

1 – Cyclic voltammetry linear scan

Cyclic voltammetry is the most popular electrochemical method. It provides both qualitative and quantitative information as well as a fast and reliable characterization tool. The cyclic voltammetry linear scan method is a particular format of cyclic voltammetry during which a linear potential sweep profile is applied to the electrochemical cell and the response of the cell is measured continuously. This allows to measure both the faradic and the capacitive currents. Therefore, this particular form of cyclic voltammetry is well suited for monitoring changes in the double layer structure or electrochemical reactions characterized by fast electron transfer kinetics.

Two forms of cyclic voltammetry linear scan are supported in NOVA:

- Cyclic voltammetry linear scan: with scan rates up to 250 V/s
- Cyclic voltammetry linear scan high speed: for scan rate over 250 V/s

Note: both methods require at least the optional linear scan generator (either the SCANGEN or the SCAN250 module). For linear scan high speed, an additional fast sampling ADC module is required (ADC750 or ADC10M).

Depending on the hardware configuration of the instrument, the maximum scan rate will be different:

- SCANGEN or SCAN250: maximum scan rate – 250 V/s
- SCANGEN or SCAN250 with ADC750: maximum scan rate – 10 kV/s
- SCAN250 with ADC10M: maximum scan rate – 250 kV/s

2 – The CV linear scan command

NOVA provides a *CV linear scan* command¹ which can be used to perform potentiostatic linear scan cyclic voltammetry measurements. The command is located in the Measurement – cyclic and linear sweep voltammetry group of commands.

Figure 1 shows an overview of the *CV linear scan* command and its parameters.

¹ The *CV linear scan* command requires the SCAN250 or SCANGEN module. This command is hidden from view when the required modules are not specified in the hardware setup and the hardware related profile is active.

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CV linear scan [0.000, 1.000, -1.000, Up, 3, 0.100]	
Start potential (V)	0.000
Upper vertex potential (V)	1.000
Lower vertex potential (V)	-1.000
Initial direction	Up
Number of start or vertex potential crossings	3
Stop on start potential or vertex potential	Vertex
Potential interval (V)	2.44E-03
Scan rate (V/s)	0.100
Estimated number of points	2050
Interval time (µs)	24400
Signal sampler	Time, WE(1).Potential, WE(1).Current
Options	1 Options
Scan	<..array.>
Time	<..array.> (s)
WE(1).Potential	<..array.> (V)
WE(1).Current	<..array.> (A)
Index	<..array.>

Figure 1 – Overview of the CV linear scan command

Note: as a timed command, the *CV linear scan* command must be located within a Timed procedure.

The *CV linear scan* command has the following parameters

- **Start potential (V):** defines the start potential, in Volts.
- **Upper vertex potential (V):** defines the upper vertex potential, in Volts. The upper vertex potential must be larger than the lower vertex potential.
- **Lower vertex potential (V):** defines the lower vertex potential, in Volts. The lower vertex potential must be smaller than the upper vertex potential.
- **Initial direction:** defines the initial direction of the scan (up/down).
- **Number of start or vertex potential crossings:** defines the number of times that the scan should cross the start or a vertex potential value in order to stop the measurement.
- **Stop on start potential or vertex potential:** defines whether the scan should stop on the start potential or on a vertex potential².
- **Potential interval (V):** defines the length of the potential interval between two consecutive data points used in the CV linear scan, in Volts. This value must be positive.
- **Scan rate (V/s):** defines the scan rate, in Volts per second³.
- **Signal sampler:** defines the specific sampler used during the CV linear scan measurement. By default, Time, Potential applied and WE(1).Current are measured, but additional electrochemical signals can be added to the sampler. Moreover, the Scan signal, which provides the scan number, will be added to the data.
- **Options:** defines the options used during the CV linear scan measurement (automatic current ranging and cutoffs).

² Stopping on the start potential is only possible when using the SCAN250 module.

³ Because of the maximum sampling rate of the ADC164 module, the scan rate (in V/s) divided by the potential step (in V) should always be lower than 12.000 s⁻¹.

The *CV linear scan* command in NOVA provides a flexible framework for the definition of the scan parameters. In a typical cyclic voltammetry experiment, it is assumed that the start and stop potentials should be the same. With NOVA, this is not the case anymore, and the user is free to define any type a potential scan using the set of parameters available.

