1 – Chrono methods high speed (ADC750 / ADC10M module)

The term *Chrono methods high speed* includes all the measurements of electrochemical signals during a well-defined sequence of steps, using the smallest possible interval time.

In NOVA, time resolved measurements are possible using three different measurement strategies:

- **Using the *Record signals (> 1 ms)* command:** this command can be used at any point in a procedure to record the signals defined in the signal sampler for a specified amount of time and using a well-defined interval time. The smallest possible value of the interval time is 1.3 ms. The *Record signals (> 1 ms)* command does not apply a potential or current value. It simply samples the signals defined in the sampler using the specified parameters. More information is provided in the C*hrono methods* tutorial (available in the Help menu).
- **Using the *Chrono methods* command:** this command can be used to perform time resolved measurements with interval times smaller than 1.3 ms. The lowest interval time is roughly 80 µs or 20 µs, depending on the type of instrument, and it depends on the type of signals to measure and the number of signals to sample. The measured signals are defined in the signal sampler. More information is provided in the C*hrono methods* tutorial (available in the Help menu).
- **Using the *Chrono methods high speed* command:** this command can be used to perform time resolved measurements at the smallest possible interval time. A dedicated fast sampling ADC module is required for these measurements (ADC750 or ADC10M This tutorial provides more information on the use of the *Chrono methods high speed* command. The maximum number of signals that can be measured with this methods is two (choice from: WE(1).Potential, WE(1).Current, or External).

Note

In order to use the *Chrono methods high speed* command, the optional ADC750 or ADC10M must be installed (In the rest of this document, the ADC750 or ADC10M module will be referred to as fast sampling ADC).

Table 1 provides an overview of some of the important features related to the use of the three different commands for time resolved measurements.

Command	Record signals (> 1 ms)	Chrono methods	Chrono methods high speed
Smallest interval time	1.3 ms	~ 80 µs/20 µs[1]	1.33 µs (ADC750) 0.1 µs (ADC10M)
Setpoint included	No	Yes	Yes
Real time display	Yes	No	No
Signals selection	Sampler	Sampler	Hardware defined (2)
Options support	Yes	No	No
Pause/Stop support	Yes	No	No
Fast options support	Yes	No	No
Time derivative sampling	Yes	No	No

Table 1 – Comparison of the commands for time resolved commands

2 – Using the fast sampling ADC module

The fast sampling ADC module (either ADC750 or ADC10M) is a dual channel synchronous Analog-to-Digital converter with a very high sampling rate. This optional module allows recording the electrochemical signals during high speed chrono experiments, with a very small interval time.

Note

The main difference between the ADC750 and the ADC10M module is the sampling rate. For the first module, the maximum sampling rate is 750 kSamples/s whereas it is 10 MSamples/s for the ADC10M. Both modules are dual channel ADCs. These modules are available for the PGSTAT12, 128N, 30, 302, 302N, 100 and 100N.

[1] The smallest possible interval time depends on the type of embedded controller used by the instruments. Instruments fitted with the IF030 have a smallest interval time of about 80 µs, while instruments fitted with the IF040 have a smallest interval time of about 20 µs.

2.1 – Hardware setup

In order to use the fast sampling ADC module, the hardware setup must be configured accordingly (see Figure 1).

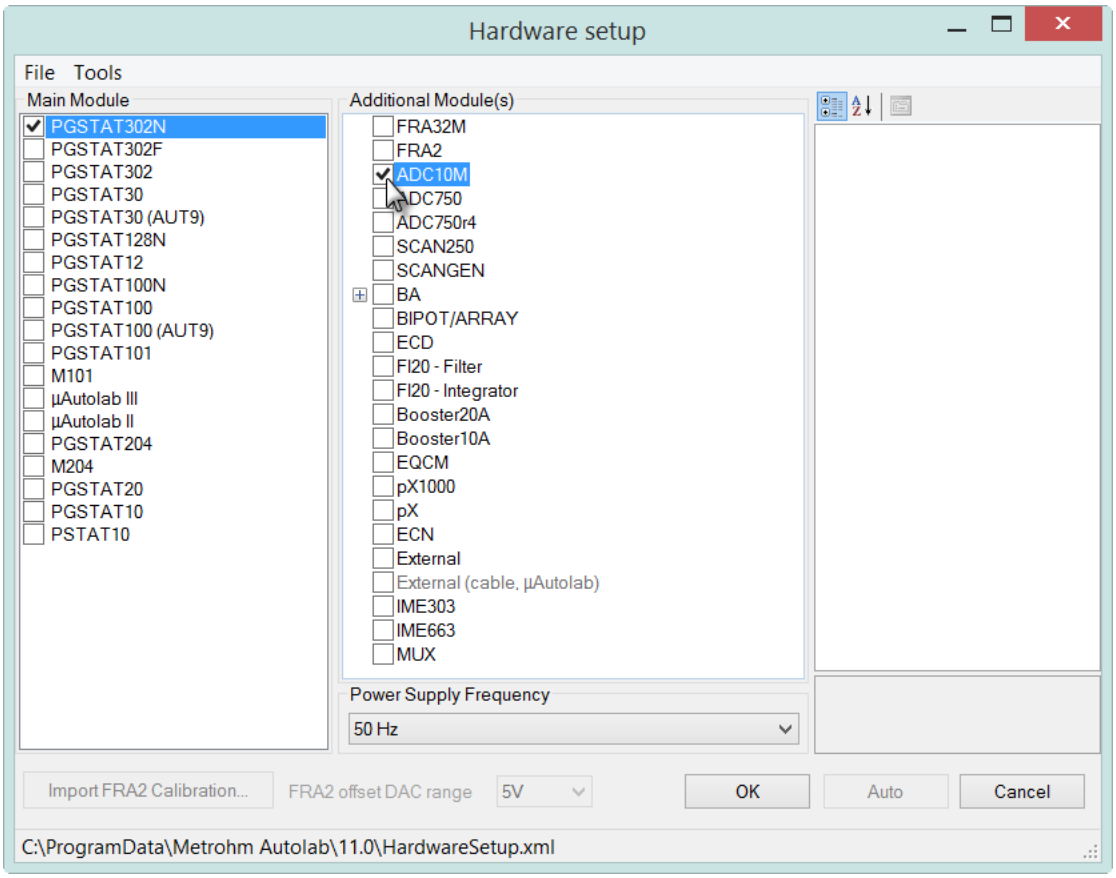

Figure 1 – Selecting the ADC10M module

Note

For ADC750 revision 4.0, please check the ADC750r4 checkbox in the hardware setup. Select the ADC750r4 checkbox if the *High speed adc module(1)* not detected message is shown in the User log after the initialization (see Figure 2). Both the ADC10M and the ADC750 have an onboard automatic recognition circuit. The revision 4.0 of the ADC750 is not fitted with this circuit and will therefore not be detectable.

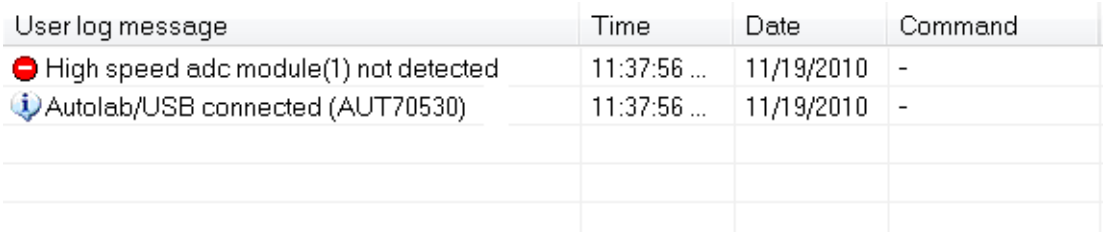

Figure 2 – Select the ADC750r4 checkbox when the *High speed adc module(1) not detected* message is shown in the User log after initialization

2.2 – The fast sampling ADC module

The fast sampling ADC modules are fitted with an on-board memory that can be used to store up to 1 million data points. When the fast sampling ADC module is used in an experiment, each new data point is stored in the on-board memory of the module until the experiment is finished. At the end of the measurement, all the stored data points are transferred to the computer for data analysis.

3 – The chrono methods high speed command

High speed chrono measurements can be performed using the *Chrono methods high speed* command.

The *Chrono methods high speed* command is similar to the *Chrono methods* command. The *Chrono methods high speed* command is designed to apply a user-defined sequence of steps on the electrochemical cell and record the response of the cell, using a high sampling rate. The sequence itself or elements of the sequence can be repeated a number of times without any interruption. When the whole sequence is finished, the data points stored in the high speed ADC module are transferred to the computer.

Note

Because the time required to transfer the measured data points from the Autolab to the computer can be a few seconds, it is not possible to display the measured data points in real time in the measurement view. However, the measured data points are displayed at the end of the experiment.

Note

The main difference between a chrono measurement using the ADC164 and using a fast sampling ADC is that in the former case, the sampling rate can be changed during the measurement and the sampling can be switched off (please refer to the Chrono methods tutorial for more information). These options are not available with a high speed ADC module, which samples the electrochemical signals at a fixed sampling rate.

The *Chrono methods* command is a timed command. This means that the timing of the measurements will be defined by the internal clock of the Autolab interface. The command can be located anywhere in the procedure editor. The green timing line will be shown on the left of the command to indicate that this is a timed command (see Figure 3).

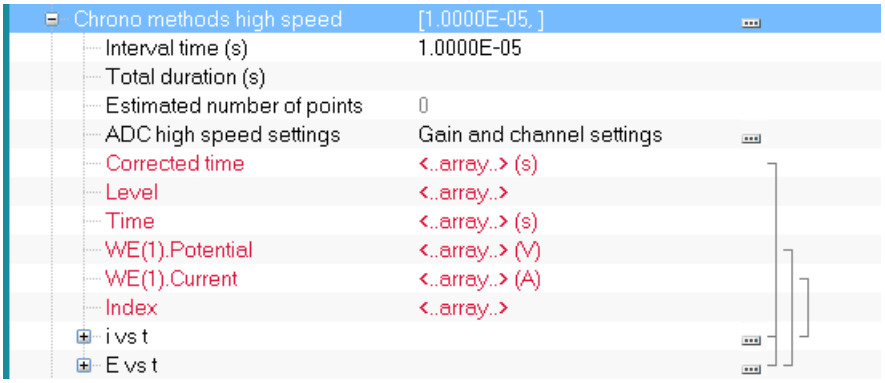

Figure 3 – The *Chrono methods high speed* command can be located anywhere in the procedure editor

The *Chrono methods high speed* command has the following parameters (see Figure 3):

- **Interval time (s):** defines the interval time, in seconds, for all the steps in the sequence. This interval time is the same for all the steps. The lowest value is defined by the high speed ADC.
- **ADC high speed settings:** defines the acquisition settings for the fast sampling ADC (gain values, signals to sample, etc…).

To use the *Chrono methods high speed* command, the sequence of steps must first be defined. To create or edit a sequence of steps, the ... button of the *Chrono methods high speed* command must be clicked (see Figure 4).

