

1 – The open circuit potential (OCP)

Open circuit potential monitoring and measurements involving the open circuit potential as a reference potential are quite common in electrochemistry. This tutorial explains how to perform open circuit potential (OCP) measurements with NOVA and how to use the measured OCP as a reference potential for consequent measurements.

2 – The OCP determination command

NOVA provides a specific command, which can be used to monitor the OCP, called *OCP determination*. This command is available from the Measurement – general group in the commands browser.

Figure 1 shows an overview of the *OCP determination* command and its parameters.

[-] OCP determination	[0.000]
Maximum time (s)	120
dE/dt limit	1E-06
Use average OCP	Yes
OCP value	0.000
Time	<..array..> (s)
WE(1).Potential	<..array..> (V)

Figure 1 – Overview of the OCP determination command



Note

The *OCP determination* command can be located anywhere in the procedure editor. This command is timed by the host computer.

The OCP determination command has the following parameters

- **Maximum time:** defines the maximum time, in seconds, during which the OCP is measured.
- **dE/dt limit:** defines an optional limit for the derivative of the OCP in time. If the option is used, the OCP measurement will stop when the measured variation of the OCP becomes smaller than the dE/dt limit. If the dE/dt limit is not reached, the measurement will continue until the maximum time is reached or until the user manually accepts the measured OCP.
- **Use average OCP (Yes/No):** defines whether the moving averaged value of the OCP, over the last five seconds, should be kept in memory or if the last measured OCP value should be used instead.



Note

The *OCP determination* command switches the cell off before the measurement. This means that after the value of the OCP has been measured, the cell must be switched on. This has to be done by the user, by switching the cell on manually or by using the *Set cell* command after the OCP determination.

3 – Using the OCP determination command

When a procedure integrating an OCP determination is executed, an additional window will be displayed while the OCP value is being monitored (see Figure 2).