3 – The CV linear scan high speed command

NOVA provides an additional *CV linear scan high speed* command⁴ which can be used to perform potentiostatic linear scan cyclic voltammetry measurements at high scan rates. This command is located in the Measurement – cyclic and linear sweep voltammetry group of commands.

Note: the *CV linear scan high speed* command is an Intermediate level command.

Figure 2 shows an overview of the *CV linear scan high speed* command and its parameters.

CV linear scan high speed		[0.000, 1.000, -1.000, Up, 3, 100.000]
Start potential (V)		0.000
Upper vertex potential (V)		1.000
Lower vertex potential (V)		-1.000
Initial direction		Up
Number of start or vertex potential crossings		3
Stop on start potential or vertex potential		Vertex
Potential interval (V)		5.3333E-04
Scan rate (V/s)		100.000
Estimated number of points		9375
Interval time (µs)		5.33
ADC high speed settings		Gain and channel settings
WE(1).Potential		<..array..> (V)
Scan		<..array..>
Time		<..array..> (s)
WE(1).Current		<..array..> (A)
Index		<..array..>
i vs E		

Figure 2 – Overview of the CV linear scan high speed command

Note: as a timed command, the *CV linear scan high speed* command must be located within a Timed procedure.

The *CV linear scan high speed* command has the following parameters:

- **Start potential (V):** defines the start potential, in Volts.
- **Upper vertex potential (V):** defines the upper vertex potential, in Volts. The upper vertex potential must be larger than the lower vertex potential.
- **Lower vertex potential (V):** defines the lower vertex potential, in Volts. The lower vertex potential must be smaller than the upper vertex potential.

⁴ The *CV linear scan high speed* command requires the SCAN250 or SCANGEN module in combination with the ADC10M or ADC750 module. This command is hidden from view when the required modules are not specified in the hardware setup and the hardware related profile is active.

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- **Initial direction:** defines the initial direction of the scan (up/down).
- **Number of start or vertex potential crossings:** defines the number of times that the scan should cross the start or a vertex potential value in order to stop the measurement.
- **Stop on start potential or vertex potential:** defines whether the scan should stop on the start potential or on a vertex potential⁵.
- **Potential interval (V):** defines the length of the potential interval between two consecutive data points used in the CV linear scan high speed, in Volts. This value **must** be positive.
- **Scan rate (V/s):** defines the scan rate, in Volts per second.
- **ADC high speed settings:** defines the acquisition settings for the fast sampling ADC (gain values, signals to sample, etc...). Since the fast sampling ADC used to measure the data points during the scan is a double channel ADC, only two electrochemical signals can be sampled (default: WE(1).Potential and WE(1).Current). An external signal can be measured instead of the WE(1).Current signal through the analog input on the front panel of the instrument (see Figure 3).

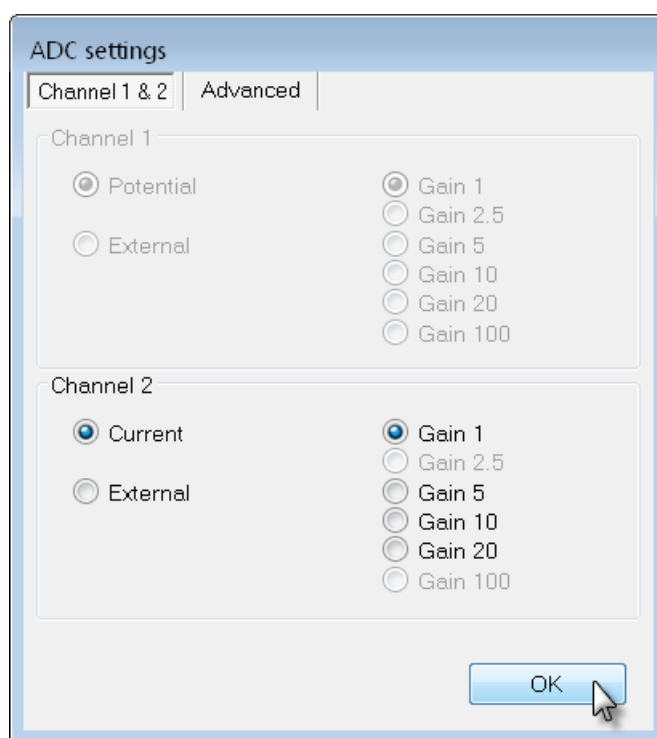


Figure 3 – The ADC settings window can be used to define the gain value of the Current (or for an external signal)

⁵ Stopping on the start potential is only possible when using the SCAN250 module.