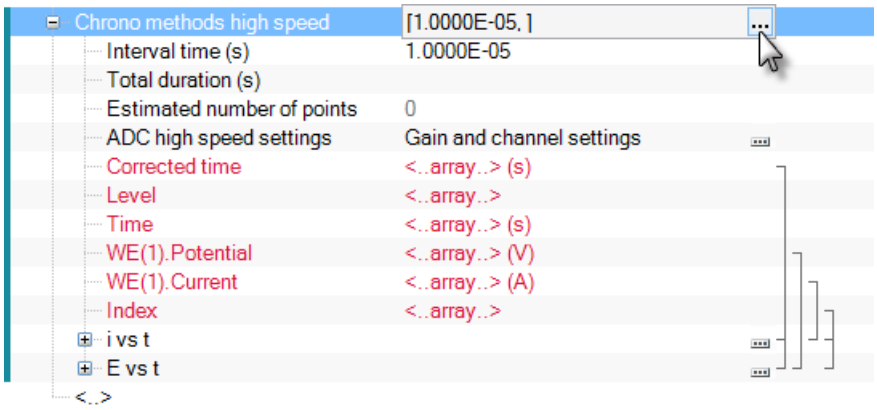

Figure 4 – Opening the *Chrono methods high speed* editor window

The *Chrono methods high speed* editor window displays three frames (see Figure 5). The frame on the top contains information on the interval time and the gain

settings. The frame on the left-hand side is used to display the sequence of steps. The frame on the right-hand side is used to specify the parameters for each step.

Warning

The interval time is defined for all the steps in the sequence. The smallest possible interval time depends on the high speed ADC module (1.33 µs for the ADC750 or 100 ns for the ADC10M).

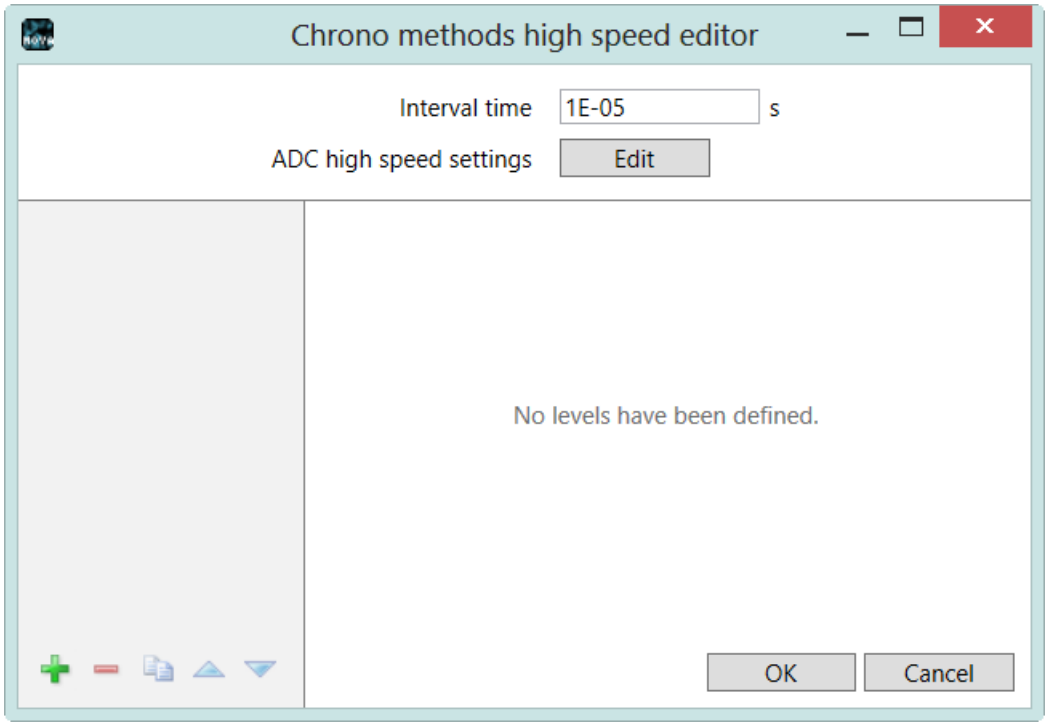

Figure 5 – The Chrono methods high speed editor window

3.1 – Creating a sequence of steps

The sequence of steps can be constructed by adding items to the sequence, using the five buttons located on the bottom end of the frame on the left-hand side of the window (see Figure 6).

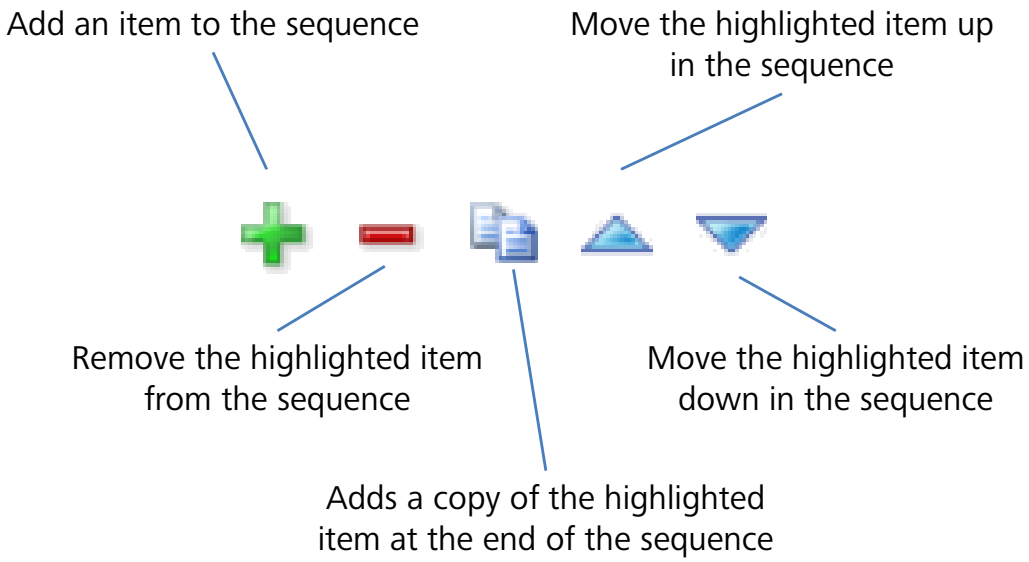

Figure 6 – The sequence can be edited using the four buttons located in the frame on the left-hand side

Five buttons are available in the frame on the left-hand side (see Figure 6):

- **Add ():** adds an item to the sequence.
- **Remove ():** removes the highlighted item from the sequence.
- **Copy ():** creates a copy of the highlighted item at the end of the sequence.
- **Move up ():** moves the highlighted item up in the sequence.
- **Move down ():** moves the highlighted item down in the sequence.

The sequence of steps can be constructed by dragging elements from the list in the left-hand side frame and adding them to the collection sequence.

The following items can be used to construct the required sequence.

- **Step**: this item creates a step in the sequence. A step is defined by three parameters – the potential (or current), the duration and the interval time. The default values for potential (or current), duration and interval time are 0, 0.001 s and 0.0001 s, respectively.
- **Repeat**: this item creates a new sub-sequence in the main sequence, in which new items can be added. This sub-sequence can be repeated any number of times and the electrochemical response of the cell is sampled during the whole sub-sequence.

To create the required sequence using the Chrono methods editor window, click the button in the frame on the left-hand side and select the required item from the popout menu (see Figure 7).

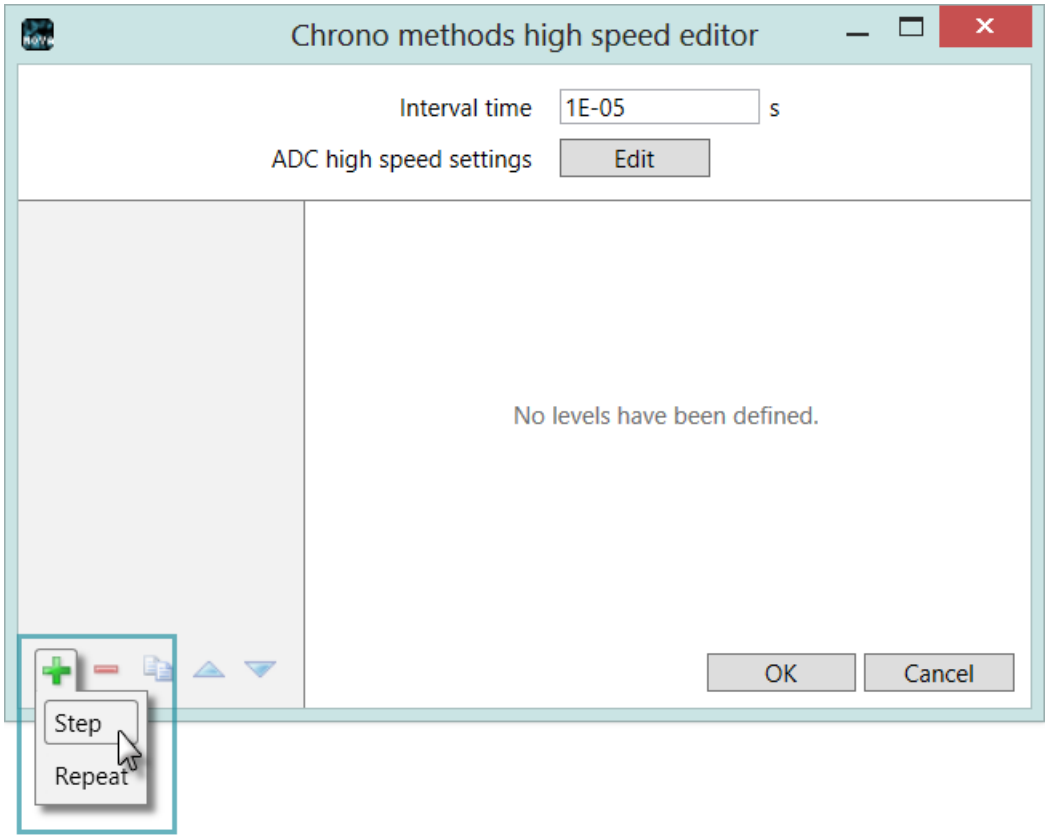

Figure 7 – Adding items to the sequence

Click the step that was added to the sequence to display the parameter details in the frame on the right (see Figure 8).

