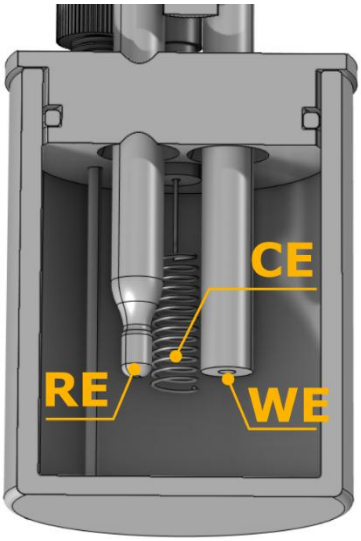
ModElChem app manual

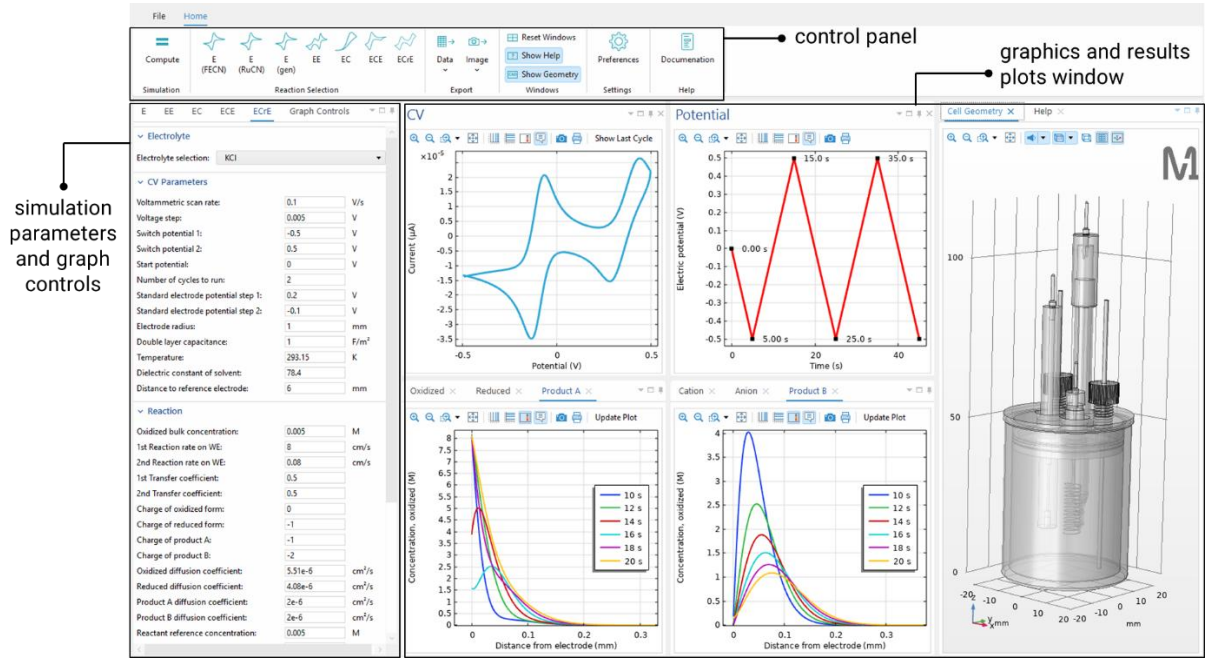
version 2.0



Contents

I. Introduction

ModElChem is a simulation software designed to simulate cyclic voltammograms (CV) for commonly encountered electrochemical reaction mechanisms, including both electron transfer and chemical steps. The application includes predefined mechanisms, while allowing users to customize input parameters. It is based on the Poisson-Nernst-Planck equations, which account for both diffusion and ion migration. A supporting electrolyte is also explicitly included in the model.



Main user interface of the application.

