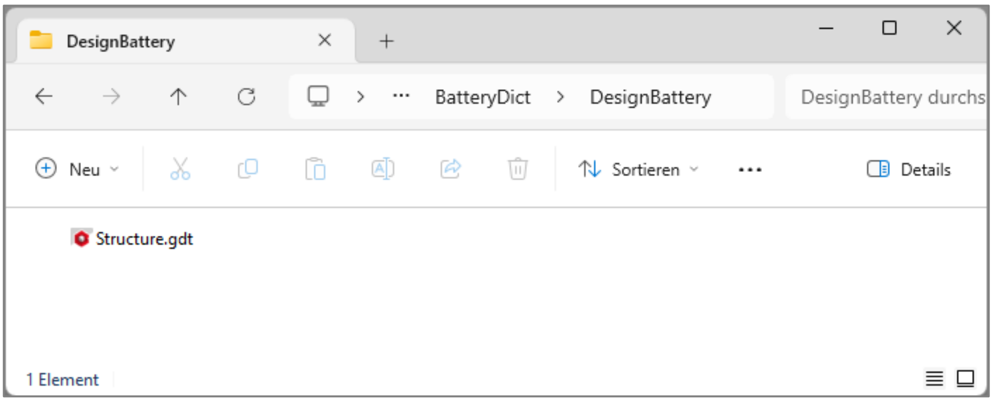
# RESULT FOLDERS

After designing a battery or running a charging simulation for a full cell or a single electrode, result files and the corresponding result folders are located in the project folder selected.



## DESIGN BATTERY FOLDER

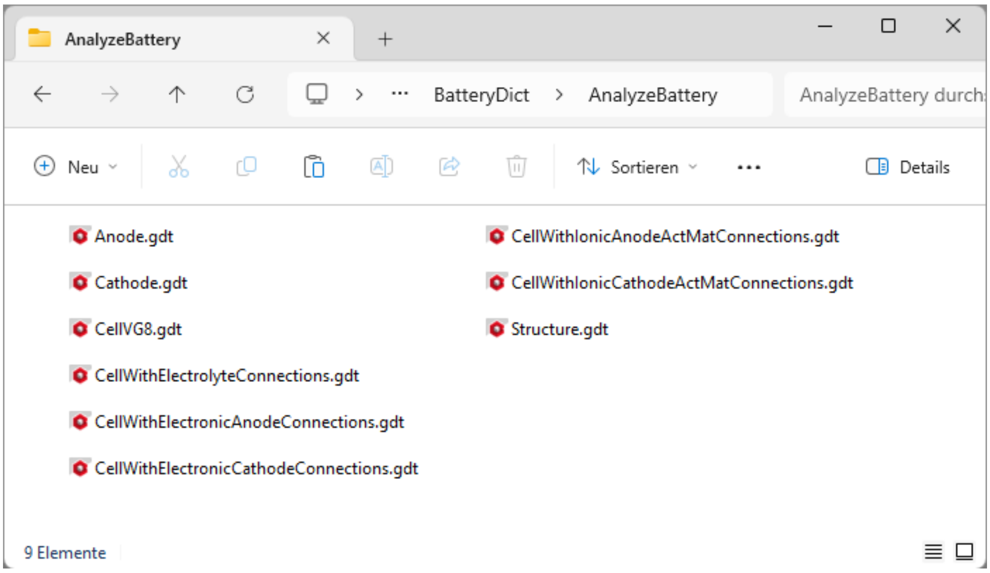
After the generation of a battery structure, a GeoDict result file (.gdr) is created in the selected project folder. A subfolder with the same name as the result file contains the generated battery structure.



The result file (.gdr) can be loaded at any time by selecting **File → Open Results (*.gdr) …** in the menu bar.