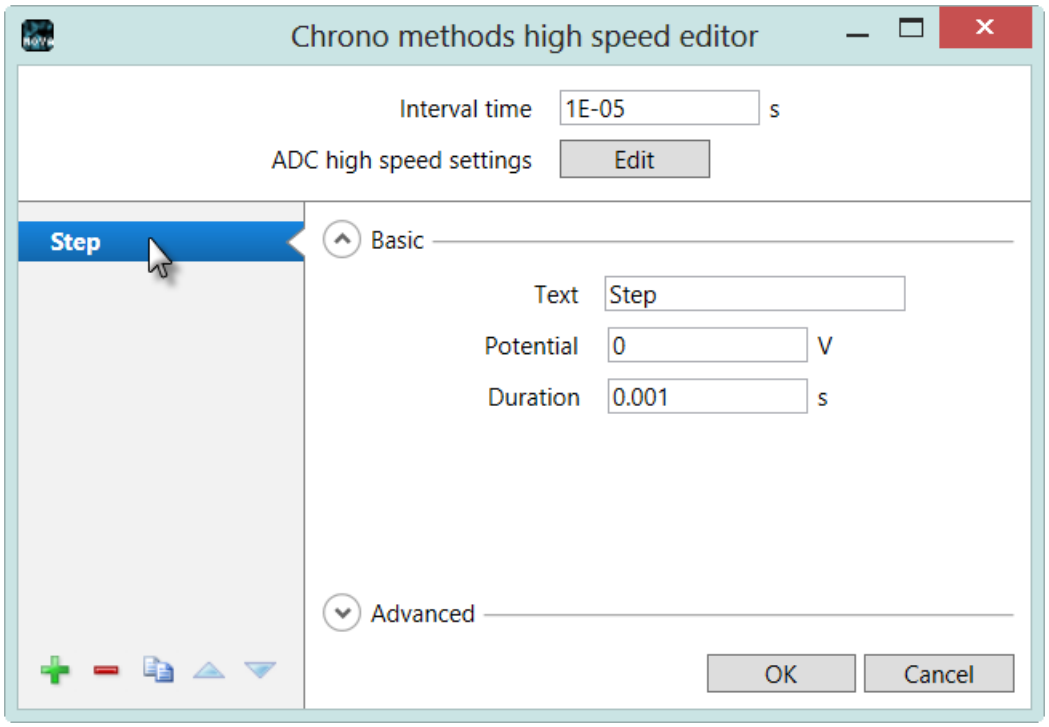

Figure 8 –The details of the step parameters are displayed in the frame on the right

The step has the following default basic parameters:

- **Text:** Step
- **Potential**[2]**:** 0 V
- **Duration (s):** 0.001

Warning

The maximum duration for a single step is 4294 seconds.

The two additional parameters, *Pre Autolab control* and *Post Autolab control*, are advanced settings that can be used to change the Autolab settings during the sequence. These parameters are available in the advanced section and their use falls outside of the scope of this tutorial (see Figure 9).

[2] In Galvanostatic mode, the Current parameter is displayed instead of the Potential parameter.

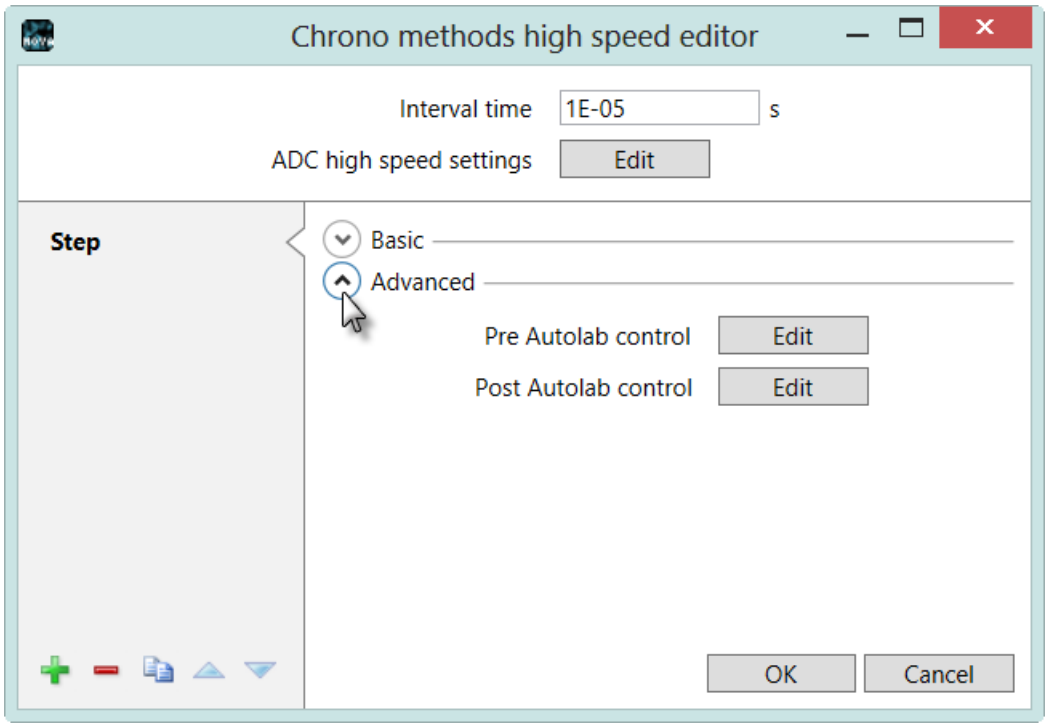

Figure 9 – Advanced parameters are available in the advanced section

It is possible to change any of the three parameters of the step. Change the duration of the step to 0.005 seconds (see Figure 10).

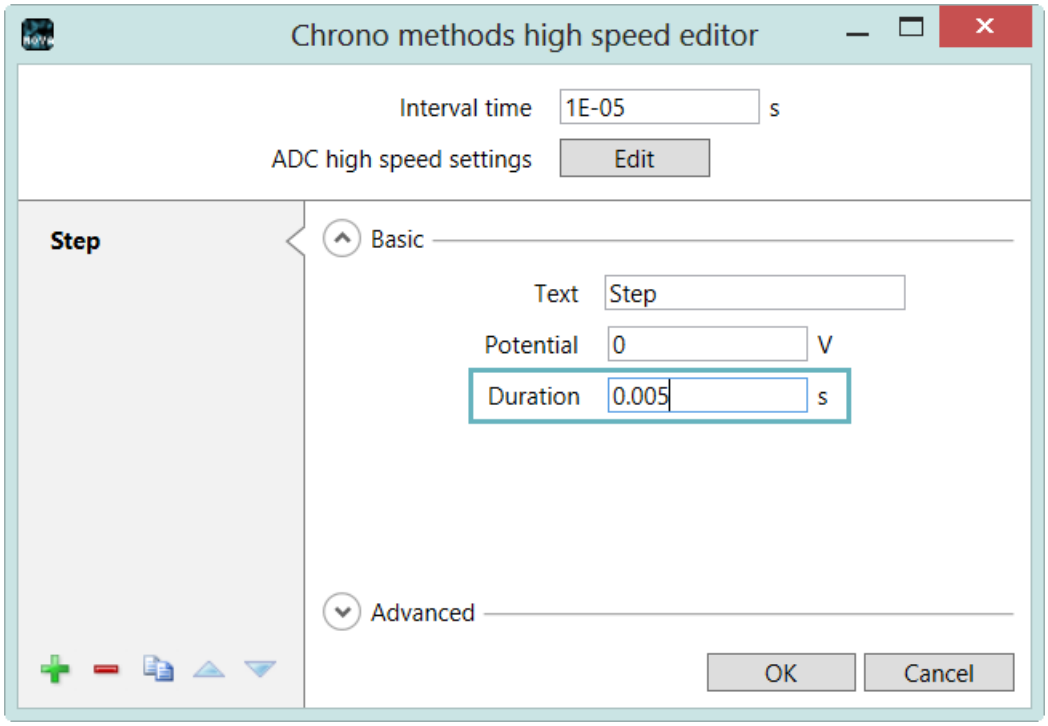

Figure 10 – Changing the duration

Using the same approach, it is possible to add additional steps to the sequence (see Figure 11).

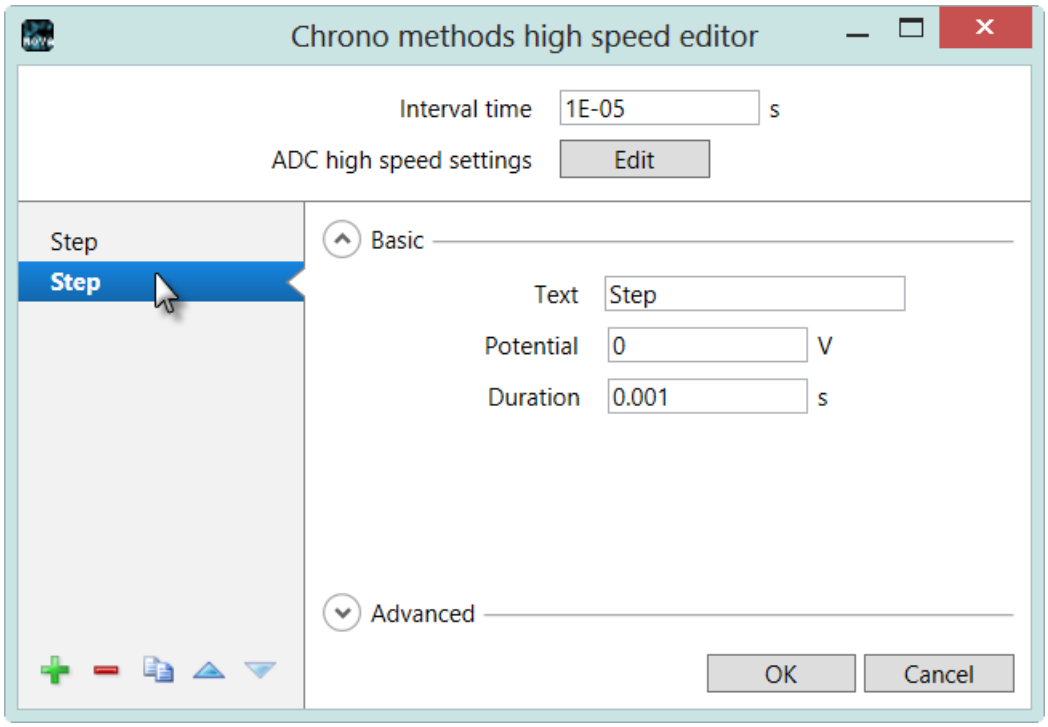

Figure 11 – Adding more steps to the sequence

It is also possible to select any item in the sequence and create a copy of it at the end of the sequence by clicking the button in the toolbar (see Figure 12).

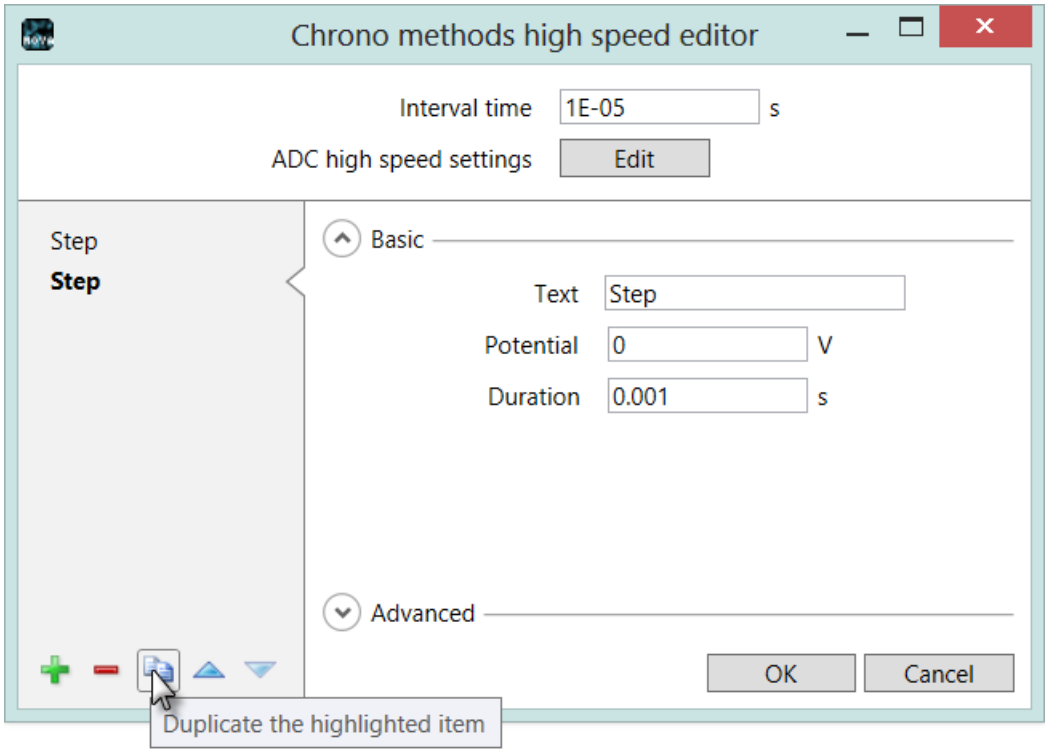

Figure 12 – Using the button to copy the highlighted item

The copied item is always added at the end of the sequence (see Figure 13).