4 – Using the *CV linear scan* command

The Autolab Cyclic voltammetry linear procedure provides a good example of the use of the *CV linear scan* command (see Figure 4).

Commands	Parameters	Links
Cyclic voltammetry linear scan		
Remarks	Cyclic voltammetry linear scan: requires SCA...	...
End status Autolab		...
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Instrument		
Instrument description		
⊖ Timed procedure		
⊕ Autolab control		...
⊕ Set potential	0.000	
⊕ Set cell	On	...
⊕ Wait time (s)	5	
Optimize current range	5	
⊖ CV linear scan	[0.000, 1.000, -1.000, Up, 3, 0.100]	
Start potential (V)	0.000	
Upper vertex potential (V)	1.000	
Lower vertex potential (V)	-1.000	
Initial direction	Up	...
Number of start or vertex potential crossings	3	
Stop on start potential or vertex potential	Vertex	...
Potential interval (V)	2.44E-03	
Scan rate (V/s)	0.100	
Estimated number of points	2050	
Interval time (μs)	24400	
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Scan	<..array..>	
Time	<..array..> (s)	
WE(1).Potential	<..array..> (V)	
WE(1).Current	<..array..> (A)	
Index	<..array..>	
⊕ i vs E		...
⊕ Set cell	Off	...
<.>		
<.>		

Figure 4 – The Autolab linear scan procedure

The Autolab linear scan procedure performs a single scan, from 0 V to an upper vertex potential of 1 V, then to a lower vertex potential of -1 V and finally stopping at the upper vertex potential, 1 V. The number of vertex potential crossings is three. The scan rate is 100 mV/s and the initial scan direction is upwards (i.e. from the start potential to the upper vertex potential). Figure 5 shows the potential profile of this experiment.

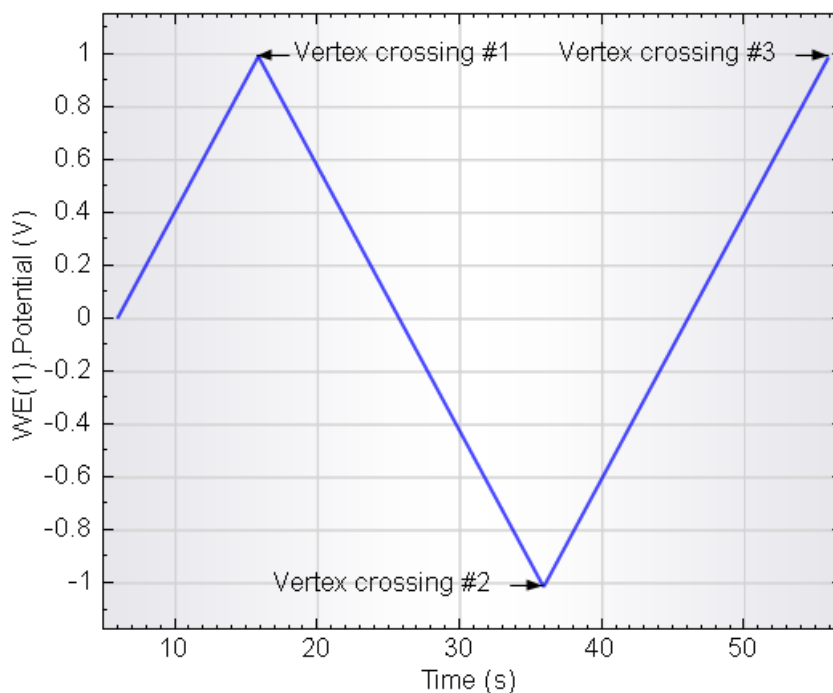


Figure 5 – The potential applied profile with the two stop crossings used in the Autolab Linear scan procedure

The *CV linear scan* command does not have a Stop potential value. It is possible to stop at the start potential⁶ or at either one of the vertices.