II. Geometry and system description

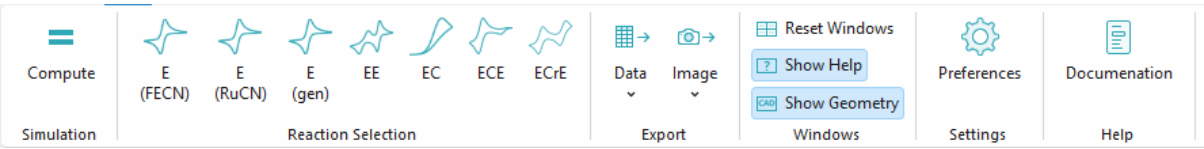
The graphical interface on the right side of the application displays the 3D geometry of a standard three-electrode electrochemical cell. Despite the 3D visualization, the simulations are performed in a 1D model perpendicular to the working electrode surface.

III. Control panel

The control panel, shown below, provides access to core app functionalities. These include:

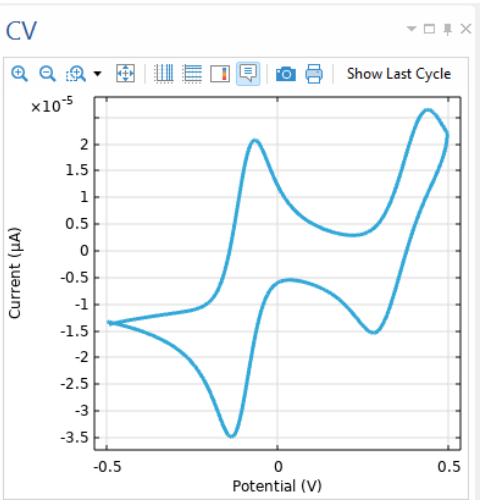
- Selecting a reaction mechanism
- Running simulations (“Compute”)
- Exporting results as text files or images
- Resetting the layout
- Showing/hiding geometry and help menus

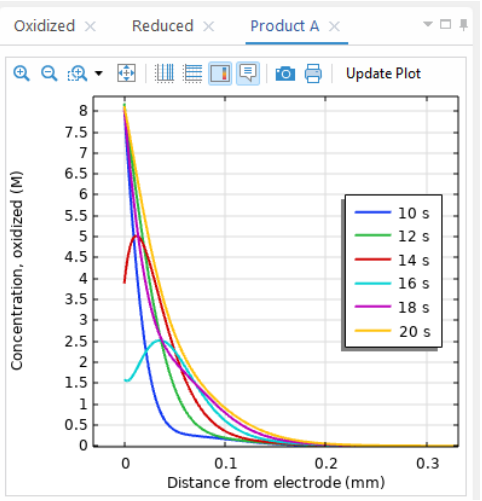
The “Preferences” menu allows users to switch between different color themes (light, dark, and blue), manage licenses (described later), and access this documentation for further guidance.



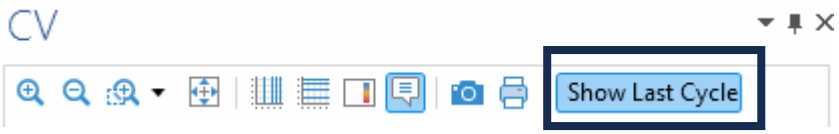
IV. Simulation properties and plotting options

The primary output of the simulation is the cyclic voltammogram (CV), along with concentration profiles for the oxidized, reduced, and other product species.

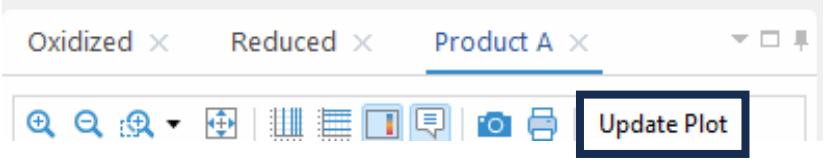




CV and oxidized/reduced/product A specie concentration output from the calculation