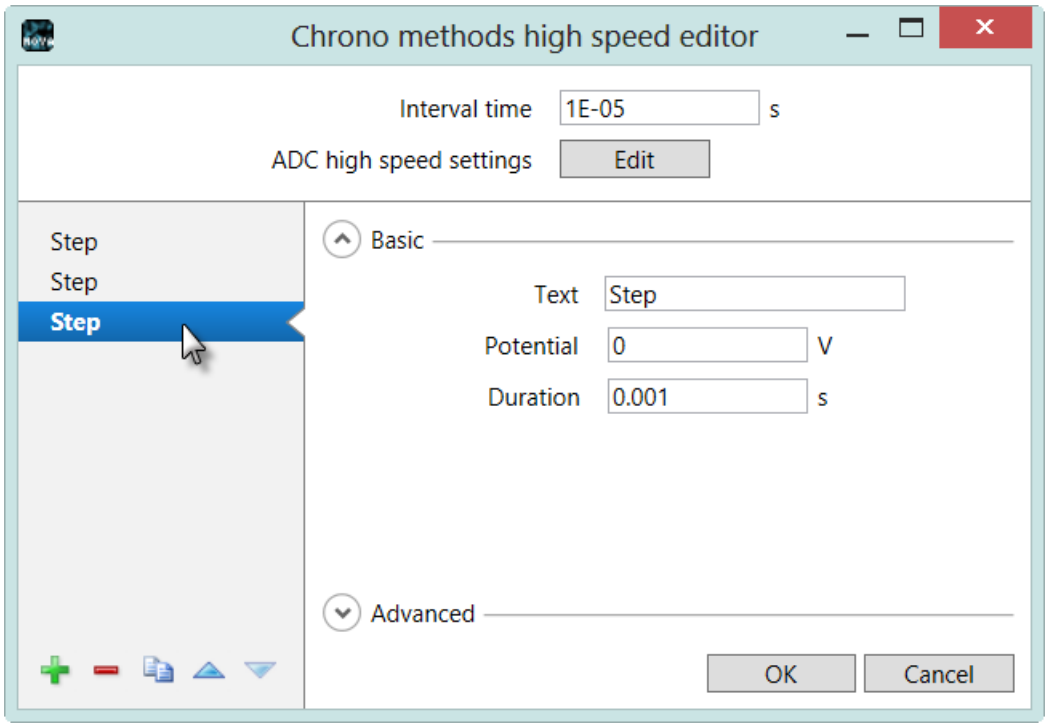

Figure 13 – The copied item is always added at the end of the sequence

The parameters for each step can be edited independently by clicking each individual item in the sequence on the left-hand side. The highlighted item in the sequence is shown in bold lettering (see Figure 14).

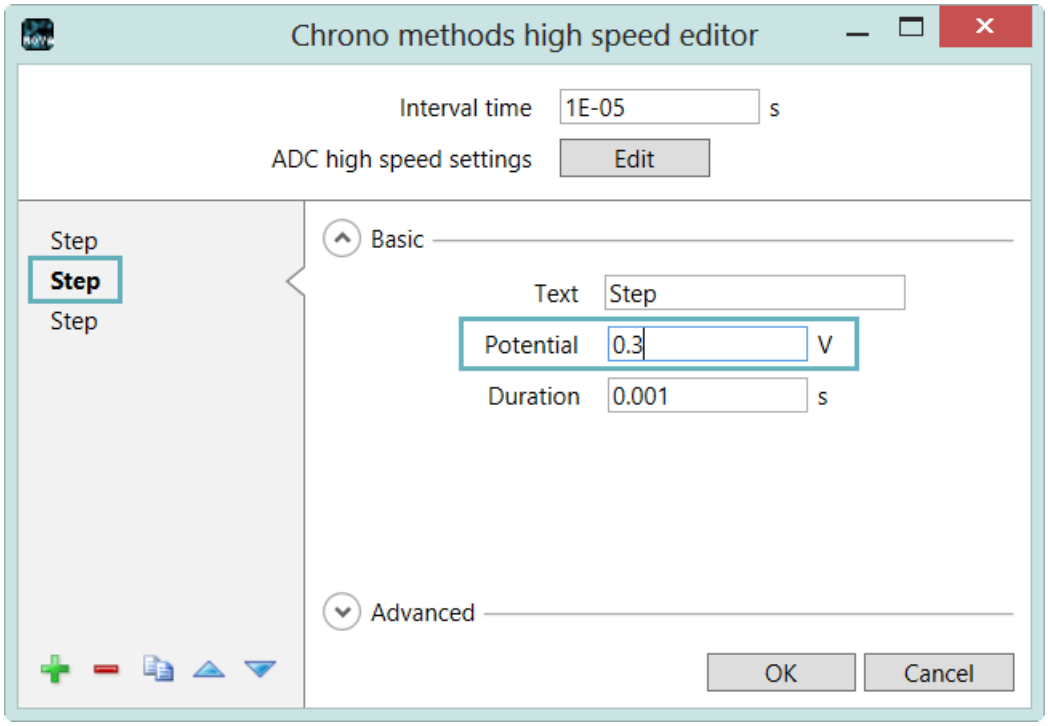

Figure 14 – Changing the potential for the steps in the sequence

Set the duration of each step to 0.005 seconds and click the OK button to close the editor and validate the defined sequence. This will update the parameters of the *Chrono methods* command in the procedure editor view (see Figure 15).

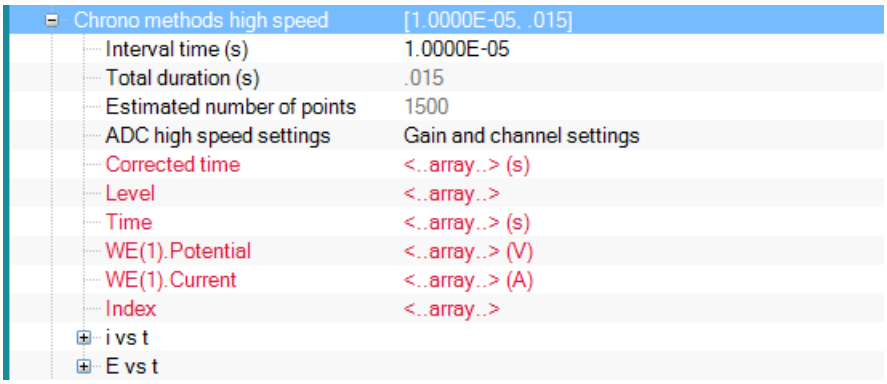

Figure 15 – The updated Chrono methods high speed command

The parameters and properties of the *Chrono methods high speed* command are the following:

- **Interval time (s):** 1.0000E-5
- **Total duration (s):** 0.015 – each step has a duration of 0.005 seconds
- **Estimated number of points:** 1500 – 500 data points are recorded for each step
- **ADC high speed settings:** defines the acquisition settings for the *Chrono method high speed* command

3.2 – Specifying the interval time

The interval time used in the *Chrono methods high speed* command must be the same for all the steps specified in the sequence. The interval time can be defined in the procedure editor directly, as shown in Figure 16.

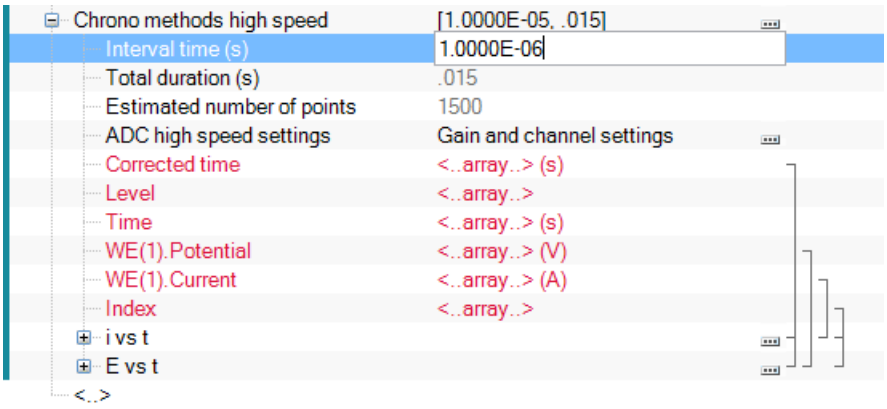

Figure 16 – Specifying the interval time in the procedure editor

The interval time can also be defined in the *Chrono methods high speed* editor, as shown in Figure 17.

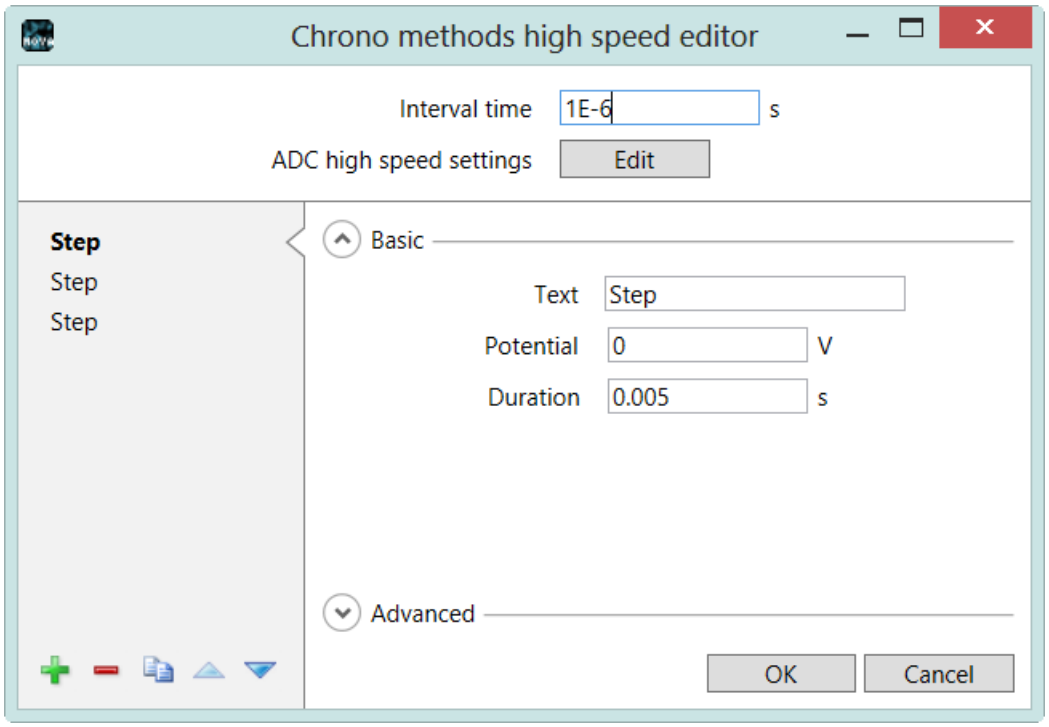

Figure 17 – Specifying the interval time in the *Chrono methods high speed* editor

4 – A measurement using the *Chrono methods high* speed command

A Chrono methods high speed tutorial folder is located in the **Program Files\Metrohm Autolab\Nova 1.11\Shared Databases\Tutorials** folder (see Figure 18). Using the database manager, set this folder as the Standard database.