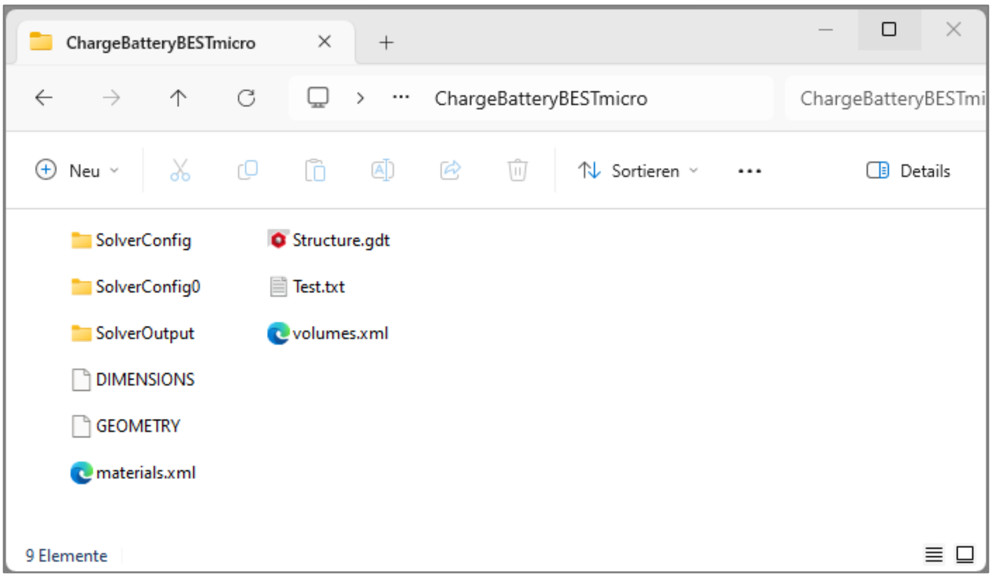
## ANALYZE BATTERY FOLDER

In the folder created for a battery analysis, the input structures used for both electrodes, as well as GeoDict structure files showing electronic and ionic connections in the active materials, the electrolyte, and the binder and carbon black are available.



## BESTmicro: the Charge Battery or Charge Electrode Folder

After running a charging simulation with BESTmicro, a GeoDict result file (.gdr) is created in the selected project folder. A subfolder with the same name as the result file contains three subfolders called **SolverConfig**, **SolverConfig0** and **SolverOutput**.



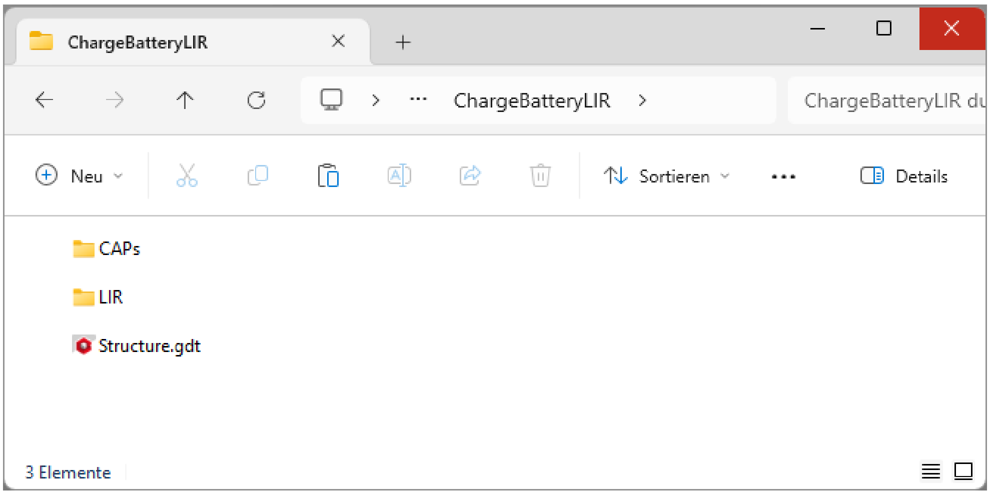
**SolverConfig** and **SolverConfig0** contain files with the input parameters for the charging simulation.

The **SolverOutput** folder contains some log-files from the solver, as well as a subfolder **output** with *.cap files containing volume fields. Such a *.cap file is written for the initial state, for the final state, and for each time step with intermediate output. These volume files can be loaded from the **Load *.cap** button under the Data Visualization tab of the Result Viewer or directly from the GeoDict GUI by selecting **File → Load Volume File ...** in the menu bar.

The additional files as well as the two additional folders **configuration** and **geometry** in **SolverOutput** contain some internal solver information and cannot be loaded in the GeoDict GUI.

## LIR: THE CHARGE BATTERY OR CHARGE ELECTRODE FOLDER

If the charging simulation was run with LIR solver, the result folder contains two subfolders. The folder **CAPs** contains the volume files for initial, final and each time step with intermediate output. The folder **LIR** contains files for each time step computed.

