Lesson 4:

This lesson demonstrates how current points in target curves can be excluded in a fitting project. This option becomes important if the current measured in a certain region is known to be affected by instrumental artefacts which cannot be reproduced on the basis of the simulation model. In the present lesson such a situation is modelled for a chrono-amperometric experiment where the theoretical current may become much higher as the limiting current that can be measured with the instrument. Note that the maximal current that can be measured in the optimal current range (i.e. the current range required to achieve a reasonable resolution for diffusion controlled decay of the long-time current) is usually restricted to a few milli-amperes while the current theoretically expected immediately after the potential jump tends towards infinity for a sufficiently fast charge-transfer process. (In a real experiment, the artefact resulting from such an instrumental limitation is even amplified by IR-drop and/or double layer effects which will be disregarded in the present lesson).

In the first part of this lesson a few theoretical current curves are simulated for a simple but relatively fast charge-transfer process under chrono-amperometirc conditions. It will be shown then that the correct parameter values are retrieved if the theoretical curves play the role of target curves in a fitting project. In the second part of this lesson the theoretical curves are modified such as to model "ideal" experiments measured with an instrument providing a maximum current of *5mA* in the underlying current range. That means, the experimental current curve is assumed to be totally free of errors with the only exception that any current value larger than *5mA* is truncated to this limit. It will be demonstrated then that large parameter errors will be obtained when using these current curves in the fitting project. However, it will shown at the end of these lesson, that reasonable results are obtained again if current points mimicking the instrumental limiting current are excluded from the fitting process.

It is assumed in the following that the reader has already worked through the previous lessons and is familiar with the procedures and operations described there in greater detail.

I. Preparation of target curves

For the purposes of the present lesson it is most educational to use theoretical (simulated) chrono-amperometric current curves as target curves for the fitting project.

1. Start *DigiElch*, click on New and create a new CA-Simulation Document

2. Click on Simulation -> Edit Properties ( ), make sure that the Chemical Reactions page is activated, enter the reaction equation for a simple charge-transfer mechanism using the default names *"Ox"* and "*Red"* and complete the input in the following way:

	Charge-Transfer Reaction	E° (V)	α / λ (eV)	ks (cm/s)
1	Ox + e = Red	0	0.5	1

	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	Ox	1E-005	0.001	0.001
2	Red	1E-005	0	0
3				

3. Go to Simulation Parameters, modify **Scan** and **Geometry** in the following way

Scan ☑ use same time (s) in all scan segments

Segment	Estart (V)	Eend (V)	time (s)
1	0.3	0	0.001
2	0	0.3	0.001
3			

Time steps/segment 500

Geometry: Planar; Area (cm²) 0.1

and enter "***Data-0***" as **Simulation Name**

Simulation Name: Data-0

4. Close the CA-Properties dialog and click on Simulation -> Run -> Fixed Grid Simulation ( ).

5. If the simulation has completed, click on Simulation -> Duplicate ( ). Then go to Simulation Parameters, enter *0.01* as *Eend (V)* for scan segment 1 (resulting in an overvoltage of *+10 mV* for the first potential step) and enter "***Data+10mV***" as "Simulation Name".

Scan ☑ use same time (s) in all scan segments

Segment	Estart (V)	Eend (V)	time (s)
1	0.3	0.01	0.001
2	0.01	0.3	0.001

Time steps/segment 500

Simulation Name: Data+10mV

6. Repeat step 4. and 5. using an overvoltage of *+20 mV*, *-10 mV* and *-20 mV*. Assign the names "***Data+20mV***", "***Data-10mV***" and "***Data-20mV***" to these simulations. In this way a simulation document containing 5 chrono-amperometric simulations referring to overvoltages of *+20 mV, +10 mV, 0 mV, -10 mV* and *-20 mV* has been generated. The screen display associated with these simulations is sown in the following picture:

   For the convenience of the user, this simulation document is stored in the "OriginalData.cas"-file contained in the Lesson4.zip archive. The user may simply open this document instead of executing steps 1 to 6.