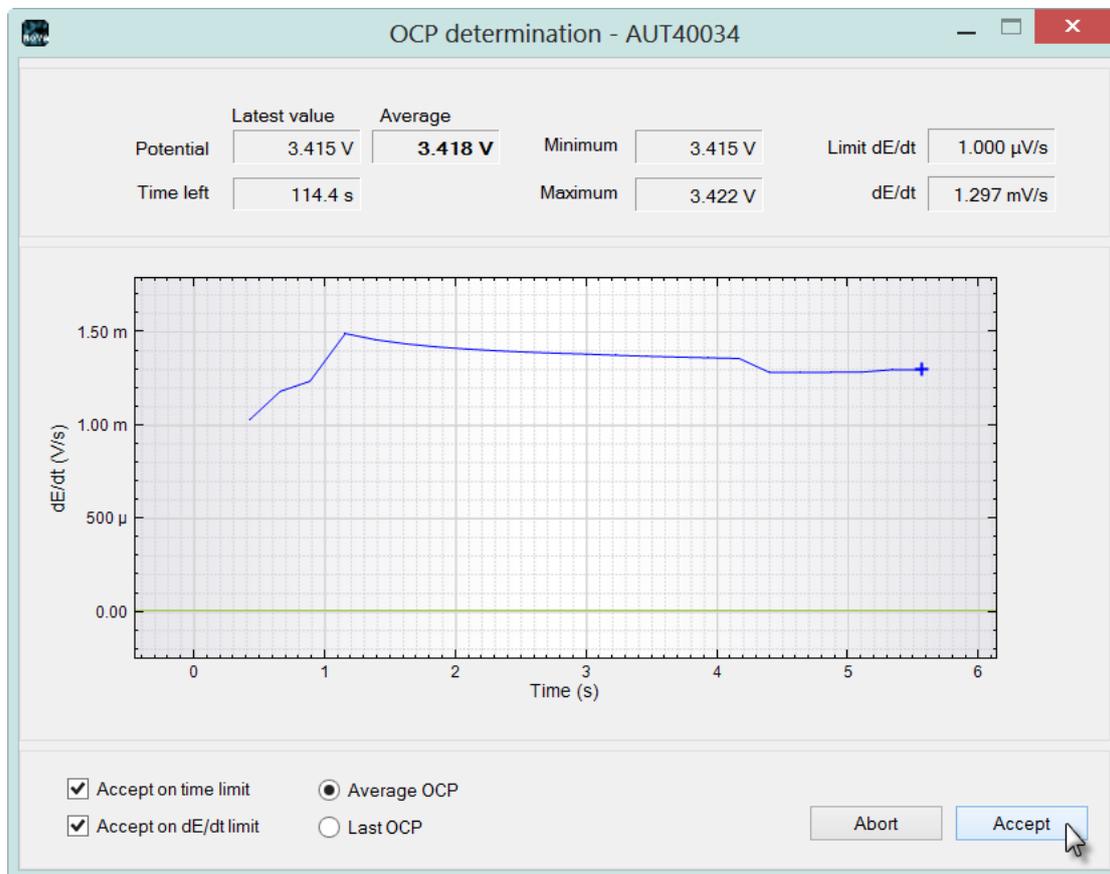


Figure 2 – The OCP determination window



Note

The serial number of the instrument is shown in the window header.

The OCP determination window is updated in real time and displays the dE/dt value, in V/s during time.

The OCP determination window has three sections. The top section displays the numerical values of the last measured value of the OCP, as well as the maximum and minimum value, the dE/dt value, the average OCP and the remaining time (see Figure 3).



Figure 3 – The values displayed in the top section of the OCP determination window



Note

The dE/dt value is calculated using the values over the last five seconds. This means that at the beginning of the OCP determination this field could be empty.

The middle section displays the variation of the measured OCP in time. The green line displayed on the same graph corresponds to the optional dE/dt limit defined in the procedure setup (see Figure 4).

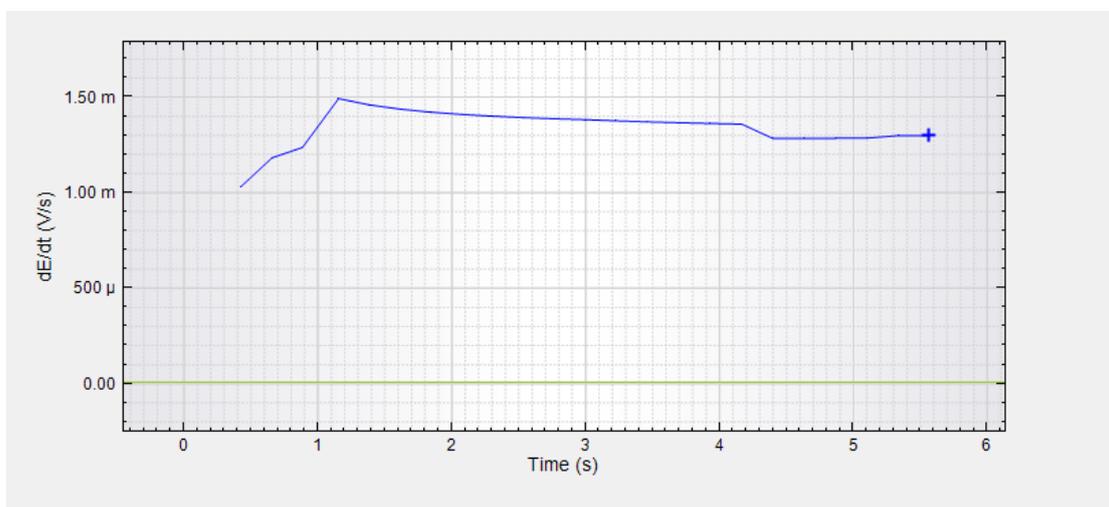


Figure 4 – The graphical display of the variation of the measured OCP in V/s

The bottom section allows to change the OCP determination parameters while the measurement is running. It is possible to activate and deactivate the time limit and the dE/dt limit and switch from average OCP to last measured OCP. Two buttons are provided in the lower right corner of the OCP determination window (Figure 5).

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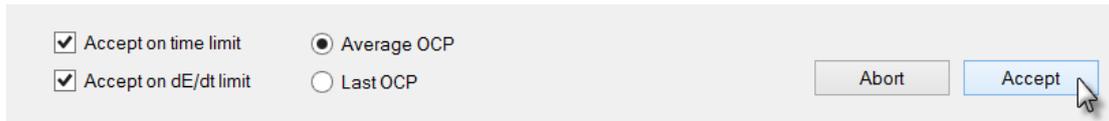


Figure 5 – The bottom part of the OCP determination command allows to control the measurement parameters

Click the **Accept** button to stop the OCP determination and continue with the rest of the procedure. Click the **Abort** to stop both the OCP determination and the procedure.

