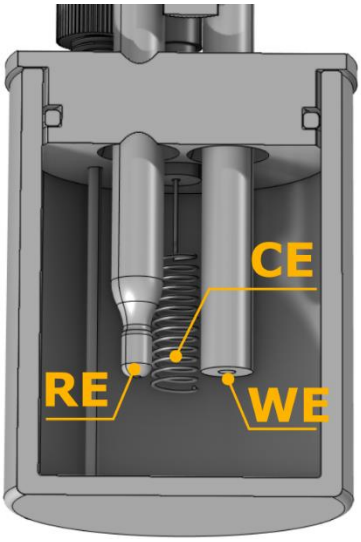
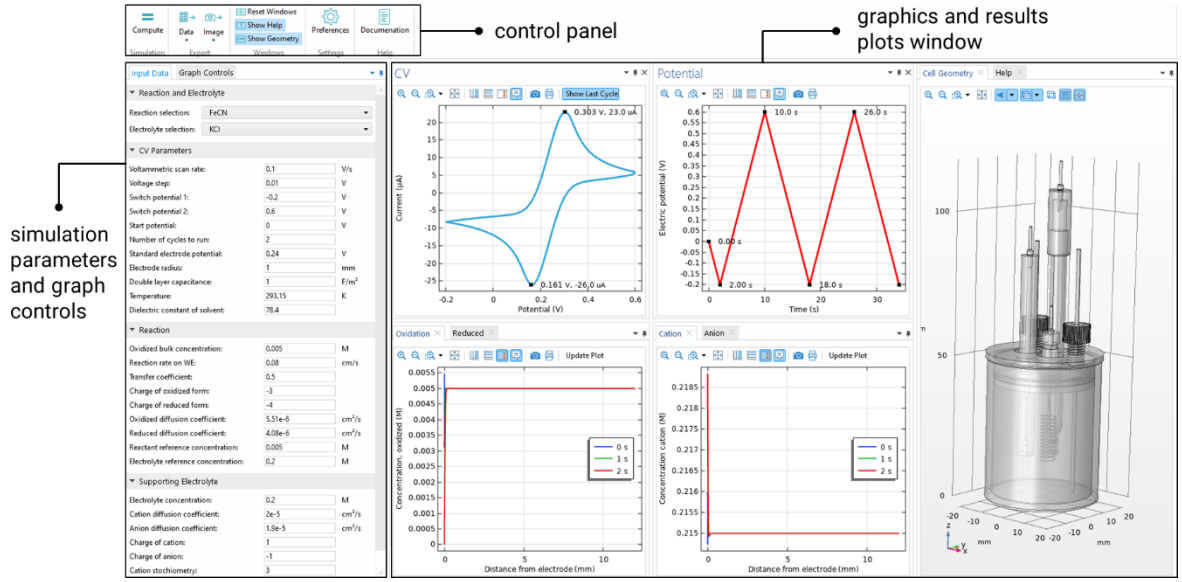
ModElChem® app manual



Contents

I. Introduction

The ModElChem® app simulates cyclic voltammograms (CV) of 1e- outer-sphere redox reactions with the general formula: $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red}$. The model is based on the Poisson-Nernst-Planck equations, thus considering both diffusion and migration. A supporting electrolyte is also explicitly included in the model.



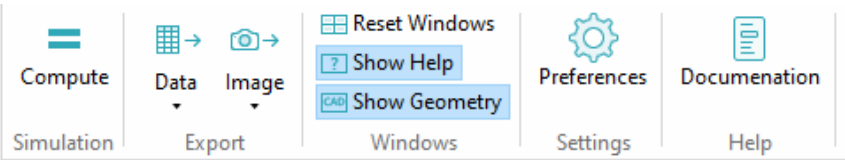
Main user interface of the application.

II. Geometry and system description

The 3D geometry of the three-electrode electrochemical cell is shown in the right graphical window. However, in practice the model is solved in 1D perpendicular to the surface of the working electrode.