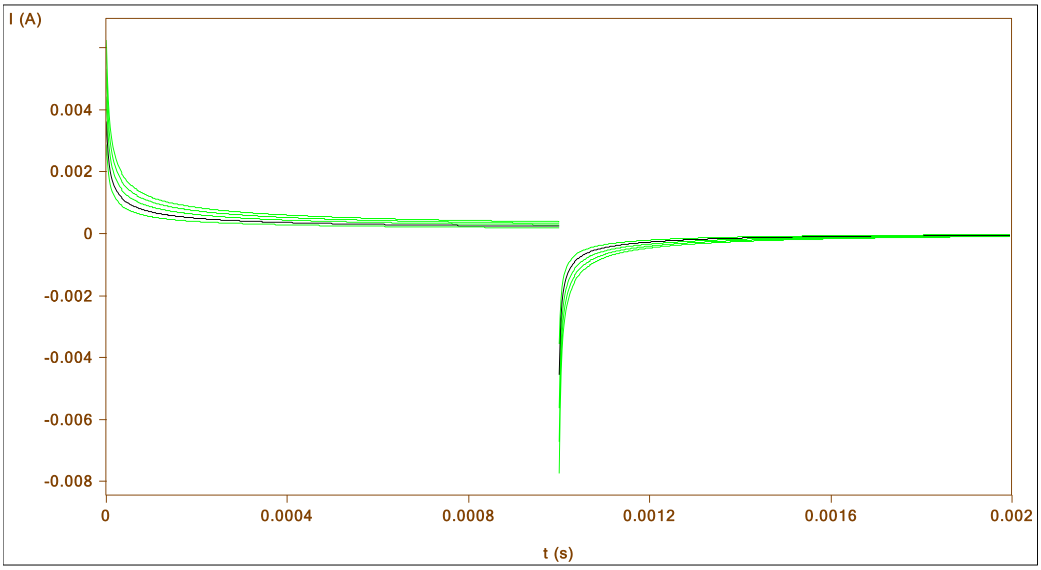


Figure 1

II. Running a fitting project using the simulated curves as target curves

We will show now that the exact charge-transfer parameters, *E°(V)*, *ks (cm/s)*, and the exact diffusion coefficient, *D (cm²/s)*, will be retrieved by the fitting procedure when using the above current curves in a fitting project based on a simple charge-transfer mechanism.

1. Click on Document -> Add Simulations to RAM-Disk (+). Bypass the appearing dialog box by clicking on **OK**. Then you may close the simulation document.

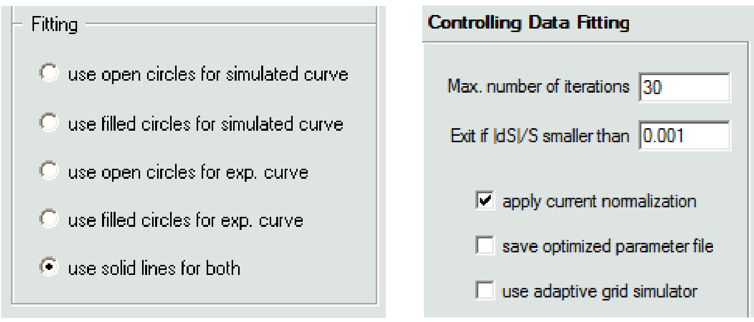
2. Create a new CA-Simulation Document, click on Data Fitting->Prepare Fitting Project, enter the reaction equation for a simple charge transfer mechanism and starting parameters which are distinctly different from those used in the target curves and select *E°(V)*, *ks (cm/s)* and *D (cm²/s)* for being optimized by the fitting procedure (see step 10. in Lesson2 for more details):

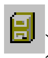
	Charge-Transfer Reaction	E° (V)	α λ (eV)	ks (cm/s)
1	Ox + e = Red	0.05	0.5	0.1

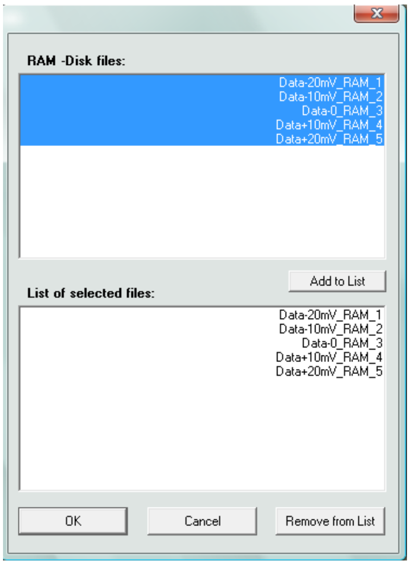
	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	Ox	2E-005	0.1	0.1
2	Red	2E-005	0	0

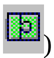
Also do not forget to link the diffusion coefficients of *Ox* and *Red* (see step 11 in Lesson2 for more details).

