

Current-Voltage Analysis Tool for Solar Fuel Production (CATS)

The current-voltage analysis tool for solar fuel production (CATS) is an app that analyzes data collected during operation of solar-driven electrochemical devices, such as PV-electrolyzers and photoelectrochemical (PEC) devices. It makes use of current-voltage data, parameters that are easily accessible for many devices of interest. The program captures the time-dependence of loss mechanisms at play during PEC device operation and opens the door for real-time optimizations of operational parameters like the feed humidity to minimize performance losses. Currently, the program is useful for applications where the current-voltage polarization response of the photoabsorber and electrolyzer are pre-recorded, and changes over time can be estimated based on the pre-recorded current-voltage scans. More complicated scenarios, that involve permanent degradation of the PV component or detailed calculations of the electrolyzer current-voltage characteristics, may be included in future versions of this software. Aside from the possibility of deconvoluting loss mechanisms, this software can also reveal possible performance benefits by convective PV cooling when the photoabsorber is integrated into the electrolysis cell. The latter can highlight why certain device architectures may be beneficial over others. This app requires MATLAB Runtime to be installed which will be automatically downloaded when the installer file (CATS_Installer.exe) is opened. In general, this app consists of 3 parts. On the left side, the parameters for the calculations process can be changed. In the middle, the calculated or imported data can be displayed. On the right side, there are buttons that start the calculation processes.

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I. Current-voltage (IV) synchronizing (optional)

To enable the deconvolution of loss mechanisms, it is necessary to have a common timescale for both current and voltage data.

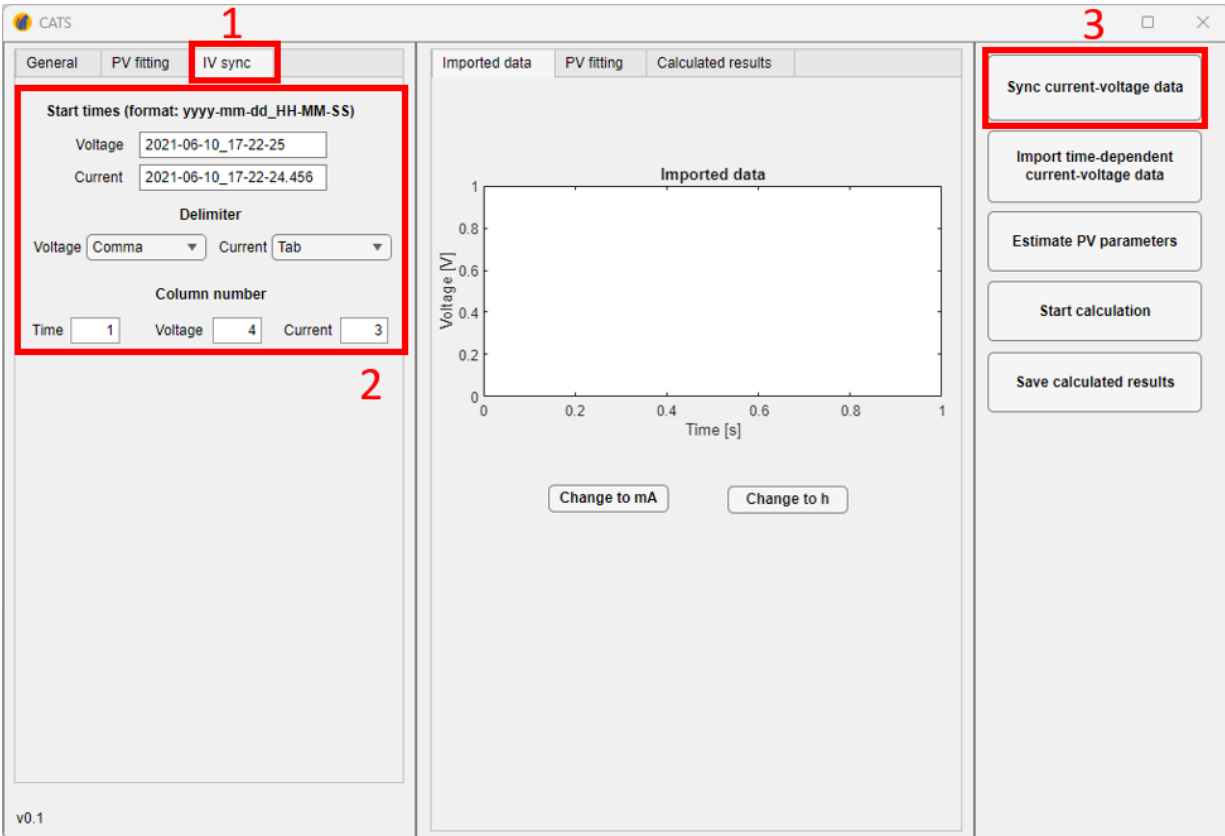


Figure 1. Synchronize current and voltage data

1. If the recorded current and voltage data are saved in separate files and need to be synchronized to a common timescale first, go to the IV sync tab on the left (**Figure 1**).
2. Set the correct values
 - Enter the recording start times for the voltage and current files.
 - Specify the variable delimiter for the voltage and current files.
 - Set the column numbers for time, current and voltage. The time column number needs to be the same for both current and voltage files.
3. Press the sync button to start the synchronization process
 - Select the voltage data file and wait for the import to proceed.
 - Choose the current data file and wait for the import to proceed.
 - A wait bar will appear and show the estimated remaining time for the synchronization process (**Figure 2**). This process attempts to use 90% of the available RAM (memory) and may take several minutes, depending on the size of the files and computer specifications.