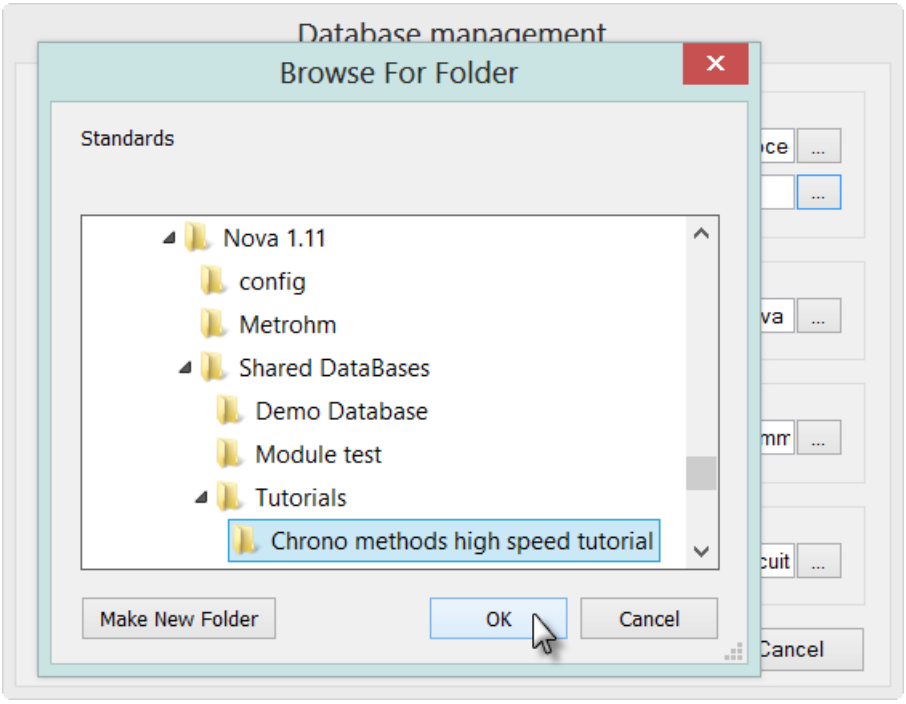

Figure 18 – Loading the Chrono methods high speed tutorial database

Three procedures are included in this tutorial procedure. All the procedures are intended to be used with the standard Autolab dummy cell (see Figure 19).

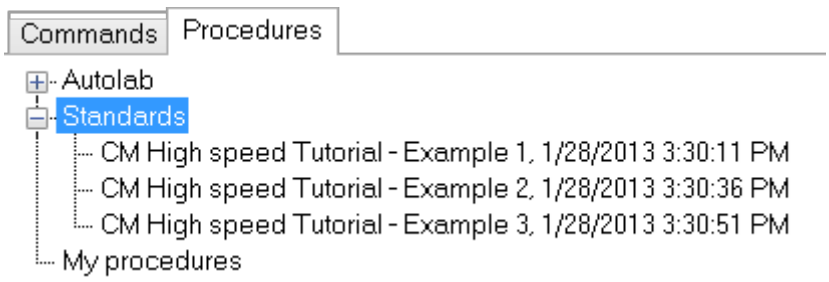

Figure 19 – The three Chrono methods high speed tutorial procedures

4.1 – Chrono methods Tutorial – Example 1

Select the *CM High speed Tutorial – Example 1* procedure from the Standard group. Connect the dummy cell (c) to the instrument and start the measurement.

The procedure will perform a measurement on the dummy cell using the following sequence, using an interval time of 10 µs:

- **Step 1** – Potential 0 V, duration 0.005 s
- **Step 2** – Potential 0.3 V, duration 0.005 s
- **Step 3** – Potential -0.3 V, duration 0.005 s
- **Step 4** – Potential 0 V, duration 0.005 s

Press the Start button to run the measurement. A message box will be displayed before the measurement starts (see Figure 20).

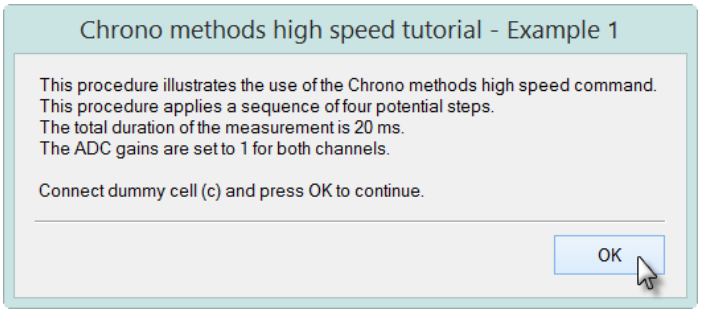

Figure 20 – The message box shown during the example 1 tutorial procedure

When the measurement is finished, the measured data points are displayed in the measurement view (see Figure 21).

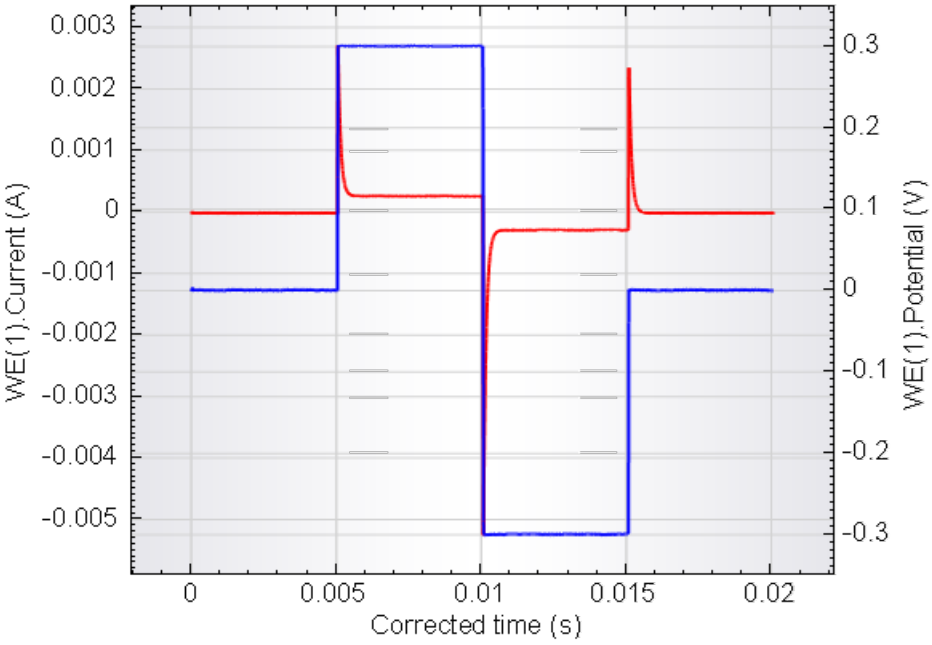

Figure 21 – The potential (blue combi plot) and current (red combi plot) profiles plotted vs Corrected time measured during the tutorial 1 procedure (the data is displayed at the end of the measurement)

As expected, the current of the working electrode, WE(1).Current, goes through three spikes, after each of the potential steps. The data points are measured with an interval time of 10 µs. With the ADC750 module, the interval time can be further decreased to 1.33 µs while with the ADC10M, the smallest possible interval time is 100 ns.

5 – ADC high speed settings

The *Chrono methods high speed command* uses the optional high speed ADC modules to sample two electrochemical signals. Both modules (ADC750 or ADC10M) have specific data acquisition settings that can be edited for the experimental conditions. These settings can be edited by clicking the Edit button in the Chrono methods high speed editor (see Figure 22).

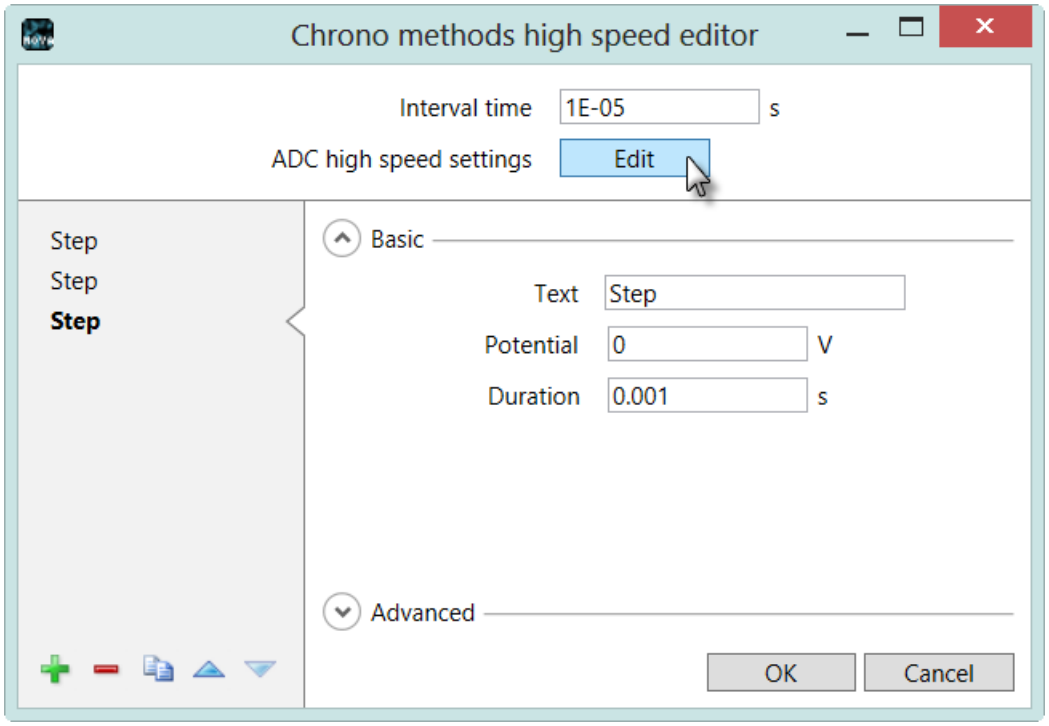

Figure 22 – Editing the ADC high speed module settings

The settings can also be edited by clicking on the ... button located next the ADC high speed settings in the procedure setup (see Figure 23).