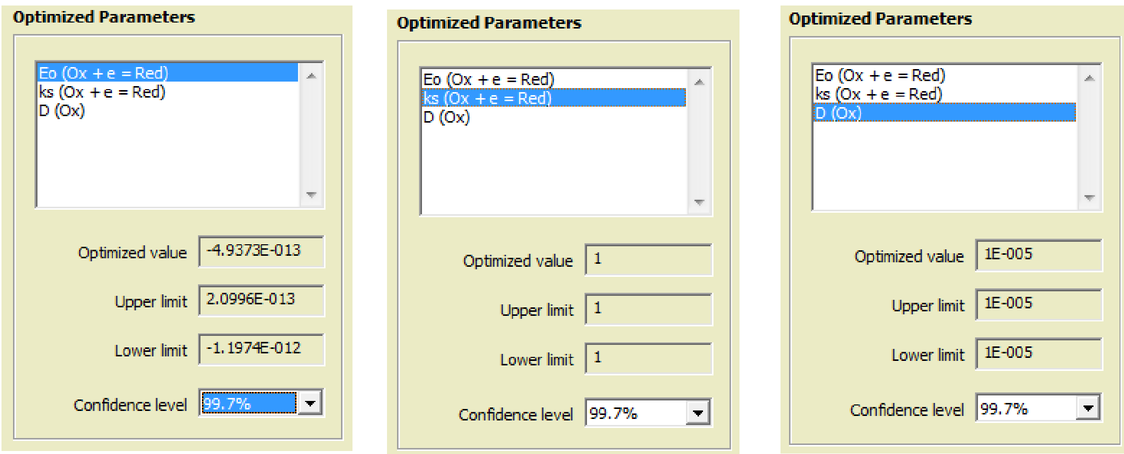
Before closing CA-Properties with **OK** go to Preferences and modify the default settings as follows



3. Click on Data Fitting->Select Data Target Curves form RAM-Disk (), select the five files and click on **OK**



4. Click on Data Fitting->Run Fitting Procedure () and watch how the program is trying to find the "best fit". After having completed the 30 iterations, the agreement between simulated and target curves is perfect and the exact parameter values are retrieved by the fitting procedure within a numeric rounding error of about 10^{-12} :



This is not surprising because the target curves are simulated ones obtained with these parameter values.

III. Running a fitting project using target curves in which an instrumental artefact is mimicked

Now we are going to modify the target curves such as to mimic an instrumental artefact. It is assumed for this purpose that the current curves simulated above are used for mimicking ideal experimental curves measured with an instrument that is built up from operational amplifiers working with a ±15V power supply. It is also assumed that the experiments were measured in a current range working with a *3kΩ* resistance in the feedback loop of the current follower so that a maximum absolute current of *5mA* can be provided by the instrument. That means any absolute current value larger than *5mA* is truncated to this value while the rest of the current curve is assumed to be totally free of errors for the sake of simplicity. The current curves modified in this way are included in the "ModifiedData.cas"-file contained in the Lesson4.zip archive. They are shown in the following picture:

These files can be prepared by exporting (in use-format) the simulations produced as described above in step 1 to 6. (For convenience, the data are saved in "OriginalData.cas"-file contained in the Lesson4.zip archive). Open each use-file with an ASCII-editor and replace any current value larger than *+5mA* with *+5mA* and any current value smaller than *-5mA* with *-5mA*.