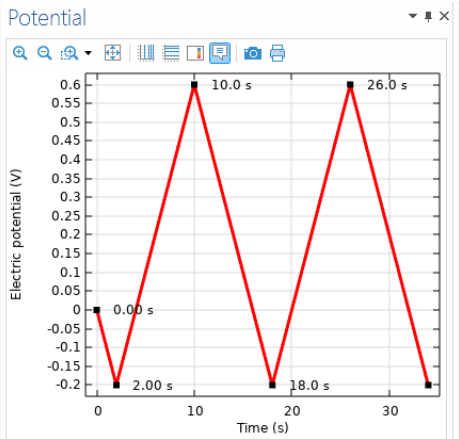


Buttons above each plot allow users to zoom, reset view, take snapshots, and more. A toggle option is available to display only the final CV cycle (enabled by default).



For concentration plots, use the “Update Plot” button to refresh the display after changing any plotting parameters (see next section for details).

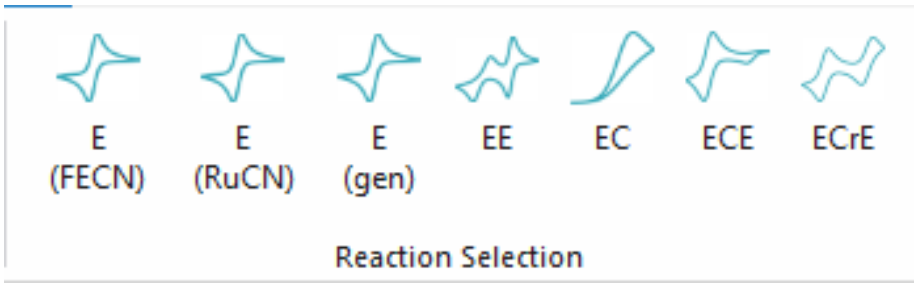
The graphical interface also shows the potential sweeping profile used in simulations. A standard triangular waveform is applied, sweeping the potential linearly between two switching potentials: *Switch potential 1* and *Switch potential 2*.



V. Simulation parameters

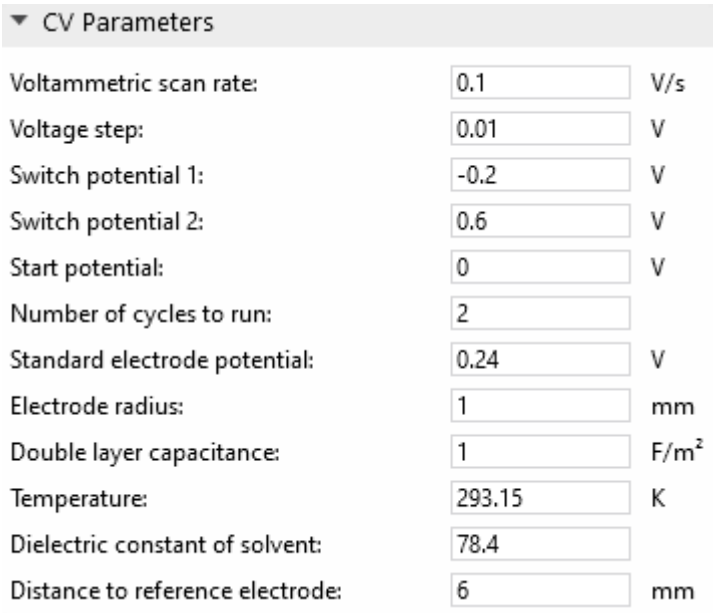
First the reaction and the supporting electrolyte can be chosen from the control panel (reaction) and drop-down menu (electrolyte) shown below. Five different reaction mechanisms are predefined: 1 electron transfer reactions (E), 2 electrons transfer reactions (EE), electron transfer followed by chemical reaction (EC), electron transfer, followed by chemical chemical reaction (irreversible) followed by second electron step (ECE) and electron transfer, followed by reversible chemical chemical reaction followed by second electron step (EC_rE). In addition, three different 1e- reactions are predefined for the E mechanism. The general formulas of the reactions are given below.