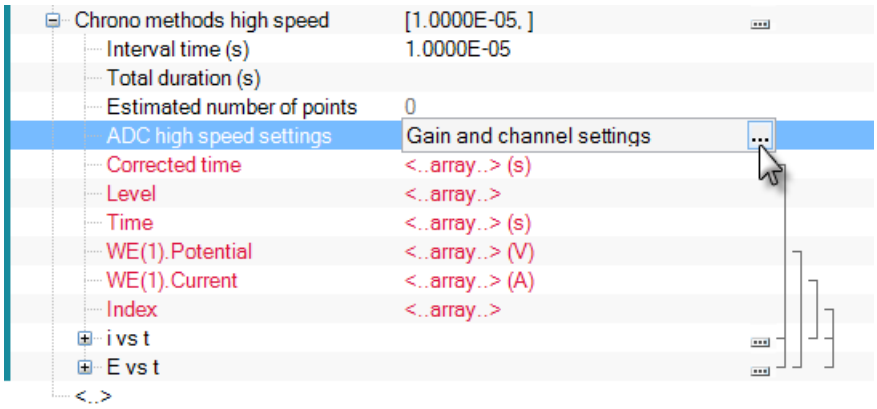

Figure 23 – Click the ... button to open the ADC high speed settings

This will open the ADC settings window (see Figure 24).

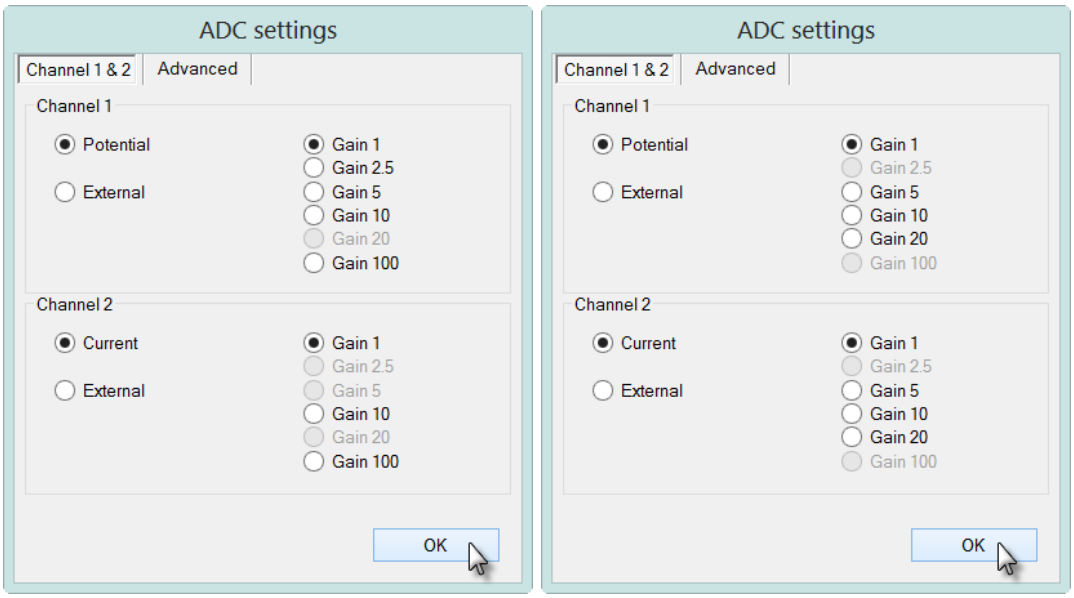

Figure 24 – The high speed ADC module acquisition settings (right – ADC750, left – ADC10M)

Both modules have two ADC channels and each channel can be configured independently. Channel 1 can sample the potential or an external signal, while channel 2 can sample the current or an external signal. The gain settings for each channel can be set using the ADC settings window (see Figure 24).

Note

Using the high speed ADC, it is also possible to record external signals. This can be indicated in the ADC settings window (see Figure 24). The location of the external inputs is indicated by the front panel labels on the instrument (see Figure 25).

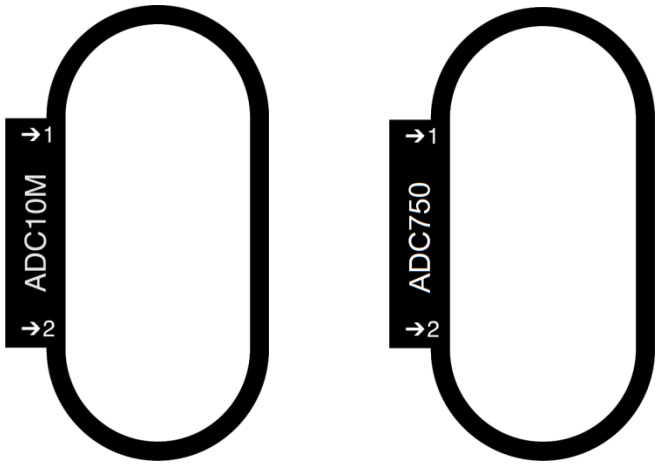

Figure 25 – Module labels for the ADC10M (left) and the ADC750 (right) indicating the locations of the external inputs of the fast sampling ADC module on the front panel of the instrument

5.1 – Chrono methods Tutorial – Example 2

Select the *CM High speed Tutorial – Example 2* procedure from the Standard group. This procedure will perform the same measurement as in Example 1, but using a higher gain setting for ADC channel 1, which is used to measure the WE(1).Potential.

Connect the dummy cell (c) to the instrument and start the measurement.

Press the start button to run the measurement. A message box will be displayed before the measurement starts (see Figure 26).

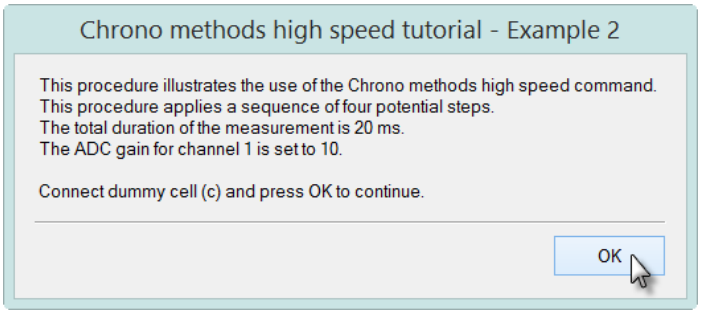

Figure 26 – The message box shown during the example 2 tutorial procedure

When the measurement is finished, the data will be displayed in the measurement view (see Figure 27).

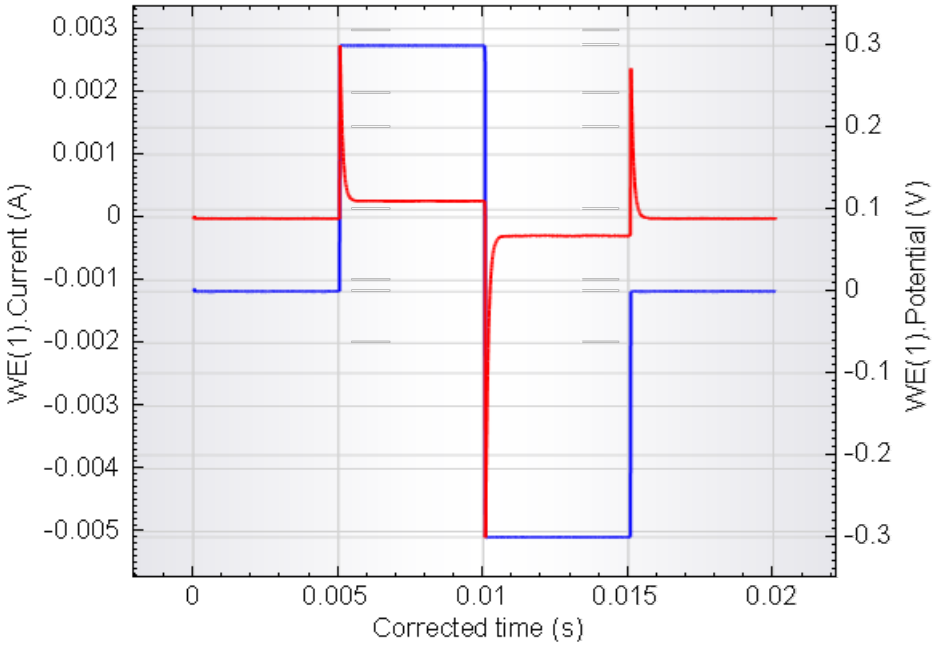

Figure 27 – The potential (blue) and current (red) profiles plotted vs Corrected time measured during the tutorial 2 procedure (the data is displayed at the end of the measurement)

Careful comparison of the WE(1).Potential values measured during the first two tutorial procedures shows how the ADC gain settings can help to improve the

signal-to-noise ratio[3]. In the first measurement, the gain setting for channel 1 was set to 1, whereas it was set to 10 for the second measurement. Since the input range of both ADC channels is 0-10 V, setting the gain value to 10 for the WE(1).Potential channel significantly increases the resolution of the signal (see Figure 28).

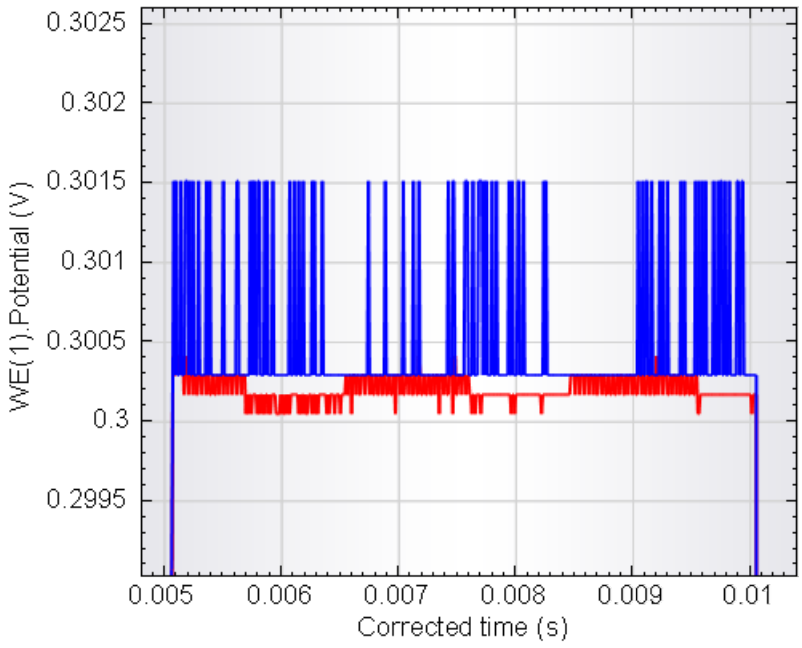

Figure 28 – Comparison of the measured WE(1).Potential signals during the second step of the sequence. Blue curve corresponds to tutorial 1 (gain 1) and red curve corresponds to tutorial 2 (gain 10)

6 – Using Repeats

The *Chrono methods high speed* command offers the possibility of using a Repeat in the sequence editor.

Inserting a Repeat in the Chrono methods high speed sequence, creates a sub sequence in which new steps can be added.

To add a Repeat item to the sequence, select the last item in the sequence and click the button. Select the Repeat item from the popout menu (see Figure 29).

[3] Switch to the analysis view to compare the measurements.