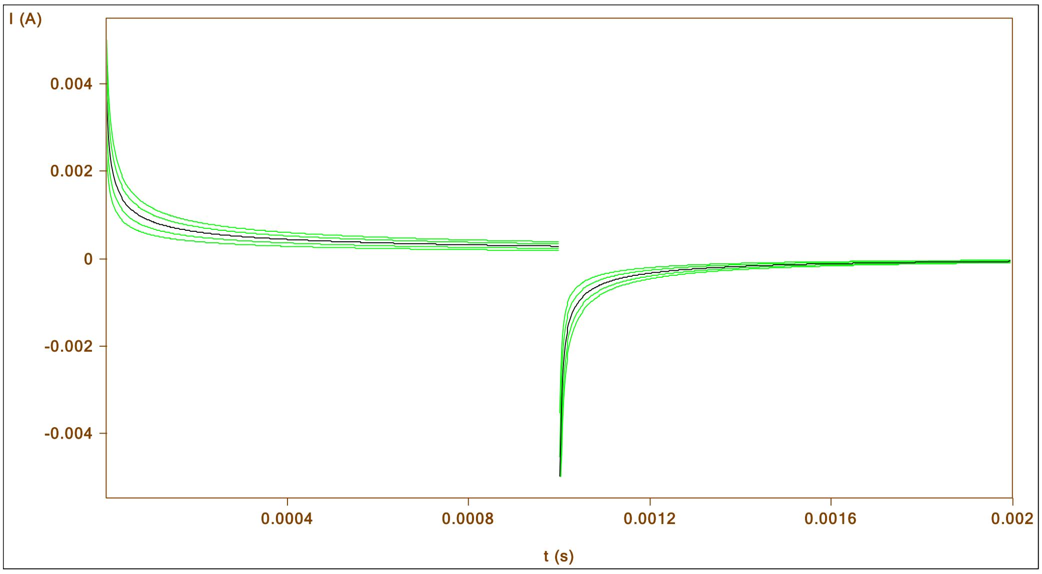
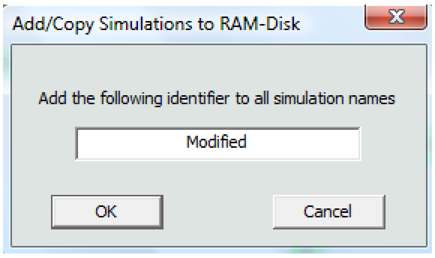
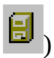


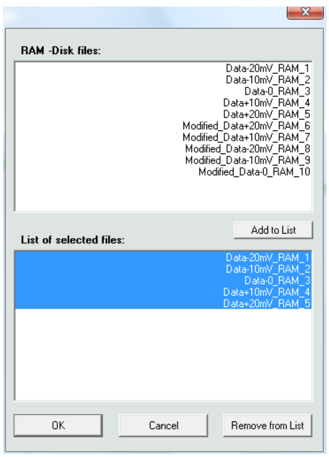
Figure 2

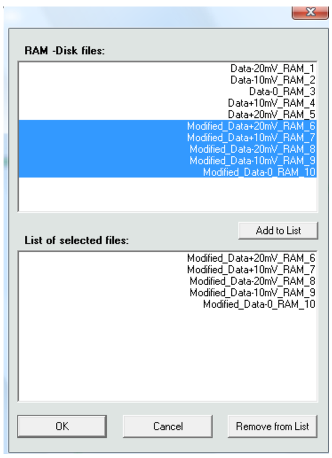
Theoretically the most reliable information about the nature of the charge transfer process is just contained in the current values following immediately after the potential jump. It should be clear for this reason that it makes no sense to use "experimental" curves as target curves in a fitting project if these current points are known to be falsified (either artificially as for the purposes of the present lesson or) by real instrumental artefacts resulting indeed from a not sufficiently high current supply or from a not ideal compensation of IR-drop and coupled double layer charging effects. (Note that a short time current of several amperes may be required for re-charging the double layer of a macro-electrode on a microsecond time-scale.) This will be demonstrated now by using the current curves shown above as target curves in a fitting project.

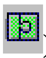
5. Open the "ModifiedData.cas"-file. Click on Document -> Add Simulations to RAM-Disk () and enter "Modified" in the appearing dialog box to make it easier to distinguish the modified files from the original ones. Then close the "ModifiedData.cas"-document in order to return to the Fitting Menu.