4 – Measurement view update

Once the OCP determination is finished, the procedure progress in the measurement view is updated, indicating the measured OCP value (see Figure 6).

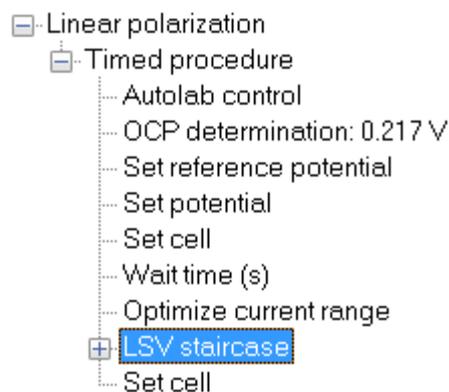


Figure 6 – The procedure progress is updated after the OCP determination

5 – Using the OCP value

Once the OCP value has been measured, it can be used in the rest of a NOVA procedure. The OCP value can be used in two different ways:

1. As a reference voltage for **all** the potential values specified in the procedure.
2. As a reference voltage for specific potential values in the procedure.

5.1 – Setting the OCP value as the reference for all potential values

In order to set the OCP value as a reference potential value for all the potential values used in the rest of the procedure, the *Set reference potential* command must be used (see Figure 7).

[-] OCP determination	[0.000]
Maximum time (s)	120
dE/dt limit	1E-06
Use average OCP	Yes
OCP value	0.000
Time	<..array..> (s)
WE(1).Potential	<..array..> (V)
[-] Set reference potential	0.000
Reference potential (V)	0.000
<..>	

Figure 7 – Using the *Set reference potential* command in combination with the *OCP determination* command

The *Set reference potential* command defines an offset value for all the potential values used in the procedure. It has a single parameter:

- **Reference potential (V):** this is the value of the offset added to all the potentials used in the procedure.

In order to use the measured OCP as a reference potential, the OCP value of the OCP determination command must be linked to the Reference potential parameter of the Set reference potential command (see Figure 7).



Note

To reset the reference potential it is necessary to add the *Set reference potential* command in the procedure again and set the value to 0 V. This will remove the OCP value as reference potential for the subsequent measurement.

When the OCP value is linked to the Set reference potential command, all the consecutive potentials are expressed with respect to the OCP.

5.2 – Setting the OCP value as the reference for specific potential values

When only a few potential values specified in the procedure need to be applied with respect to the measured OCP, it is possible to indicate this directly in the procedure editor using a right-click menu (see Figure 8).

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Commands	Parameters	Links
Cyclic voltammetry potentiostatic		
Remarks	Cyclic voltammetry potentiostatic	...
End status Autolab		...
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Instrument	AUT40007	
Instrument description		
Autolab control		...
OCP determination	[0.000]	
Set potential	0.000	
Set cell	On	...
Wait time (s)	5	
Optimize current range	5	
CV staircase	[0.000, 1.000, -1.000, 0.000, 2, 0.1000000]	
Start potential (V)	0.000	
Upper vertex potential (V)	1.000	
Lower vertex potential (V)		
Stop potential (V)		
Number of stop crossings		
Step potential (V)		
Scan rate (V/s)		
Estimated number of points		
Interval time (s)	0.024400	
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Potential applied	<..array..> (V)	
Time	<..array..> (s)	
WE(1).Current	<..array..> (A)	
Scan	<..array..>	
WE(1).Potential	<..array..> (V)	
Index	<..array..>	
i vs E		...
E vs t		...
Set cell	Off	...
<..>		

Figure 8 – Each applied potential value can now be specified versus the OCP or versus the reference electrode (REF)

Each potential to be applied can be specified versus the reference electrode (REF) or versus the measured open circuit potential (OCP).

When the potential is specified versus the reference electrode (REF), the potential will be applied on the cell using an implicit offset potential of 0 V. When the potential is specified versus the open circuit potential, the potential will be applied using an implicit offset potential equal to the OCP value.