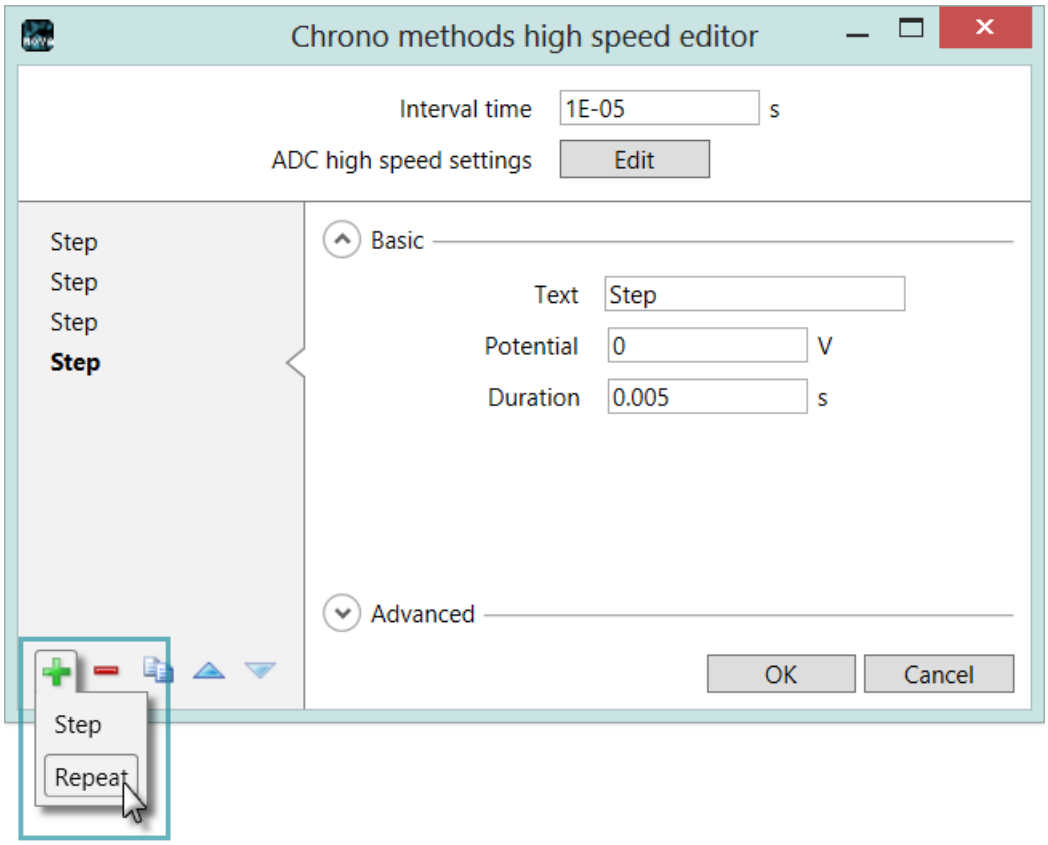

Figure 29 – Inserting a Repeat item creates a new sequence in the editor

A new item will be added to the sequence (see Figure 30).

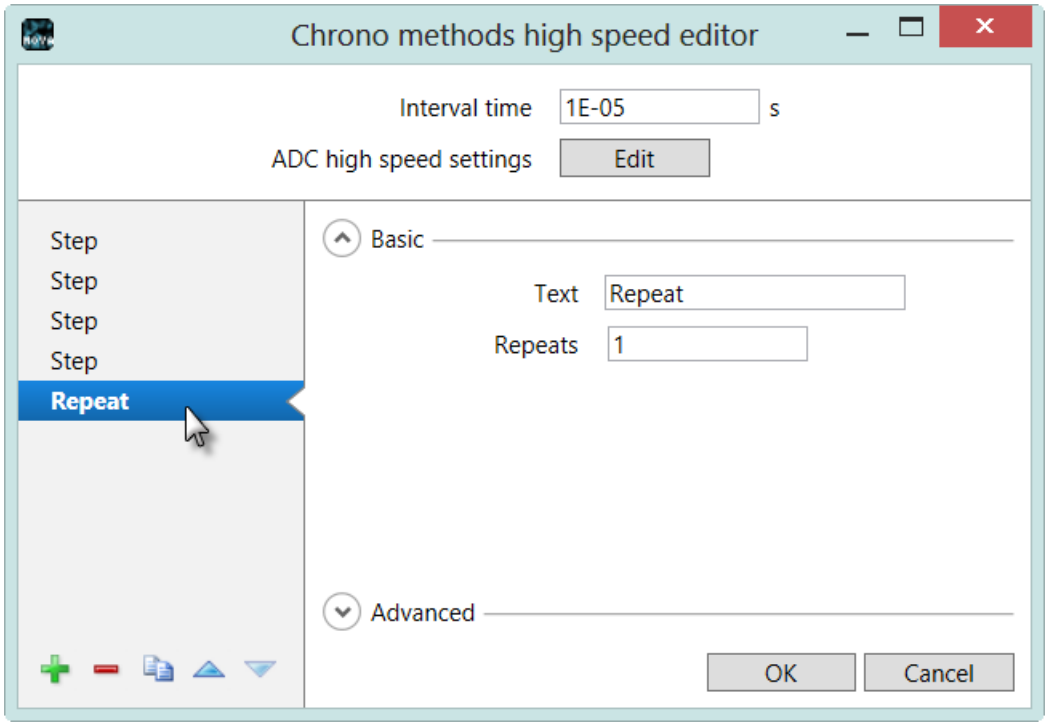

Figure 30 – The Repeat item creates a new sequence

Any steps added to the Repeat sequence will be repeated n times, where n is the number of repeats specified in the Chrono methods high speed editor.

Using the same approach as in the previous examples, select the Repeat item and add two steps using the button (see Figure 31).

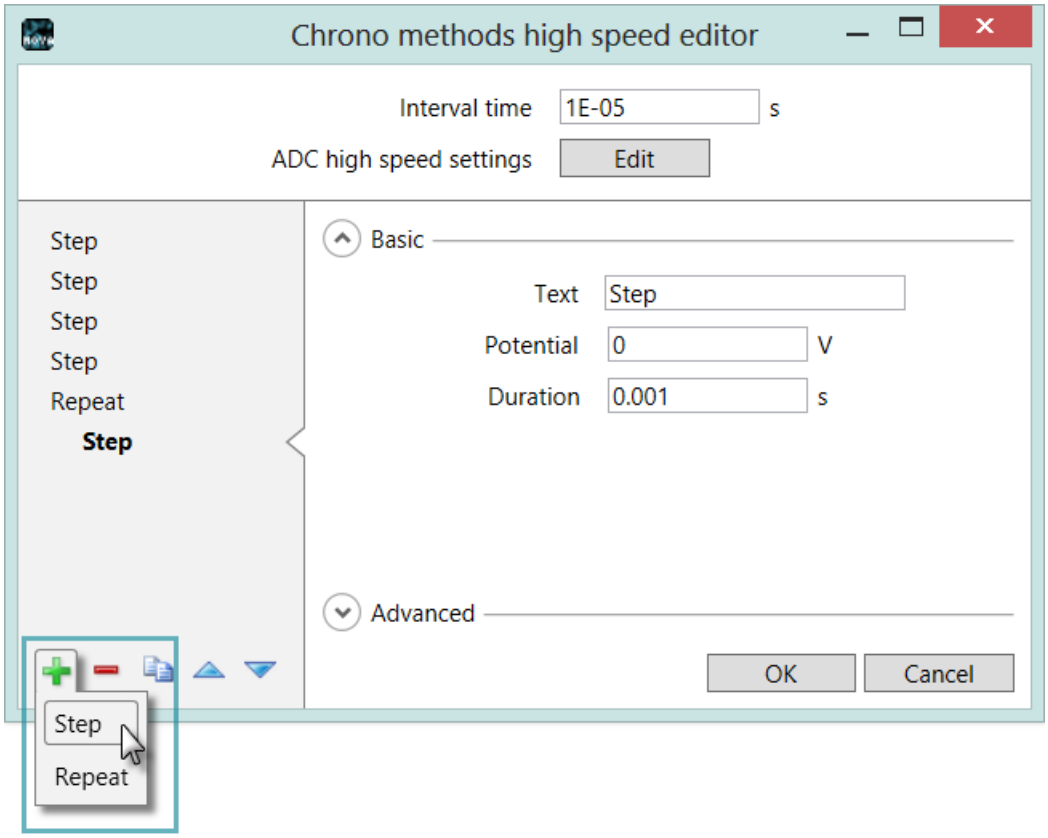

Figure 31 – Adding two steps to the Repeat

Change the potential of the first step of the recurrent steps to 0.5 and the potential of the second step to -0.5. Change the duration of both steps to 0.001 s (see Figure 32).

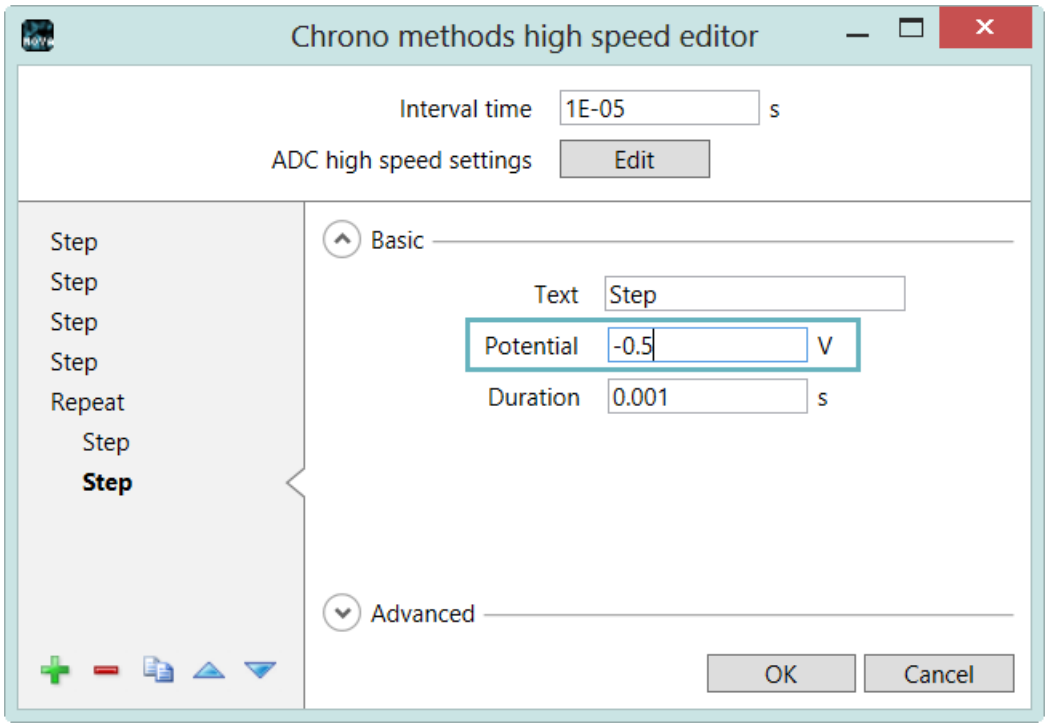

Figure 32 – Adjusting the parameters of the two steps

Select the Repeat item in the sequence to highlight the whole sub-sequence (see Figure 33).