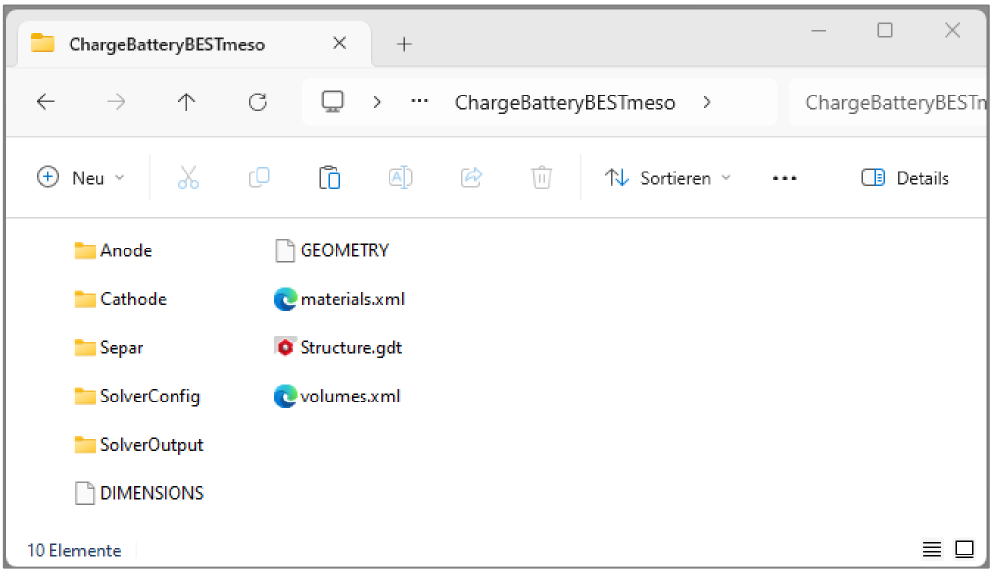


CAPs
LIR
Structure.gdt

3 Elemente

## BESTMESO: THE CHARGE BATTERY FOLDER

The result folder of a homogenized simulation with BESTmeso contains subfolders with information about the solver configuration and output. Additionally, subfolders with the effective material parameters of electrolyte and active materials, derived from the microstructure, are available.



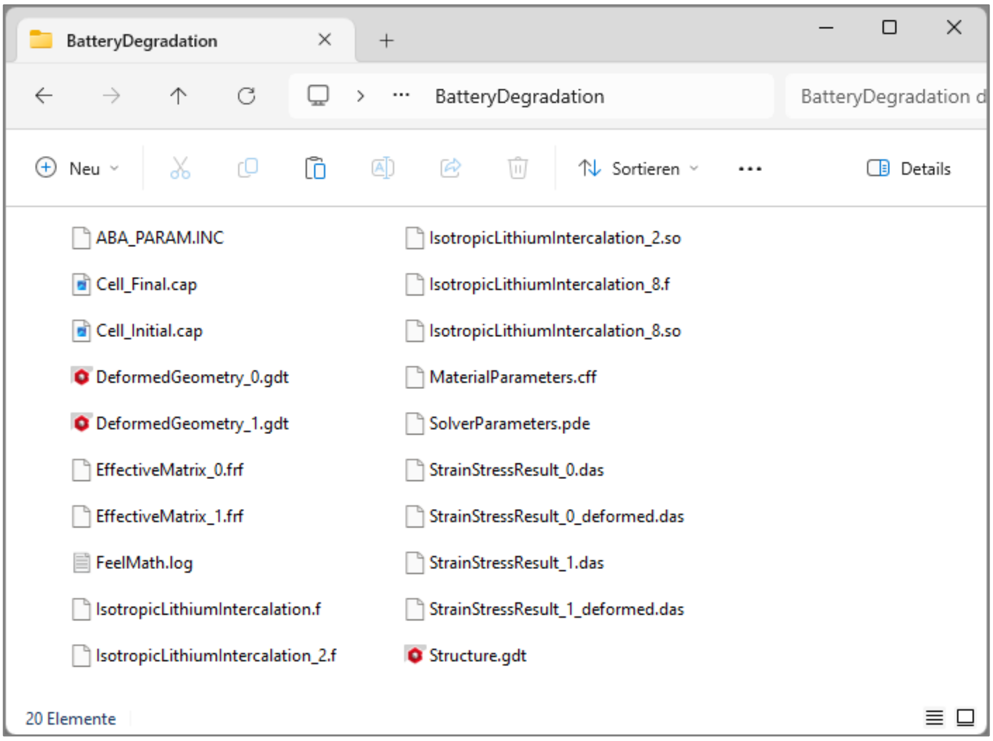
Anode
Cathode
Separ
SolverConfig
SolverOutput
DIMENSIONS
GEOMETRY
materials.xml
Structure.gdt
volumes.xml

10 Elemente

## DEGRADATION FOLDER

The result folder of a degradation simulation contains the initial and final .cap file of the previously run charging simulation and the *.das files with the volume fields created in the mechanical simulation for the undeformed geometry. If selected on the Output tab, see page 97, it contains additionally the deformed geometry and the *.das files for the deformed geometry for each step.

The other files are needed internally for running the mechanical simulation.



ABA_PARAM.INC
Cell_Final.cap
Cell_Initial.cap
DeformedGeometry_0.gdt
DeformedGeometry_1.gdt
EffectiveMatrix_0.frf
EffectiveMatrix_1.frf
FeelMath.log
IsotropicLithiumIntercalation.f
IsotropicLithiumIntercalation_2.f
IsotropicLithiumIntercalation_2.so
IsotropicLithiumIntercalation_8.f
IsotropicLithiumIntercalation_8.so
MaterialParameters.cff
SolverParameters.pde
StrainStressResult_0.das
StrainStressResult_0_deformed.das
StrainStressResult_1.das
StrainStressResult_1_deformed.das
Structure.gdt

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