For all the measurement commands that allow the potential parameters to be edited in the procedure editor, the right-click menu can be used. For the *Chrono methods* command, which uses a dedicated editor, this toggle is provided in the editor itself, as shown in Figure 9.

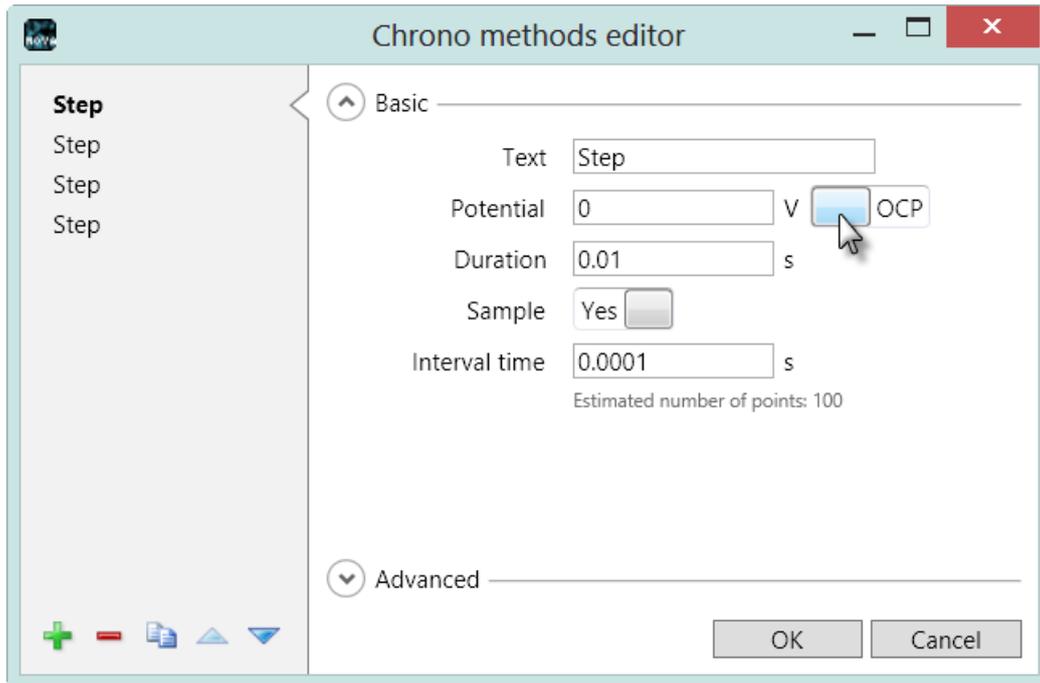


Figure 9 – The REF/OCP toggle is provided in the *Chrono methods* command editor



Note

The REF/OCP toggle is not available for the pulse potentials used in Square wave voltammetry, Differential pulse voltammetry, Differential normal pulse and Normal pulse.

6 – A measurement involving the OCP determination

An OCP tutorial folder is located in the **Program Files\Metrohm Autolab\Nova 1.11\Shared Databases\Tutorials** folder (see Figure 10). Using the database manager, set this folder as the Standard database.