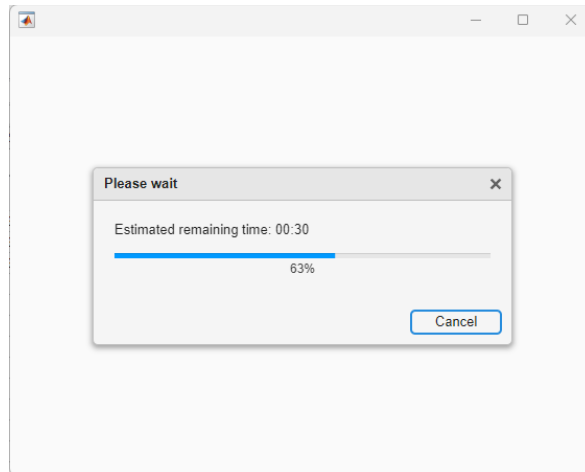


Figure 2. Wait bar indicating the estimated remaining time needed for synchronizing

- Specify the name and folder for saving the synchronized file in the window that appears as soon as the synchronization process has finished.

II. Import of synchronized current-voltage data

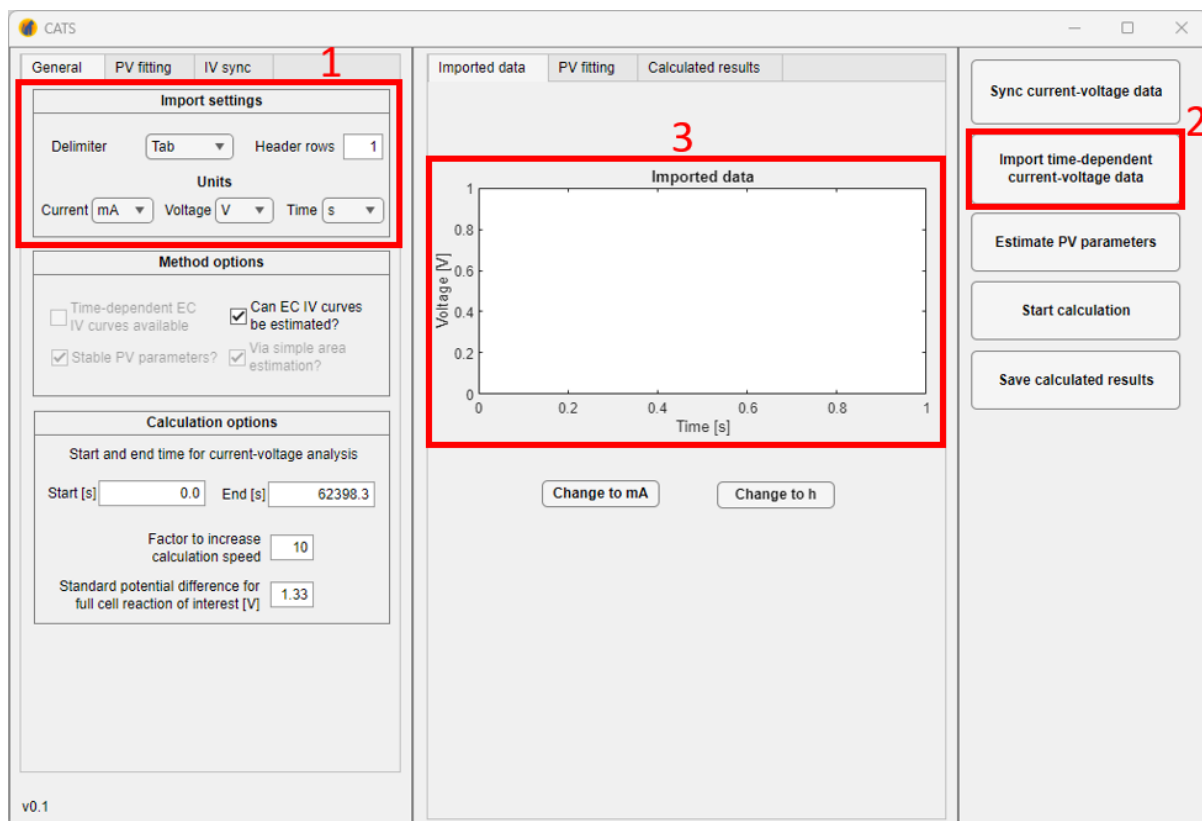


Figure 3. Import synchronized current-voltage data

1. Choose import settings (**Figure 3**).
 - Header rows are the number of rows before your data starts. If there are only the column names, the number of header rows should be 1.
 - Pick the units and column numbers of current, voltage and time in the synchronized data file.
2. Click the import button. This process should be fairly quick if your data file is saved locally.
3. The imported data will be displayed in the graph. Check for accuracy. It is possible to change the displayed units with the buttons below the graph.