1. **E (FECN):** $\mathrm{Fe^{III}(CN)_6^{3-}} + e^- \rightarrow \mathrm{Fe^{II}(CN)_6^{4-}}$
2. **E (RuCN):** $\mathrm{Ru(NH_3)_6^{3+}} + e^- \rightarrow \mathrm{Ru(NH_3)_6^{2+}}$
3. **E (gen):** $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red}$
4. **EE:** $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red} + e^- \rightleftarrows \nu_A\mathrm{A}$
5. **EC:** $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red} \rightarrow \nu_A\mathrm{A}$
6. **ECE:** $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red} \rightarrow \nu_A\mathrm{A} + e^- \rightleftarrows \nu_B\mathrm{B}$
7. **EC_rE:** $\nu_{Ox}\mathrm{Ox} + e^- \rightleftarrows \nu_{Red}\mathrm{Red} \rightleftarrows \nu_A\mathrm{A} + e^- \rightleftarrows \nu_B\mathrm{B}$



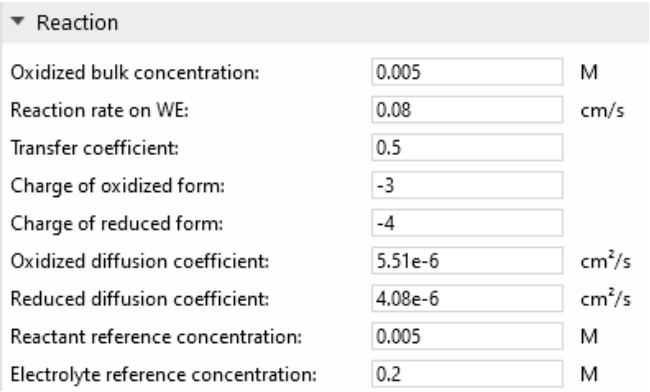
Note: when changing the reaction mechanism always do it with the button shown above, and not with the tab where the reaction parameters are shown. E EE EC ECE ECrE Switching between the tabs will not change the reaction mechanism.

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.

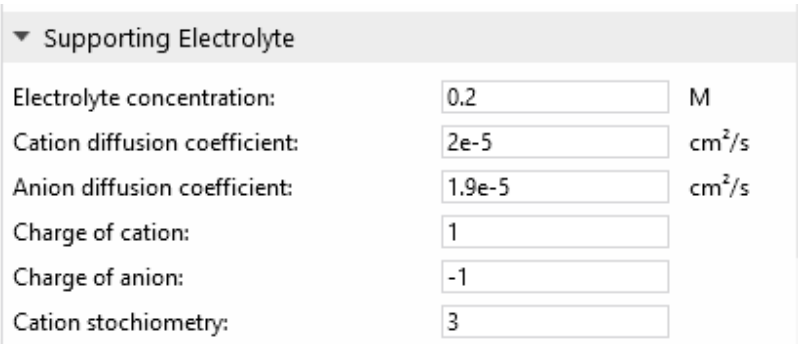


The parameters controlling the CV are found under the “CV parameters” menu. The CV potential window is given by the *Switch potential 1* and *Switch potential 2*. The *Standard electrode potential* is a parameter entering Nernst equation and affects the shift of CV curves towards lower or higher potentials. 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.