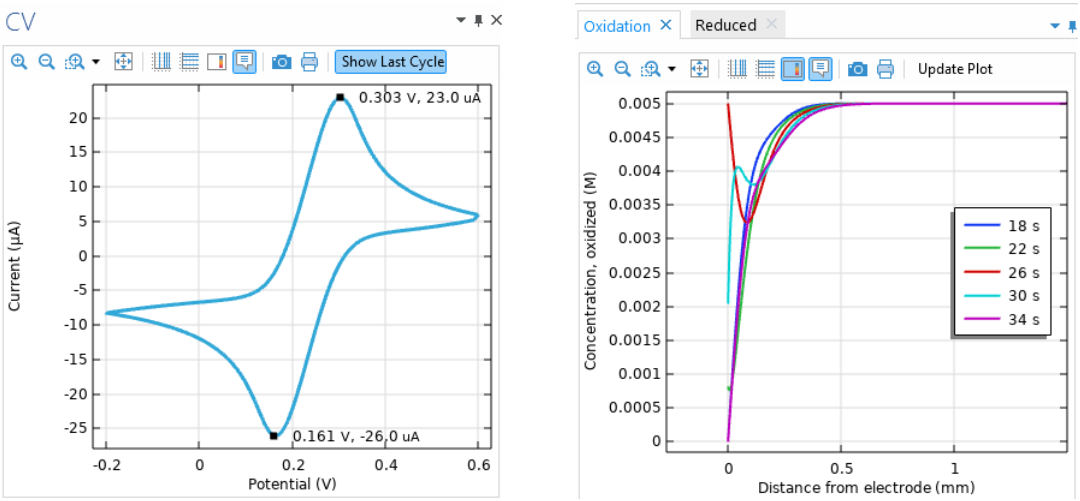
III. Control panel

The control panel, shown below, controls the app functionalities and it is used to run the simulation ("Compute"), export the simulated data to text files and images, reset the app layout, show and hide the geometry and the help menu. In the "Preference" menu one can switch between different color themes (light, dark and blue) and manage the licenses (see below), and the documentation (this file) provides more detailed description of the simulation app.



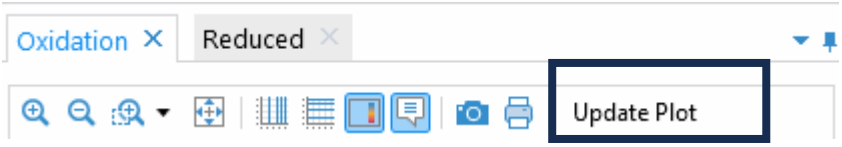
IV. Simulation properties and plotting options

The CV is the main output of the simulation together with the concentration profiles of the oxidized and reduced species.



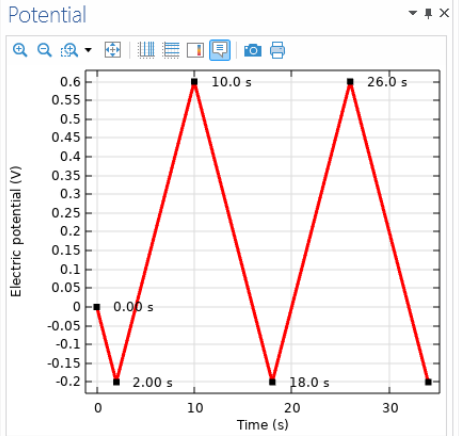
CV and oxidized/reduced specie concentration output from the calculation

The buttons above all plots can be used to zoom in, zoom out, reset the zoom, take snapshot etc. Additionally, the CV plot can also show only the last CV cycle by activating the toggle button in the window.



The concentrations windows have also an “Update Plot” button, which can be used to update the plots when the plotting parameters have been changed (see the following section for more inforamtion).

The graphical window also shows the potential sweep profile in the calculation. A standard triangular shape function is used to sweep linearly the potential between *Switch potential 1* and *Switch potential 2*.



V. Simulation parameters

First the reaction and the supporting electrolyte can be chosen from the drop-down menus shown below. Three different 1e- reactions are currently available:

1. $\mathrm{Fe^{III}(CN)_6^{3-}} + e^- \rightarrow \mathrm{Fe^{II}(CN)_6^{4-}}$
2. $\mathrm{Ru(NH_3)_6^{3+}} + e^- \rightarrow \mathrm{Ru(NH_3)_6^{2+}}$
3. Custom (general reaction) $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red}$