III. Estimate PV parameters (optional)

Material-dependent, characteristic PV parameters can be extracted from the PV IV curves by fitting the single-diode solar cell model, including the influence of series and parallel resistances, to the measured curves using the following equation^[1-3]:

$$I = I_{ph} - I_0 \left(\exp \left(\frac{q (V + I R_s)}{n k T} \right) - 1 \right) - \frac{V + I R_s}{R_{sh}} \quad (1)$$

Here, V and I are the PV voltage and current, respectively. The photo-generated current is captured by I_{ph} and I_0 is the reverse bias saturation current. The characteristic PV parameters such as ideality factor, series and shunt resistance, are captured by n , R_s and R_{sh} , respectively. For high-quality PVs, it can be assumed that the photo-generated current equals the short circuit current (I_{sc}) of the PV. Finally, q is the elementary charge, k the Boltzmann constant and T the temperature of the PV. At open circuit conditions, I is set to 0 and V substituted with the open circuit voltage (V_{oc}), resulting in the following equation for I_0 :

$$I_0 = \left(I_{sc} - \frac{V_{oc}}{R_{sh}} \right) \left(\exp \left(\frac{q V_{oc}}{n k T} \right) - 1 \right)^{-1} \quad (2)$$

To start the extraction of characteristic PV parameters from the measured IV curves using the above equations, follow these steps (**Figure 4**):