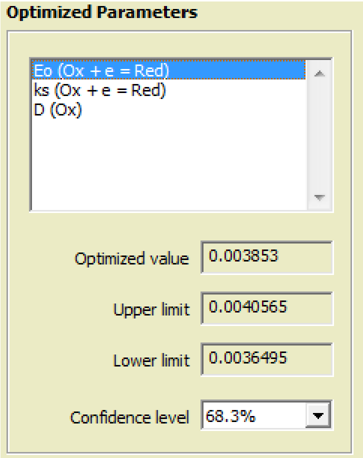


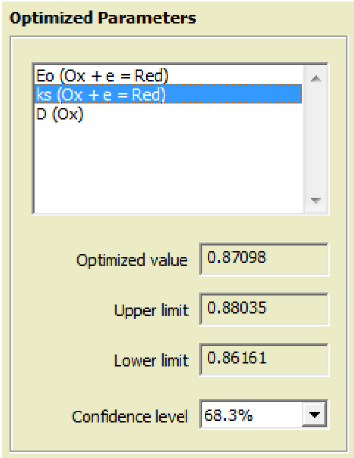
6. Click on Data Fitting->Select Data Target Curves form RAM-Disk () and remove the original target curves from **List of selected files**. Then add the modified ones and close the dialog box with **OK**.

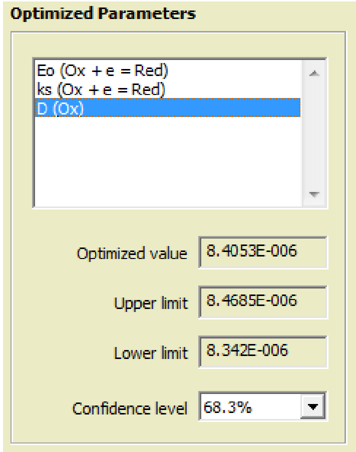




7. Click on Data Fitting->Run Fitting Procedure (). Obviously, the fitting procedure does not stay with the exact parameter values (used as starting values). After a few iterations the fitting procedure finds the minimum standard deviation with the following parameter combination:



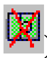
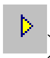
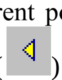
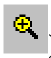


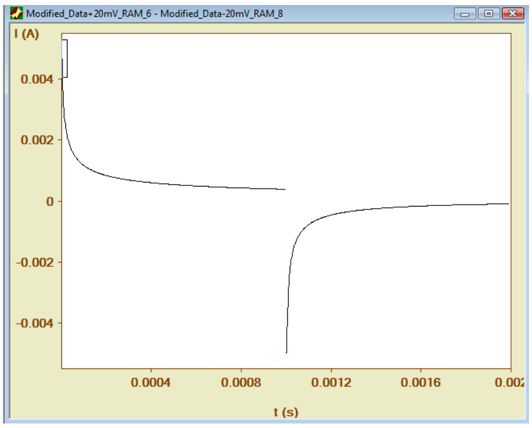


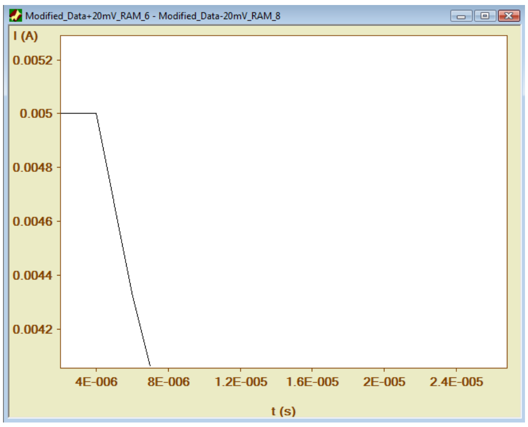
On the first glance, the agreement between target curves and simulated ones seems to be pretty good but looking at the optimized parameter values reveals that the error in the heterogeneous rate constant and in the diffusion coefficient amounts to about 15% and the standard potential has been shifted away from the correct value by about *4 mV*. Note that 5000 current points are included in the five target curves and only 8 individual current points have been modified in three files! The example demonstrates the big effect that must be expected for the chrono-amperometric determination of (fast) heterogeneous rate constants if only a few current points in the short time current following immediately after a potential jump are affected by instrumental artefacts.