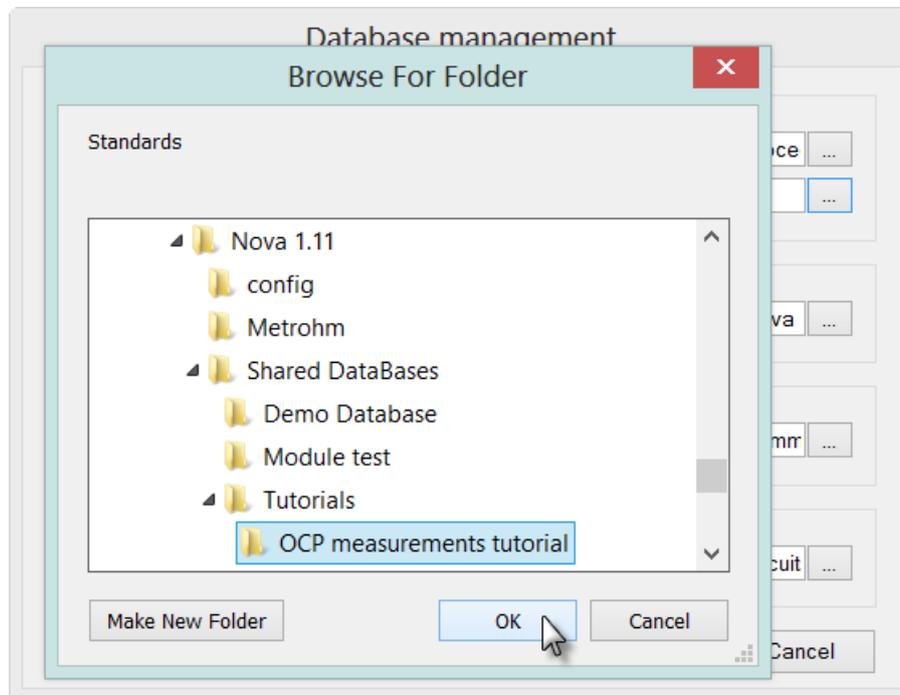


Figure 10 – Loading the OCP measurement tutorial database

The database contains two procedures designed to illustrate the use of the OCP determination command in combination with the Set reference potential command (see Figure 11).

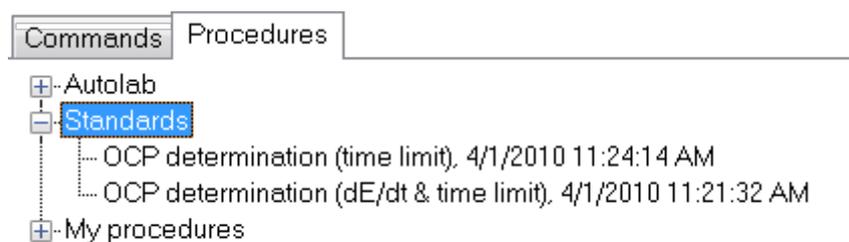


Figure 11 – The OCP determination LSV procedure

The two procedures are identical except for the optional limits during the OCP determination. The first procedure uses only a time limit for the OCP determination while the second procedure uses both a time limit and a dE/dt.

6.1 – OCP determination (time limit)

Select the *OCP determination (time limit)* procedure and connect the Autolab to dummy cell (a). Press the start button to start the measurement.

The PGSTAT101 is not equipped with the Autolab dummy cell. An optional external dummy cell can be obtained¹. It is also possible to activate the internal dummy cell, using the *Autolab control* command².

After pressing the Start button, a message will be displayed (see Figure 12).

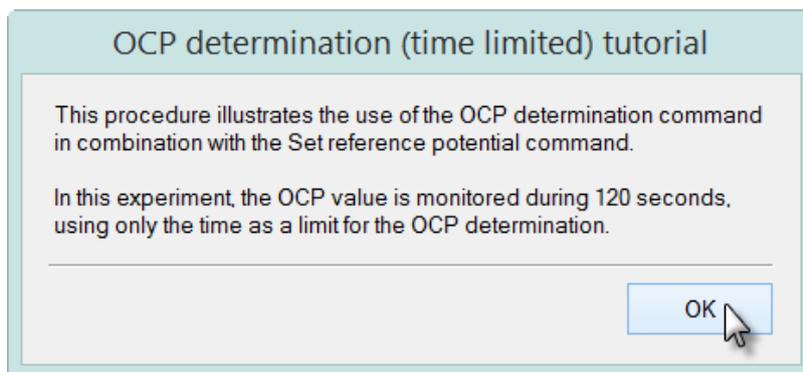


Figure 12 – A message is displayed before the OCP determination

Click the OK button to continue with the measurement. In the first part of the procedure, the OCP determination command is used to monitor the open circuit potential. The measurement will finish after 120 seconds (see Figure 13). In the second part of the procedure, the measured OCP is used to perform a linear sweep voltammetry, with a start potential of 0 V (vs OCP) and a stop potential of 1 V (vs OCP).

¹ Contact your Autolab distributor for more information.

² Please refer to the Autolab control tutorial, available from the Help menu, for more information.