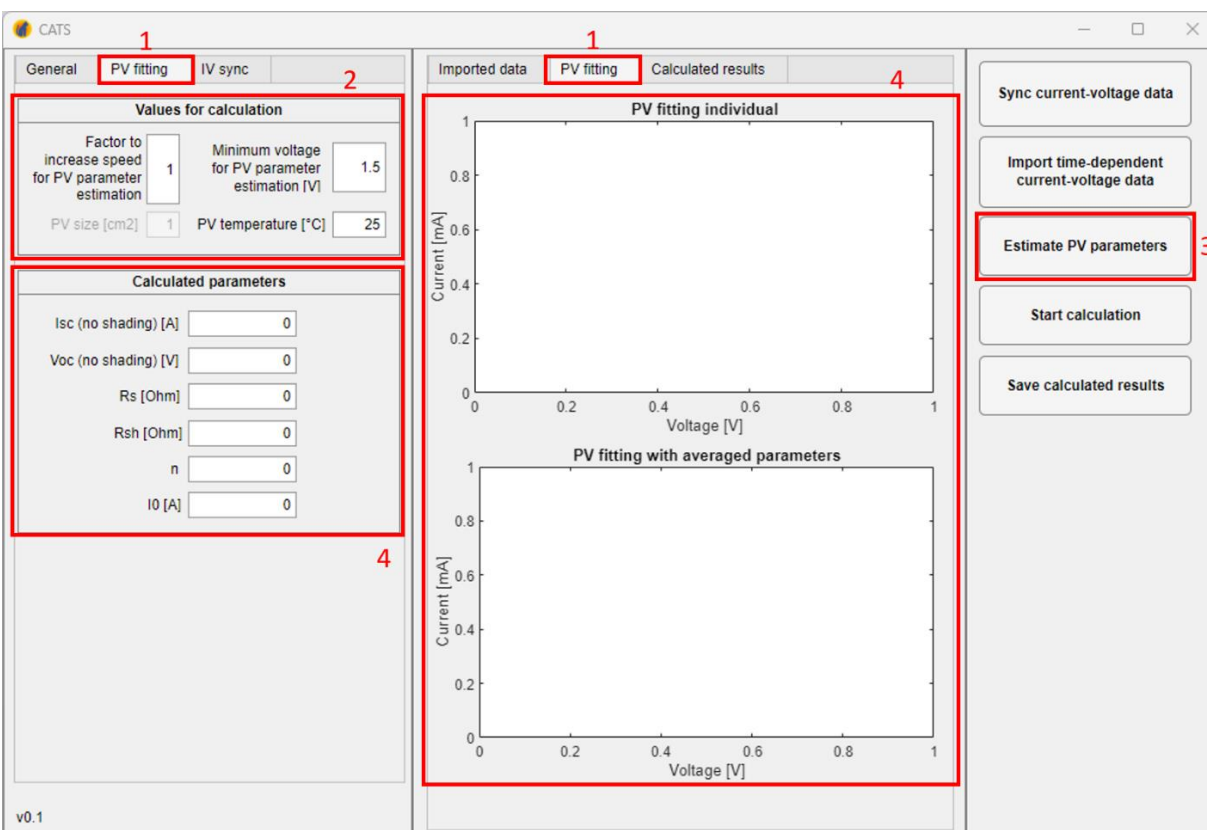


Figure 4. Estimate PV parameters

1. Go to the PV fitting tabs.
2. Set values for calculation:
 - The factor to increase calculation speed determines how many values of the PV IV curve are considered for the parameter estimation. This value needs to be an integer of at least 1, and less than the total data points. It is recommended to choose 1 unless the calculation takes too long, since any value above 1 will skip data points and reduce the calculation precision.
 - The minimum voltage for the parameter estimation determines the minimum of the voltage range that is used for the fitting process. For best results, this value should generally be set to a value around the onset potential for the electrochemical reactions of interest.
 - Set the temperature of the PV under IV curve measurement conditions.
3. Press button on the right to start the estimation process:
 - Select PV IV curves (can be multiple IV curves but they need to be in the same folder).
 - Wait for the process to be completed. Typically, it should process rather quickly, unless a large amount of data is selected.
 - It should be noted that the app attempts to use all available CPU cores for this calculation step which might slow down other applications. If this is not desired, uncheck the box 'Enable parallel computing' in the general tab on the left side of the app (which may slow down the estimation process).

4. The calculated parameters will be displayed on the left and the fitted curves will be shown together with the measured curves on the center panel. If multiple IV curves were selected in the previous step, the app will display the averaged parameters from all the extracted parameters and the difference between individual and averaged fits are shown in the graphs. If the individual fits agree well with the measured curves, but the fitted curves using the averaged parameters differ significantly from the measured curves, it indicates that the extracted PV parameters vary too much and can likely not be assumed constant during a stability experiment. For example, this could be caused by varying temperatures. In this case, it is recommended to choose a deconvolution method that does not rely on the PV parameters (see below).
5. A window will pop up asking the user to save the extracted parameters to text files. The first file contains all the parameters extracted from all the individual curves. The second file (with the ending *mean.txt*) contains the averaged parameters that are displayed in the app as described in the previous step.

Note: If higher precision in the voltage region near the V_{oc} is desired, it may be beneficial to manually fine-tune the V_{oc} value, that was extracted from the app, to improve calculation results during the deconvolution process (see IV. Deconvolute losses).

IV. Deconvolute losses

Before starting the deconvolution calculation, make sure that the time-dependent current-voltage data was imported (see II. Import of synchronized current-voltage data).

There are different methods for the deconvolution process. The method should be chosen depending on the available data and particular application. The flowchart below (**Figure 5**) can be used to help choose the right method.

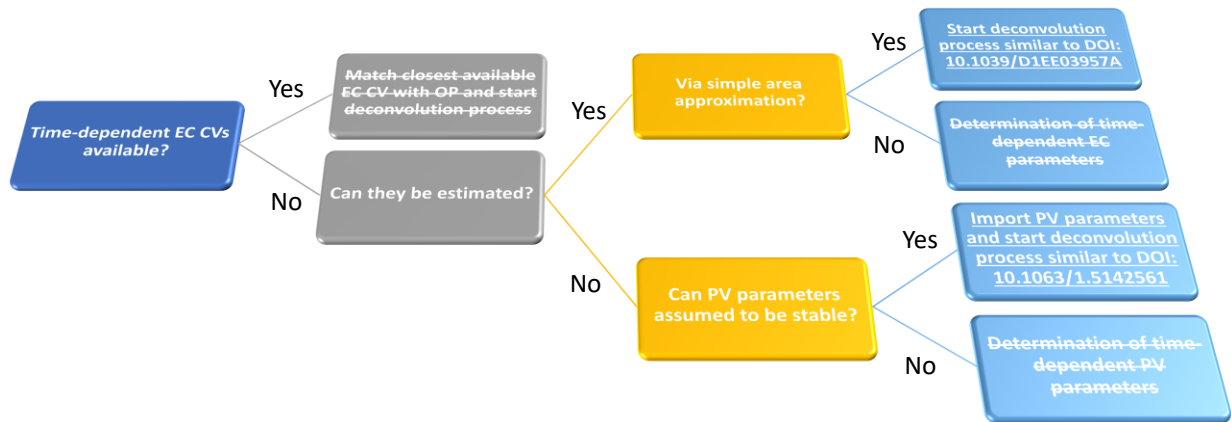


Figure 5. Pathways for deconvolution method. Some options are currently not available (indicated by the strikethrough text).

Currently, this app works with two scenarios where the operating current and voltage are either fitted to an electrochemical (EC) or photovoltaic (PV) IV-curve. For details please take a look at the respective publications (DOI: 10.1039/D1EE03957A, 10.1063/1.5142561).

a) Via EC fitting

For the EC fitting process, the EC IV-curve is estimated based on a pre-recorded EC curve multiplied with a factor that represents the available catalytic area. For example, bubbles can form during operation and stick to the surface which reduces the available area for catalytic conversion (and the respective factor). For every operating point (OP), an EC curve is fitted and the corresponding fitting factor saved, as pictured in **Figure 6** for an exemplary OP.