IV. Running a fitting project where individual current points in the target curves are excluded from being fitted

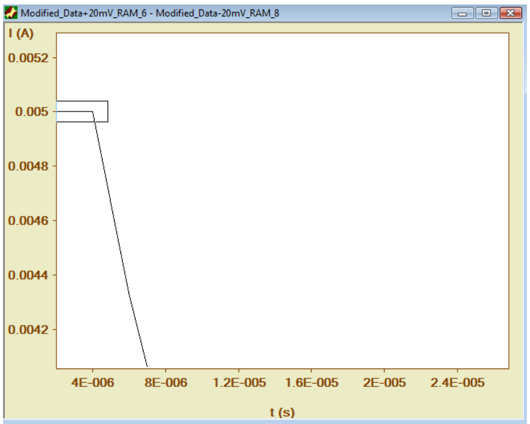
It will be demonstrated now how "wrong" current points can be excluded from the fitting project. This is easily done in the present example because we do exactly know that any current point representing the limiting current (with an absolute value of *5mA*) is likely to be artificially truncated to this value. For this reason we are going now to mark all current points amounting to ±*5mA* such that they will be excluded from data fitting. This is done as follows:

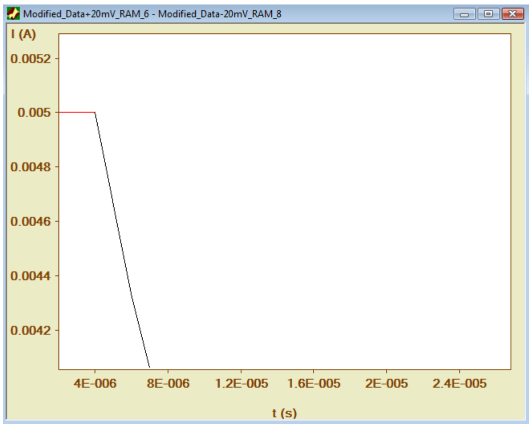
1. Click on Data Fitting -> Exclude Current Points from Fitting () to enter the Exclude Menu. The window associated with menu shows the target curve which was the active one displayed when leaving the Fitting Menu. The target curves "***Data+10mV***" and "***Data+20mV***" do not contain "wrong" current points. Thus click on View -> Activate -> Next Curve () or View -> Activate -> Previous Curve () to activate one of the remaining curves. The use the View -> Zoom () command for a better inspection of the current points by drawing a rectangle around the region containing the current points which are to be excluded from the fitting project as shown in the left picture for the target curve "***Data-20mV***". After releasing the mouse button, the zoomed display shown in the right picture is obtained





2. Then click on Exclude Data -> Define Region ( ), press down the left mouse button and (similarly as with the zoom command) draw a rectangle around the current points which are to be excluded from the fitting project as shown below in the picture on the left hand side. After releasing the left mouse button, the current points marked to be excluded from the fitting project will be drawn in red (unless the excluded region contains less than two current points) as shown in the picture on the right-hand side:



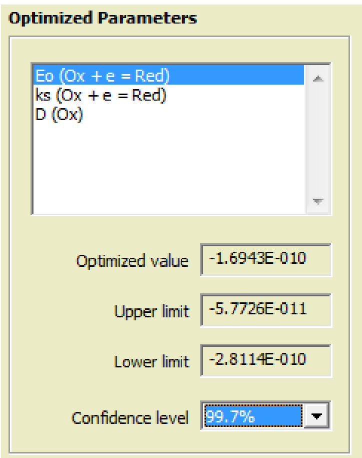


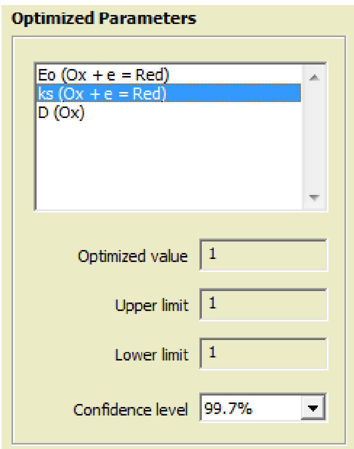
3. Click View -> Unzoom ( ) to return to the original screen display. Then proceed analogously to exclude the "wrong" current points following immediately after the potential jump at *0.001 s*.