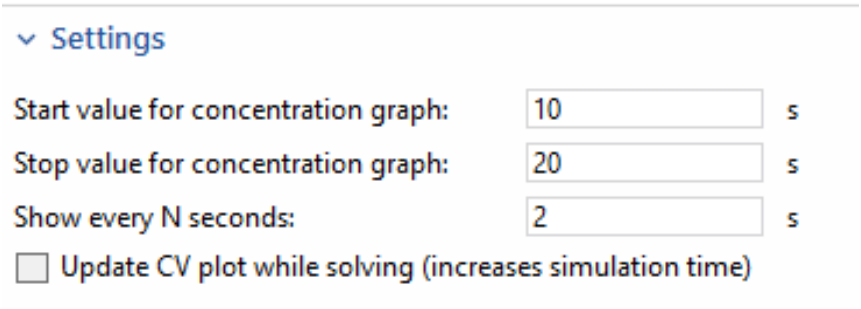
The “Distance to reference electrode” option must be chosen small enough to minimize the influence of the Ohmic drop on the CV curves. On the other hand, L also needs to be large enough to exceed the width of the diffusion layer, which varies with the scan rate. The default length of 6 mm is usually 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 experiment 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 list provided. 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 $\mathrm{Fe^{III}(CN)_6^{3-}}$ should be set to 3 and 0 for the cation and anion, respectively. This is because ferricyanide has 3 K^+ ions → $K_3\left[\mathrm{Fe^{III}(CN)_6^{3-}}\right]$. Similarly, $\mathrm{Ru(NH_3)_6^{3+}}$ has 3 Cl^- ions to compensate for the positive charge → $Cl_3\left[\mathrm{Ru(NH_3)_6^{3+}}\right]$, 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. If there are problems and the simulation gives and error, this in most cases is due to problem with convergence which stems from wrongly defined stoichiometry and charges of the species.

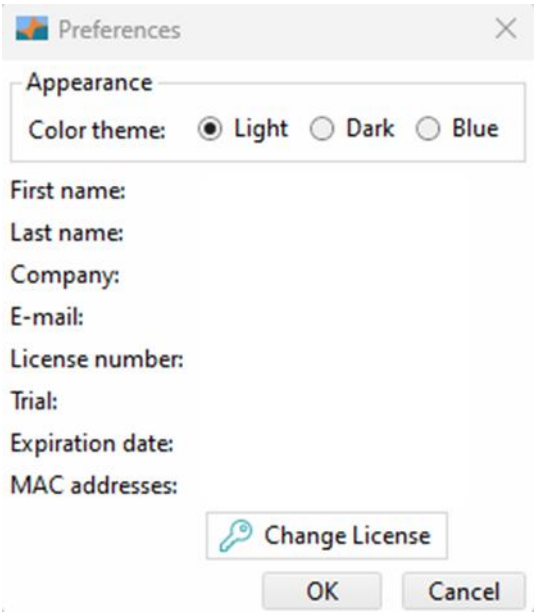


The final menu controls the concentration profiles plots. The concentrations can be plotted for a given time range, for example, from 10 to 20 seconds with an interval of 2 seconds. The potential plot window can be used to identify the time range of interest for plotting the concentrations.

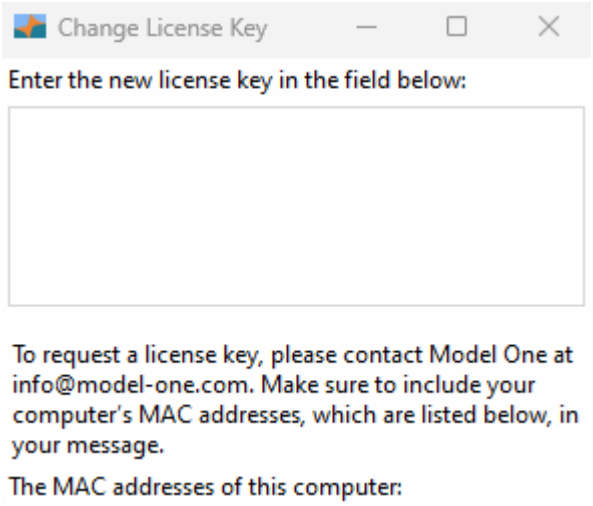
The “Update cyclic voltammetry plot while solving” is set to “OFF” by default. By turning it “ON” (checking the box) the CV plot will be plotted and updated in real time while the simulation is running. However, this makes the simulation much slower because of the plotting updating all the time. It should 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.