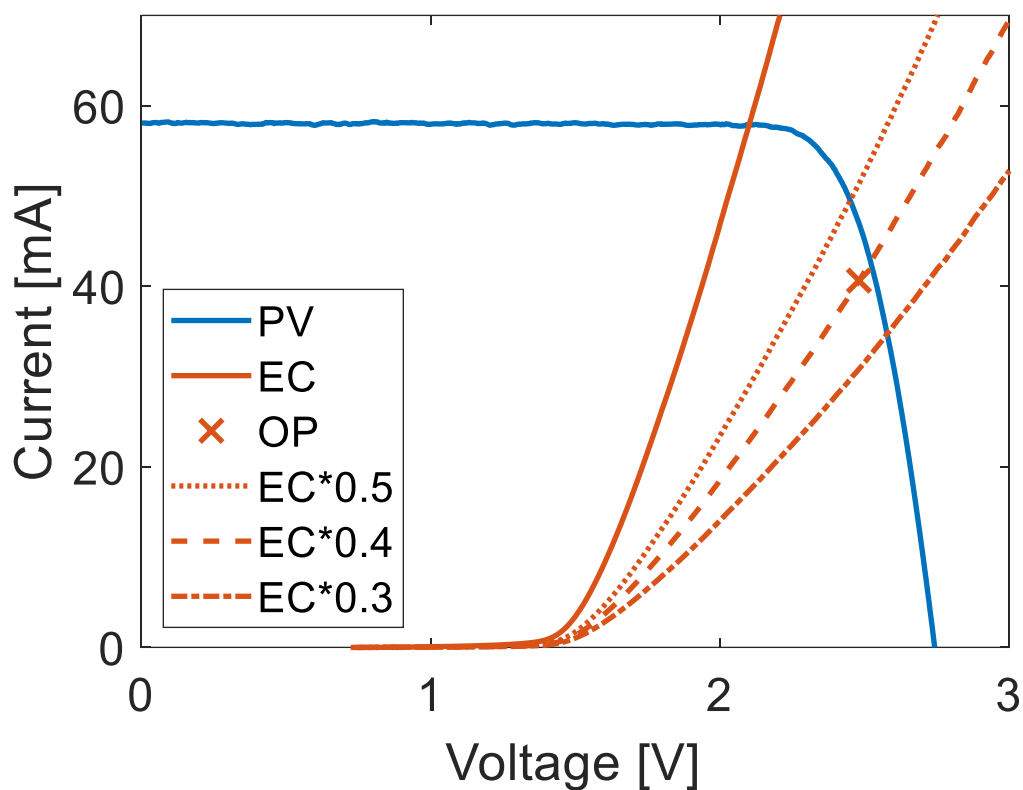


Figure 6. Exemplary fitting of the EC curve to an operating point (OP) during PEC operation. In this case, the fitting factor is 0.4, which can be interpreted as 40% of the catalytic area being available for reactions when compared to the reference EC curve.

It should be noted that this fitting factor can also be above 1 if the initially recorded EC curve was not measured under ideal conditions with parts of the catalytically active area unavailable for reactions.

To start the deconvolution process via EC-fitting, the general tab should be selected and the check marks selected as shown in **Figure 7**. Afterwards, the calculation options such as start and end time (can be 0 and Inf), speed factor and standard potential difference should be set. If the speed factor is set to 10 for example, only every 10th value is considered for the calculation process which should also be ~10 times

faster. For small datasets, it is recommended to choose 1 as the speed factor. The standard potential difference should be set according to the expected (main) reaction. For example, if the main reaction is CO_2 to CO reduction at the cathode side, coupled to the oxygen evolution reaction at the anode side, this value should be 1.33 V. After picking the correct settings, the start button (**Figure 7**) may be pushed (be sure to import the synchronized current-voltage data first, see II. Import of synchronized current-voltage data).