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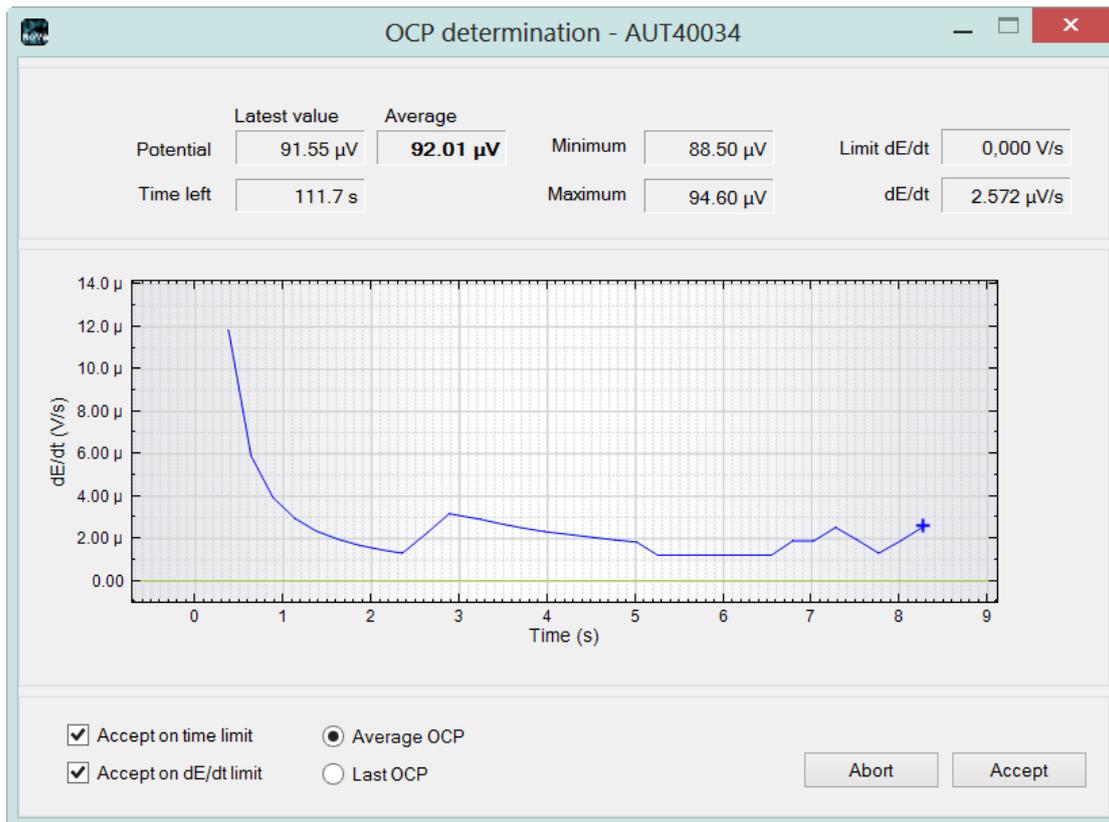


Figure 13 – Time limited OCP determination



Note

The dE/dt limit has been set to 0.000 V/s in this tutorial procedure.

Since the measurement is performed on the dummy cell (a), the OCP is close to 0 V. Figure 14 shows the potential expected in this measurement.