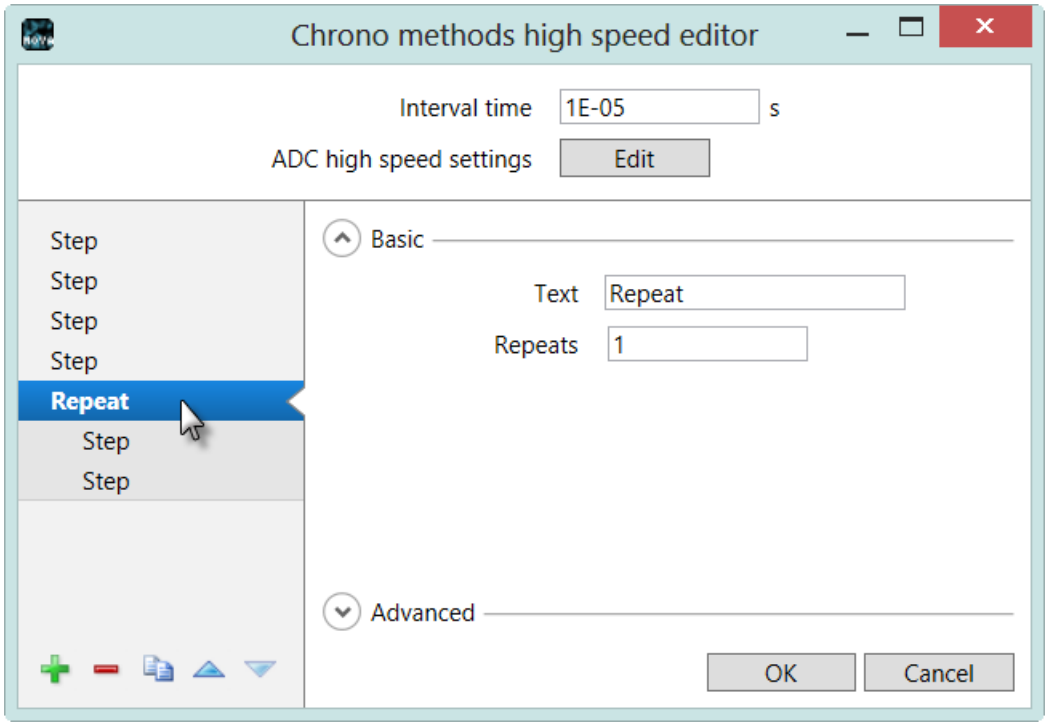

Figure 33 – Select the Repeat item in the sequence

Note

The two Steps located inside the Repeat are also highlighted in dark grey, indicating that these Steps belong to the selected Repeat item.

Change the number of repetitions to 10 (see Figure 34).

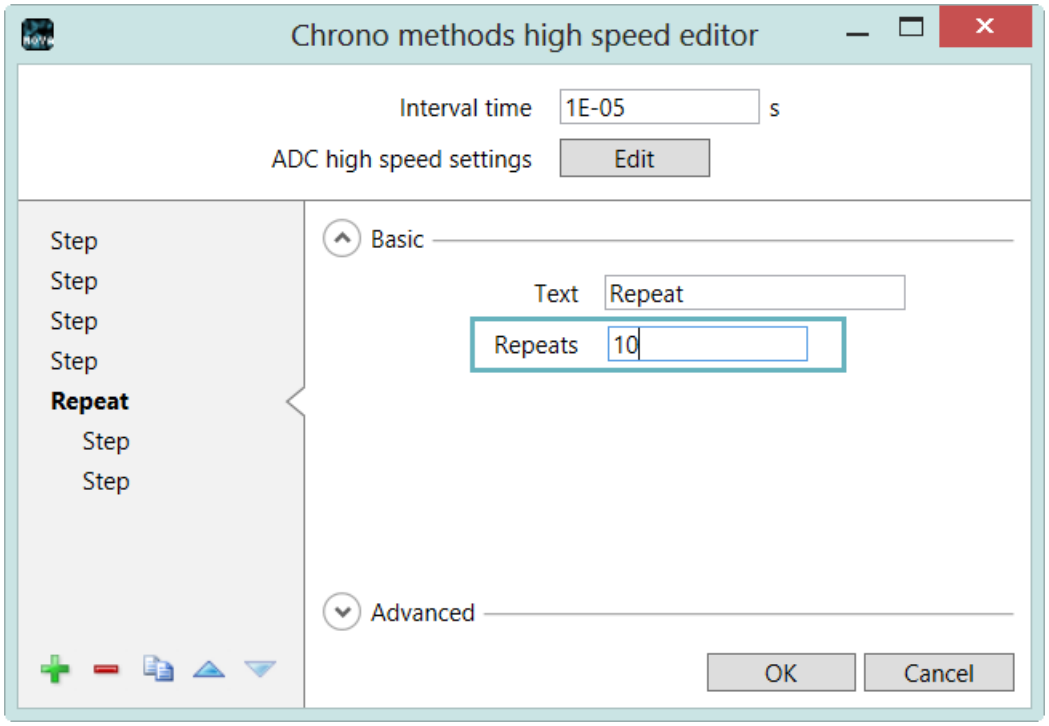

Figure 34 – Setting the number of repetitions to 10 for the whole Repeat (unsampled) sequence

Click the OK button to close the sequence editor window. The procedure editor will be updated with the new values (see Figure 35).

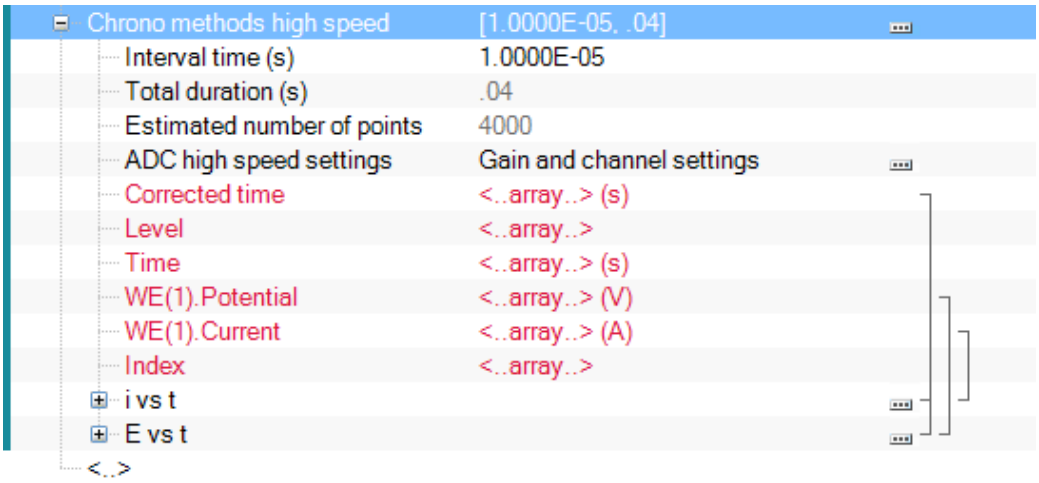

Figure 35 – The updated procedure editor

6.1 – Chrono methods Tutorial – Example 3

Select the *CM High speed Tutorial – Example 3* procedure from the Standard group. This procedure will perform the same measurement as in Example 1, followed by ten repetitions of two additional steps located in a recurrent steps sequence. Gain 10 is used for WE(1).Potential.

Connect the dummy cell (c) to the instrument and start the measurement.

Press the Start button to run the measurement. A message box will be displayed before the measurement starts (see Figure 36).

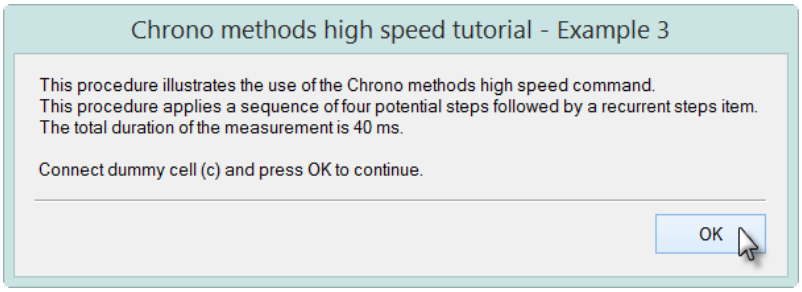

Figure 36 – The message box shown during the example 3 tutorial procedure

After the measurement, a message will be displayed indicating that it is finished. Click OK and switch to the analysis view. Load the data set into the data explorer to analyze the measured data points (see Figure 37).

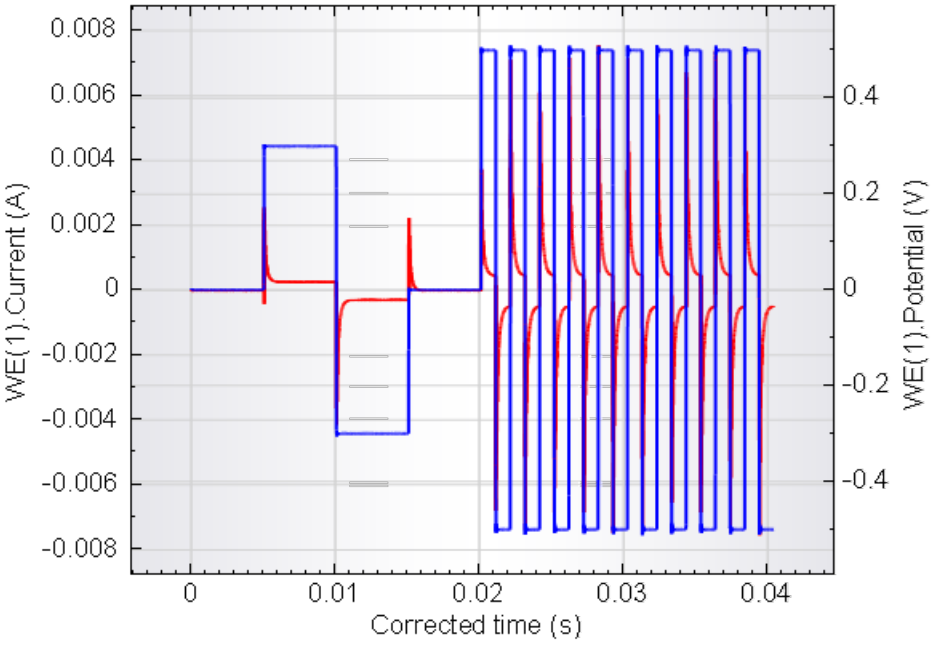

Figure 37 – The potential (blue) and current (red) profiles plotted vs Corrected time measured during the tutorial 3 procedure (the data is displayed at the end of the measurement)

The sequence starts with the four same initial steps of the previous measurements, followed by ten repetitions of two steps, with a duration of 1 ms. The current is displayed as a sequence of spikes after each potential step in the sequence, followed by exponential decays. It is important to note that all the steps are applied without any interruption.

Hardware specifications

The ADC750 and ADC10M modules are dual channel, synchronous, fast sampling A/D converters. Both modules can be installed in all the supported Autolab PGSTAT instruments, except the PGSTAT101 or M101 and the μAutolabII/III.

The ADC750 and ADC10M module can be used for chrono measurements using the smallest possible interval time. These modules can also be used in combination with the linear scan generator modules (SCANGEN or SCAN250).

Table 2 provides an overview of the fast sampling ADC module specifications.

Module	ADC10M	ADC750
Number of channels	2	2
Max. sampling rate	10 MSamples/s	750 kSamples/s
Shortest interval time	100 ns	1.33 μs
ADC resolution	14 bit	12 bit
Max. resolution, E	100 μV (Gain 10)	500 μV (Gain 10)
Max. resolution, i	0.0006 % of C.R. (Gain 10)	0.0025 % of C.R. (Gain 10)
Max. # of points	1.024.000	512.000

Table 2 – Overview of the specifications of the fast sampling ADC modules