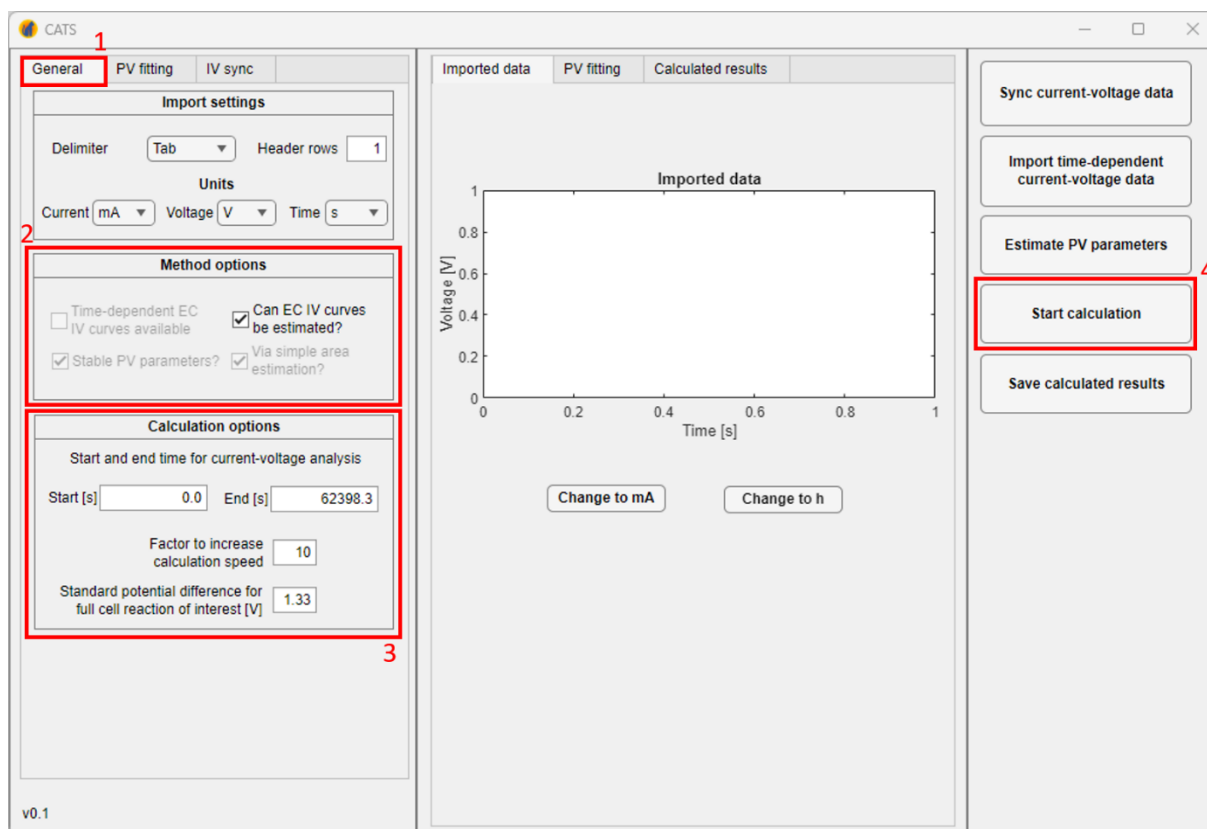


Figure 7. Start deconvolution calculation using EC fitting

After pushing the start button, the app will ask for the text files of the IV curves that should be used to compare the operating point against:

- Choose PV IV curve at room temperature (cool)
- Choose PV IV curve at equilibrium temperature (hot), if not available just pick the previous IV curve again. In the latter case, no benefits from convective PV cooling may be calculated.
- Choose EC IV curve

After the import of the three text files, the calculation starts and a wait bar appears (**Figure 8**).

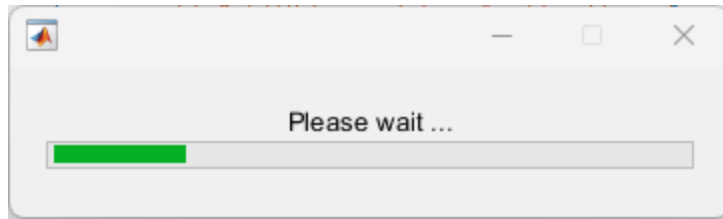


Figure 8. Wait bar for the deconvolution process

It should be noted that the app attempts to use all available CPU cores for this calculation step which might slow down other applications. If this is not desired, uncheck the box '*Enable parallel computing*' in the general tab on the left side of the app (which may slow down the calculation). Upon completion of the calculation, a window pops up which enables saving the results as a tab-separated text file. This step can be skipped and the results can be saved later by using the save button (**Figure 9**). The deconvolution results can also be seen in the calculated results tab (**Figure 9**). For details of this deconvolution method, please refer to the respective publication (DOI: 10.1039/D1EE03957A).