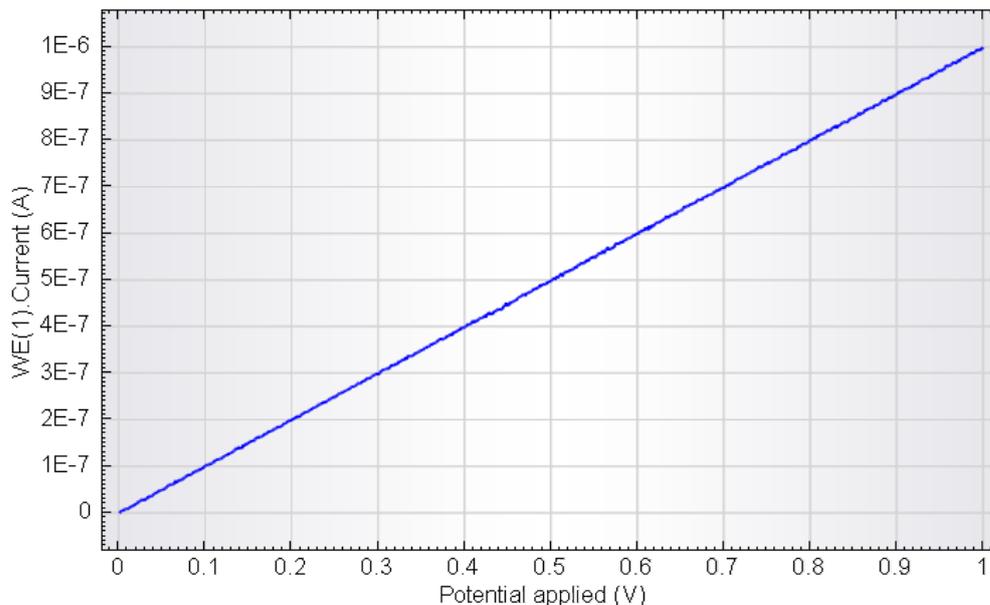


Figure 14 – The measured data obtained using the OCP determination (time limit) procedure

6.2 – OCP determination (dE/dt & time limit)

Select the *OCP determination (dE/dt & time limit)* procedure and connect the Autolab to dummy cell (a). Press the start button to start the measurement.

The PGSTAT101 is not equipped with the Autolab dummy cell. An optional external dummy cell can be obtained³. It is also possible to activate the internal dummy cell, using the *Autolab control* command⁴.

After pressing the Start button, a message will be displayed (see Figure 15).

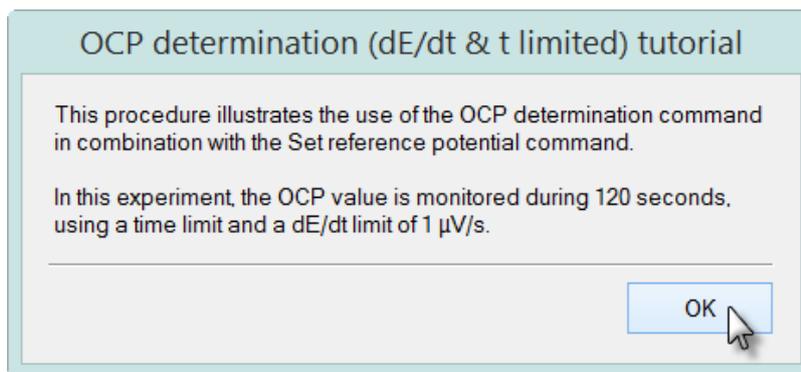


Figure 15 – A message is displayed before the OCP determination

Click the OK button to continue with the measurement. In the first part of the procedure, the OCP determination command is used to monitor the open circuit potential. The measurement will finish after 120 seconds or when the variation of

³ Contact your Autolab distributor for more information.

⁴ Please refer to the Autolab control tutorial, available from the Help menu, for more information.

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potential becomes smaller than $1 \mu\text{V/s}$ (see Figure 16). In the second part of the procedure, the measured OCP is used to perform a linear sweep voltammetry, with a start potential of 0 V (vs OCP) and a stop potential of 1 V (vs OCP).