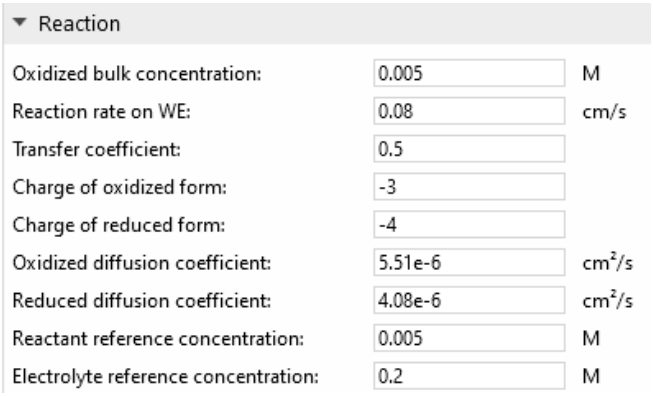
The first two reactions are validated against experimental data (see the paper: *Digital twin of a standard electrochemical cell for cyclic voltammetry based on Nernst-Planck-Poisson model*). When the reaction and supporting electrolyte are chosen the parameters in the following sections are automatically redefined.

CV Parameters

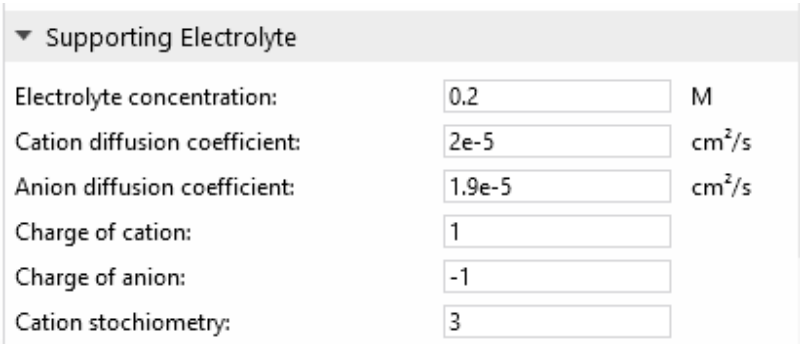
Voltammetric scan rate:	0.1	V/s
Voltage step:	0.01	V
Switch potential 1:	-0.2	V
Switch potential 2:	0.6	V
Start potential:	0	V
Number of cycles to run:	2	
Standard electrode potential:	0.24	V
Electrode radius:	1	mm
Double layer capacitance:	1	F/m^2
Temperature:	293.15	K
Dielectric constant of solvent:	78.4	
Distance to reference electrode:	6	mm

The parameters controlling the CV are found under the “CV parameters” menu. The CV potential window is given by the *Switch potential 1* and *Switch potential 2*. The *Standard electrode potential* is a parameter entering Nernst equation and affects the shift of CV curves towards lower or higher potentials. It is related to the specific reaction standard reduction potential and the reference electrode potential. Therefore, it should be varied when the reaction and/or the reference electrode change. The *Double layer capacitance* of the electrode is explicitly included in the model, however in most cases it has a negligible effect on the CV because the capacitive current is lower than the Faradaic current. The *Dielectric constant of the solvent* can also be varied if different solvent than water is used.

The “Distance to reference electrode” option must be chosen small enough to minimize the influence of the Ohmic drop on the CV curves. On the other hand, L also needs to be large enough to exceed the width of the diffusion layer, which varies with the scan rate. The default length of 6 mm is usually a good estimate.

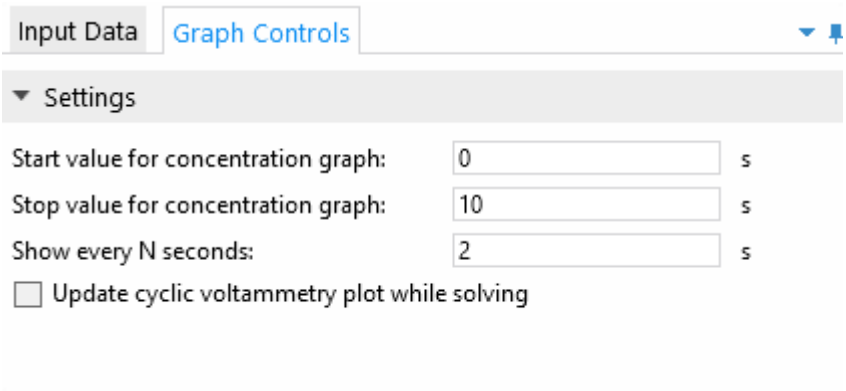


The reaction is defined by several parameters as shown in the screenshot above. The *Reactant and electrolyte reference concentrations* in most cases should be set to 1 M. However, in some cases one can get a better fit to experiments if they are set to the same values as the reactant and electrolyte concentrations, respectively, as shown in the screenshot above.