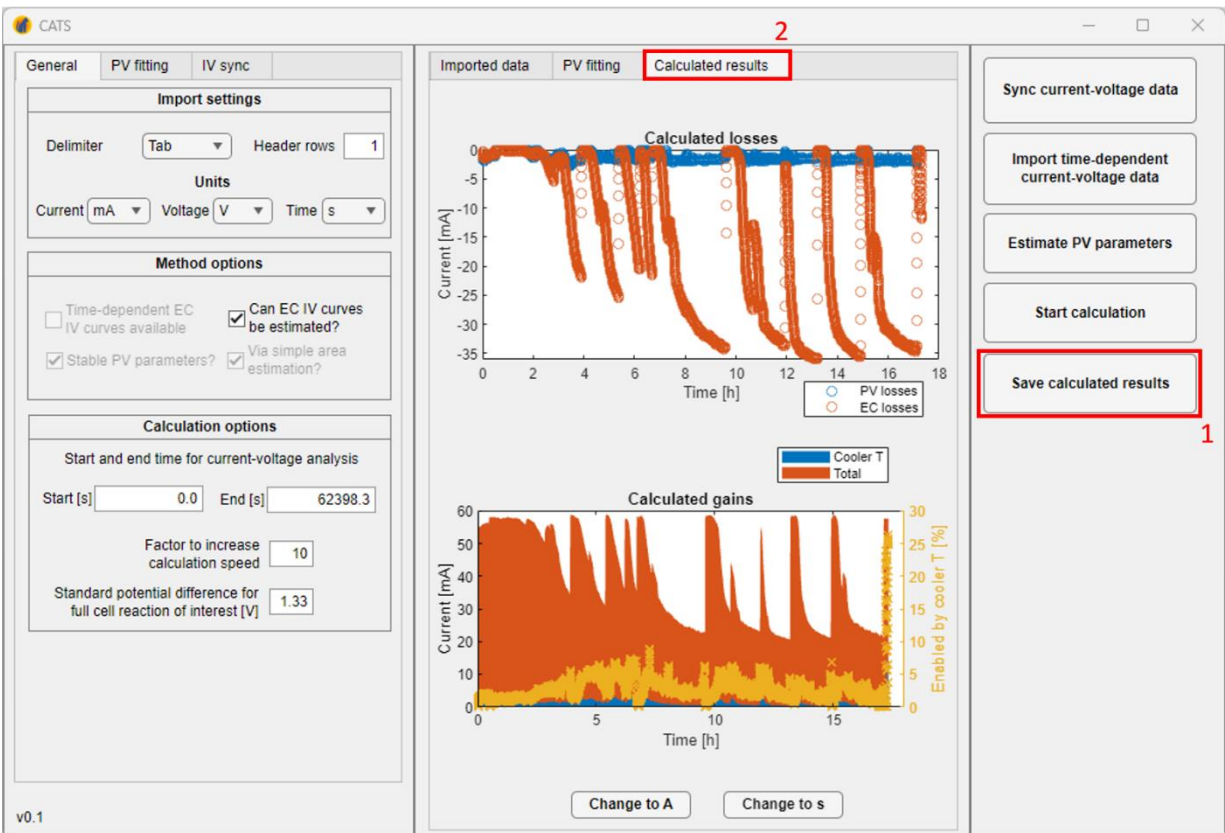


Figure 9. Exemplary results after the deconvolution calculation. The legends of the graphs may be dragged to a different position.

b) Via PV fitting

If time-dependent EC IV curves are not available for comparison with the operating point and it is also not feasible to estimate them, it is still possible to start the deconvolution calculation by using the PV fitting

approach. For this approach, it is assumed that the PV is not degrading irreversibly but PV-related performance losses are rather caused by shading of the PV, for example via water vapor condensing at its surface. Shading reduces the maximum available current (I_{ph} in **Equation (1)**) from the PV as displayed in **Figure 10**. Any operating point below the original PV curve may then be fitted to a shaded PV curve by changing the shading levels.

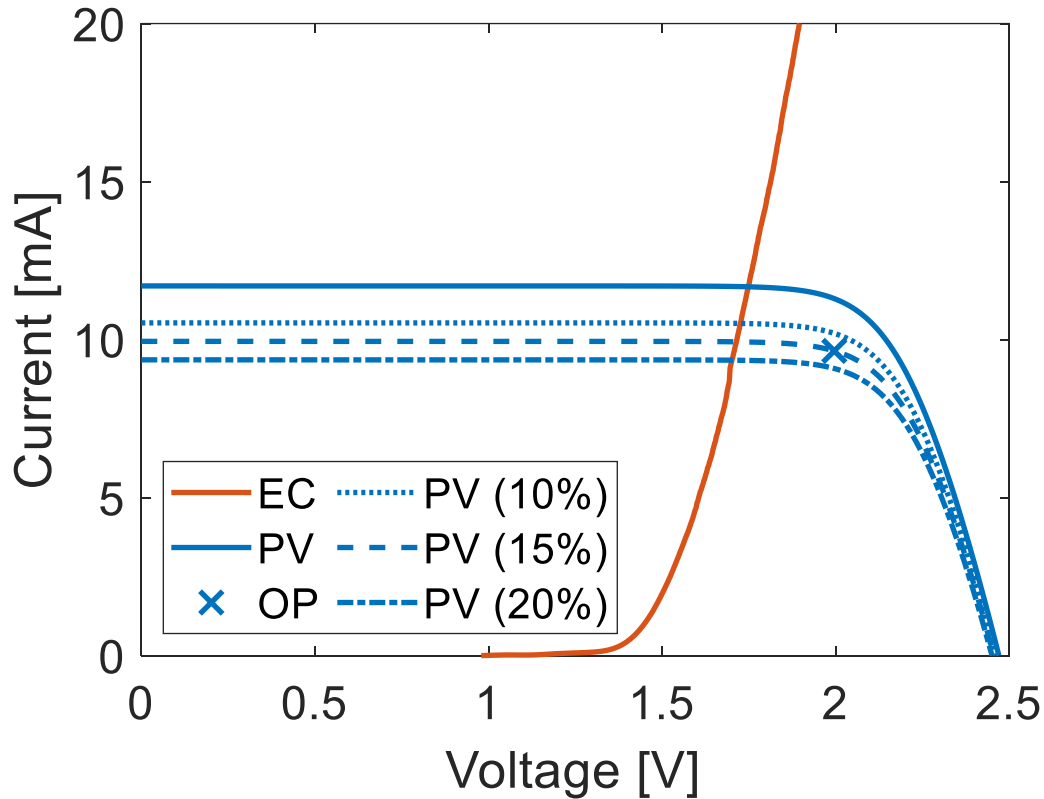


Figure 10. Exemplary fitting of the PV curve to an operating point (OP) during PEC operation. PV curves at different levels of shading (percentage values) are displayed. In this case, the OP intersects the PV curve at 15% shading level.