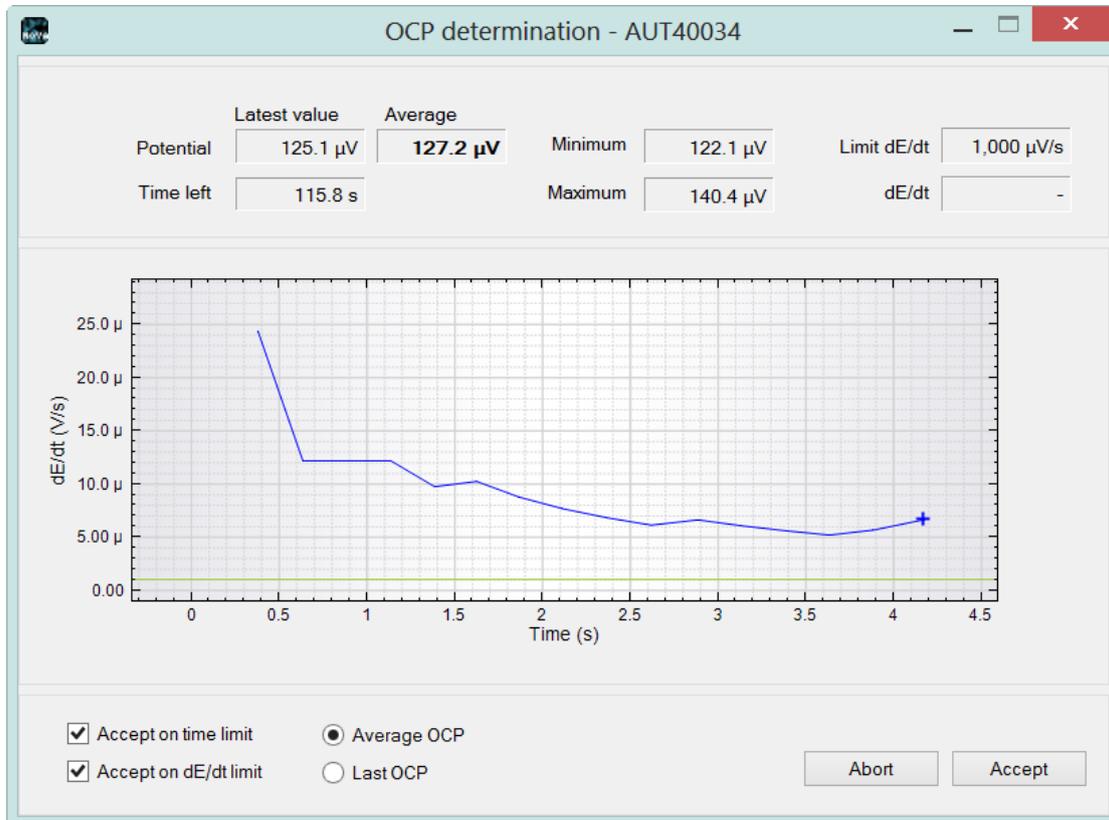


Figure 16 – Time limited and dE/dt limited OCP determination



Note

The dE/dt limit has been set to $1 \mu\text{V/s}$ in this tutorial procedure.

Since the measurement is performed on the dummy cell (a), the OCP is close to 0 V. Figure 17 shows the potential expected in this measurement.

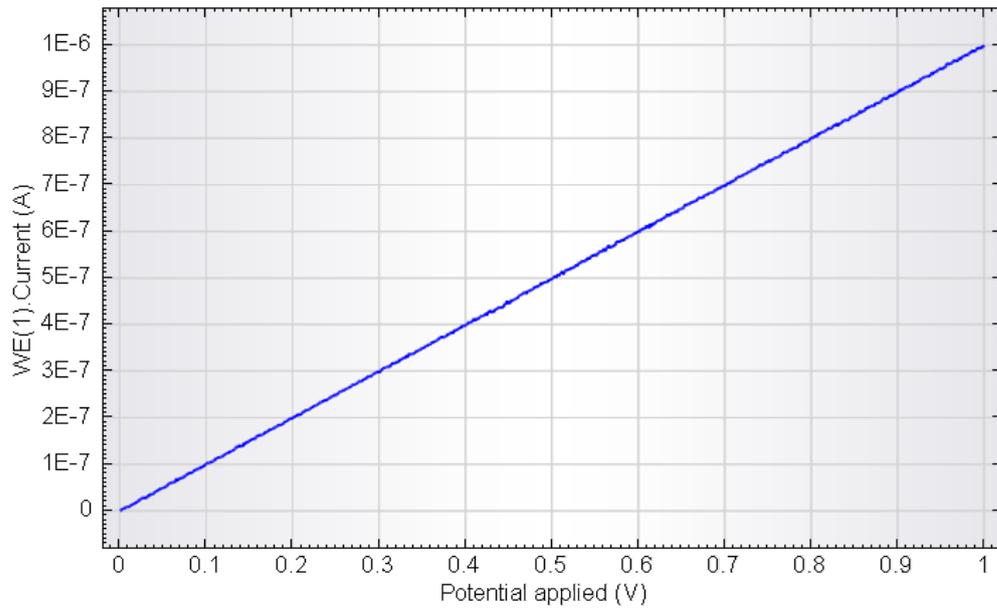


Figure 17 – The measured data obtained using the OCP determination (dE/dt & time limit) procedure