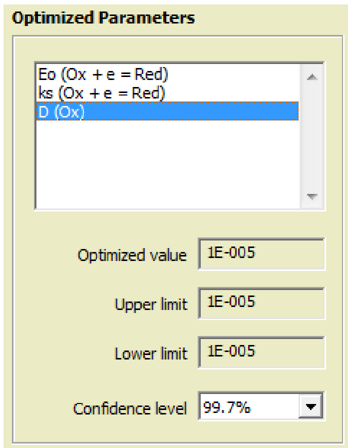
4. After having completed the target file "***Data-20mV***" use the View -> Activate -> Next Curve ( ) -command to activate the next target curve containing "wrong" current points which need to be excluded.

5. Click on Exclude Data -> Close ( ) to return to the Fitting Menu if all target curves have been completed.

6. Redo data fitting. Click on Data Fitting->Run Fitting Procedure ( ). The following parameters will be regained after a few iterations:



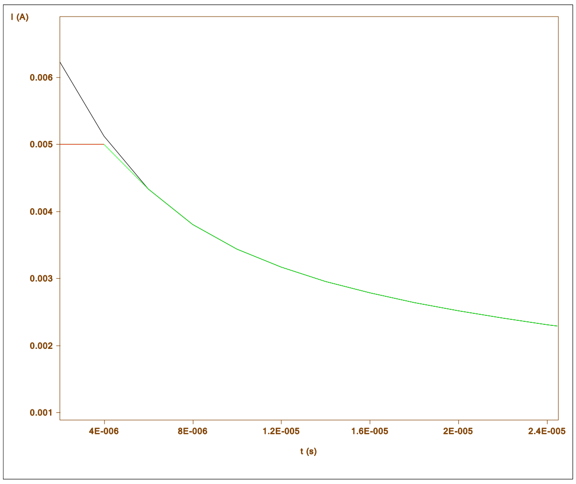


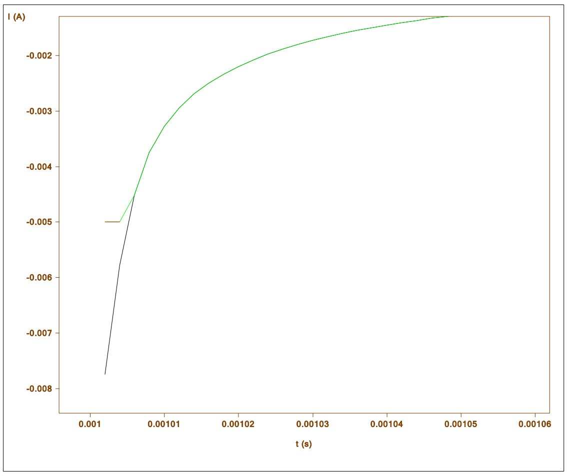


They are virtually identical with those regained using the original (unmodified simulated) target curves. Only the error level (visible only for the retrieved standard potential) seems to be insignificantly larger.

Note that the (correct) parameter values shown above will be retrieved by the fitting procedure only if really all "wrong" current points have been excluded from the fitting project. If you retrieved distinctly different parameter values, please, inspect the target curves contained in the "ModifiedData.rmd"-file of the Lesson4.zip archive. For this purpose, clear the actual content of the RAM-Disk (Document -> Clear RAM-Disk ( )) and load "ModifiedData.rmd" by means of the Document -> Load RAM-Disk command. Then select the target curves as described in step III.6. and inspect the excluded current points after activating the Exclude Menu by clicking on Data Fitting -> Exclude Current Points from Fitting ( ). After returning to the Fitting Menu and redoing the data fitting with these target curves you should yield similar results as reported above.

7. The effect of the operations described above becomes visible by comparing the simulated current curves with the “experimental” ones as shown below for the (zoomed) display of the current points following immediately to both potential jumps





The green curves represent the “***Data-20mV***”- target curve including the falsified current points plotted in red while the black lines are the simulated current curves. Obviously, there is a perfect agreement between target curves and simulated ones except for the ±*5mA*-current points mimicking the limiting current of the instrument. The latter are marked to be excluded from data fitting and their effect on the standard deviation between simulated and target curves is therefore ignored.