For PV fitting, the initial steps are similar to EC fitting, but the check mark for ‘Can EC IV curves be estimated’ should be removed (rectangle 2 in **Figure 11**). Additionally, the calculated PV parameters need to be entered on the PV fitting tab (**Figure 4**), which can be done manually or by the PV fitting step (III. Estimate PV parameters (optional)). Afterwards, the ‘Start calculation’ button may be pushed. In this case, no more files need to be imported and the calculation should start shortly after with the status indicated by a wait bar. Similar to the EC fitting approach, the details of the deconvolution calculation can be found in the respective publication (DOI: 10.1063/1.5142561).

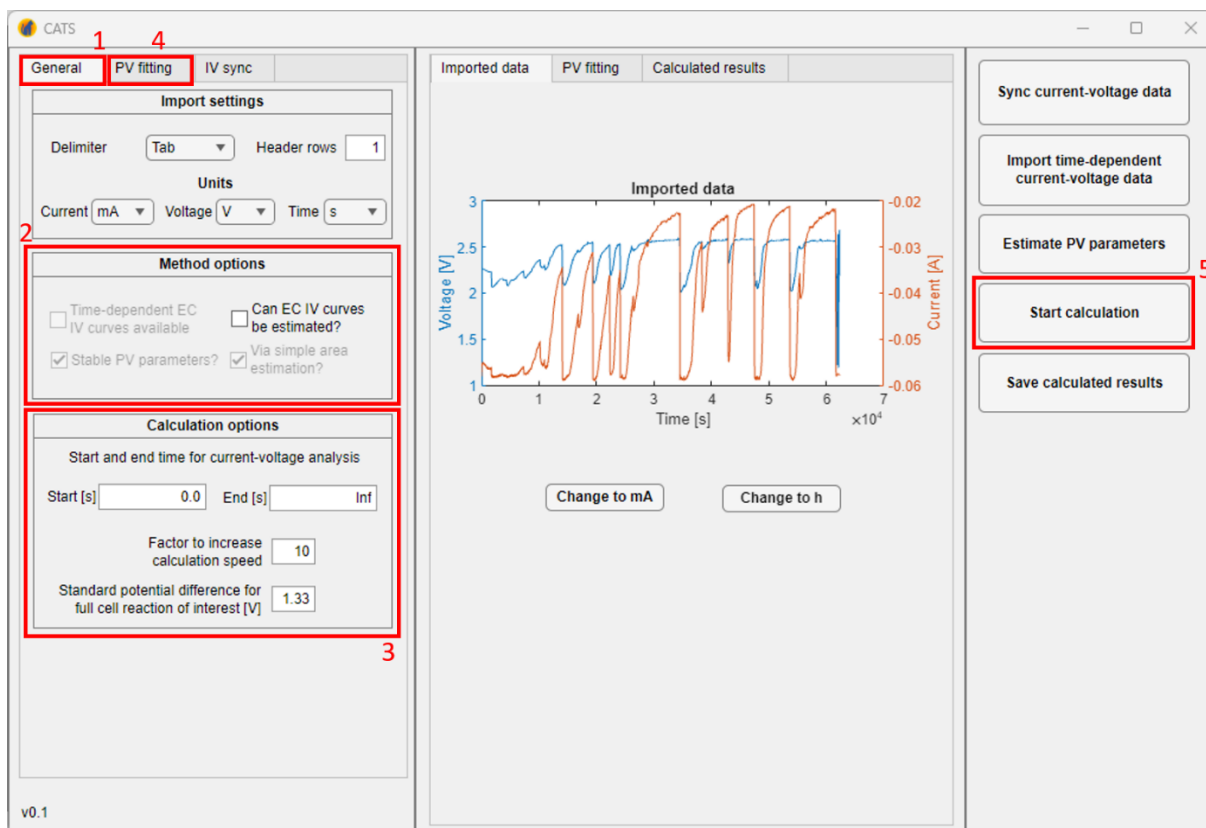


Figure 11. Start deconvolution calculation using PV fitting

V. Save data

In case the data was not saved in the previous step, it can be saved anytime before closing the software by using the '*Save calculated results*' button on the right side of the app.

VI. Acknowledgements and statement

This app uses the curve intersections function from Douglas Schwarz^[4]. The general idea of this app was developed at the Joint Center for Artificial Photosynthesis (JCAP), a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0004993. The app was then refined and converted into an executable version within the Liquid Sunlight Alliance, which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Fuels from Sunlight Hub under Award Number DE-SC0021266. The developer of this app assumes no responsibility or liability for any errors or omissions in the content of this app. The information contained here is provided on an "as is" basis with no guarantees of completeness, accuracy, usefulness or timeliness.

VII. Copyright Notice

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VIII. References

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[4] Douglas Schwarz (2023). Fast and Robust Curve Intersections
(<https://www.mathworks.com/matlabcentral/fileexchange/11837-fast-and-robust-curve-intersections>),
MATLAB Central File Exchange.