The supporting electrolyte parameters are automatically updated (except the concentration) when the electrolyte is chosen from the drop-down menu. These parameters can also be freely varied if one wants to simulate an electrolyte not found in the provided list. However, the stoichiometry of the electrolyte ions is closely linked to the specific reaction and thus they should be adjusted accordingly. The stoichiometry is important for setting-up the appropriate boundary condition concentrations and initial concentrations. If they are not correct the model

will not converge because the electroneutrality will not hold and therefore the Poisson equation will not converge. For example, the stoichiometry of the electrolyte ions in the case of $Fe^{III}(CN)_6^{3-}$ should be set to 3 and 0 for the cation and anion, respectively. This is because ferricyanide has 3 K^+ ions → $K_3[Fe^{III}(CN)_6^{3-}]$. Similarly, $Ru(NH_3)_6^{3+}$ has 3 Cl^- ions to compensate for the positive charge → $Cl_3[Ru(NH_3)_6^{3+}]$, and therefore the anion stoichiometry is 3 and cation – 0. This is valid for 1:1 electrolyte. For other types of electrolytes like 1:2, 2:1, and 2:2, the stoichiometry is adjusted automatically.

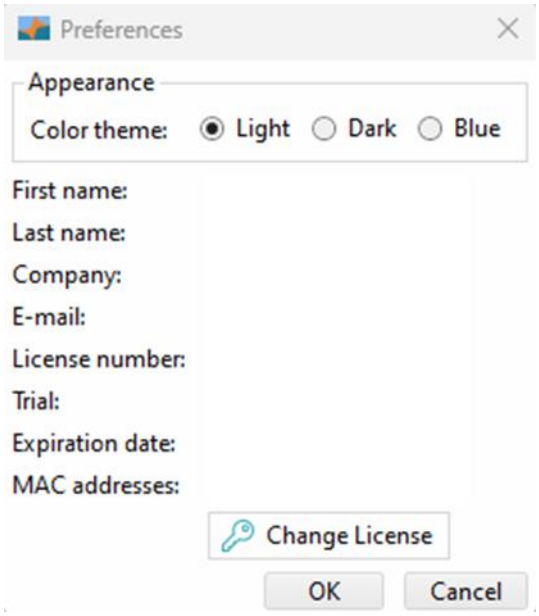


The final menu controls the concentration profiles plots. The concentrations can be plotted for a given time range, for example, from 0 to 10 seconds with an interval of 2 seconds. The potential plot window can be used to identify the time range of interest for plotting the concentrations.

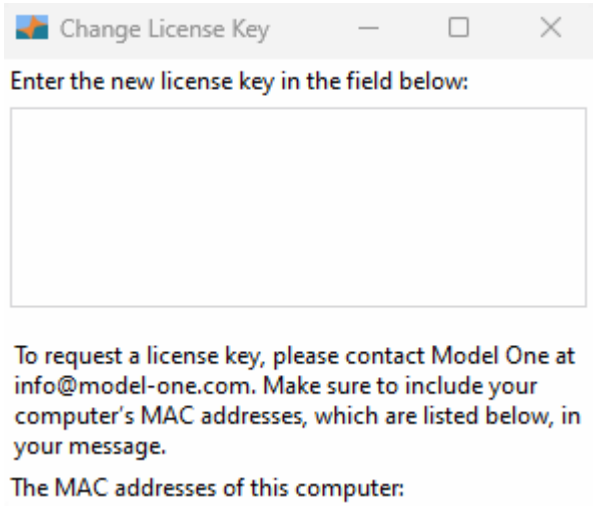
The “Update cyclic voltammetry plot while solving” is set to “OFF” by default. By turning it “ON” (checking the box) the CV plot will be plotted and updated in real time while the simulation is running. However, this makes the simulation much slower because of the plotting updating all the time. It should be noted that the potential plot is updated in real time, but this does not affect the performance.

VI. Preferences

The Preference Window can be used to set different color themes of the app as well to show the license information and to change the license.



Pressing the “Change License” will open new window where the new license key can be updated as well as displays the computers MAC address.



The MAC address of the computer can also be viewed by clicking on the “File” menu and the “Get MAC Addresses” button.