CV Linear scan vs CV staircase

During CV Linear scan, the current is monitored continuously. This allows to record the capacitive current contribution during the cyclic voltammetry measurement. In CV staircase on the other hand, the measurement is performed at the end of a potential step. Therefore, the contribution from the capacitive current is minimized.

4.1 – Changing the scan direction

In the *CV linear scan command*, the scan direction is defined by the settings of the Initial direction parameter. This parameter can be set to *up* or *down*. In the first case, the scan direction will be from the start potential to the upper vertex potential, while in the second situation, the scan direction will be the opposite (see Figure 6).

⁶ SCAN250 module only.

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Commands	Parameters	Links
Cyclic voltammetry linear scan		
Remarks	Cyclic voltammetry linear scan: requires SCA...	...
End status Autolab		...
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Instrument		
Instrument description		
Timed procedure		
Autolab control		...
Set potential	0.000	
Set cell	On	...
Wait time (s)	5	
Optimize current range	5	
CV linear scan	[0.000, 1.000, -1.000, Up, 3, 0.100]	
Start potential (V)	0.000	
Upper vertex potential (V)	1.000	
Lower vertex potential (V)	-1.000	
Initial direction	Down	
Number of start or vertex potential crossings	Up	
Stop on start potential or vertex potential	Down	
Potential interval (V)	0.100	
Scan rate (V/s)	0.100	
Estimated number of points	2050	
Interval time (μ s)	24400	
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Scan	<..array.>	
Time	<..array.> (s)	
WE(1).Potential	<..array.> (V)	
WE(1).Current	<..array.> (A)	
Index	<..array.>	
i vs E		...
Set cell	Off	...
<.>		
<.>		

Figure 6 – Changing the scan direction in the CV linear scan command

Figure 7 shows the applied potential profile used in the Autolab linear scan procedure, when the initial direction is set to *down*.

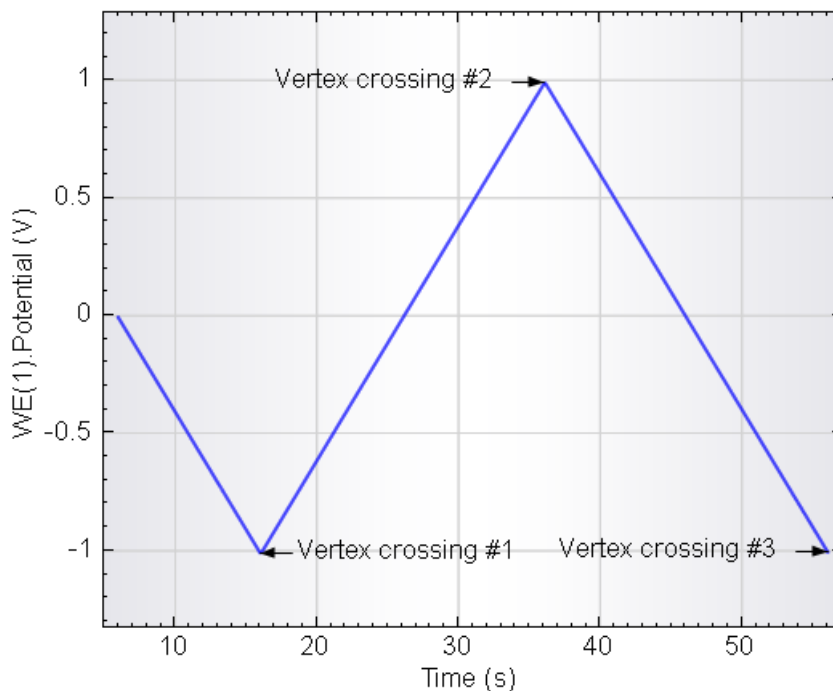


Figure 7 – The potential profile applied used in the Autolab linear scan procedure, with the initial direction parameter set to *down*

4.2 – Changing the number of scans

The number of scans in the *CV linear scan* command is defined by the number of start or vertex potential crossings. This unusual definition of the number of scans has many advantages that will be illustrated in this tutorial.

Depending on the settings, two start or vertex potential crossings are required for one cycle. This means that it is possible to define fractions of cycles during the potential scan.

Figure 8 shows the potential profile obtained with the Autolab linear scan procedure, using four vertex potential crossings instead of three.

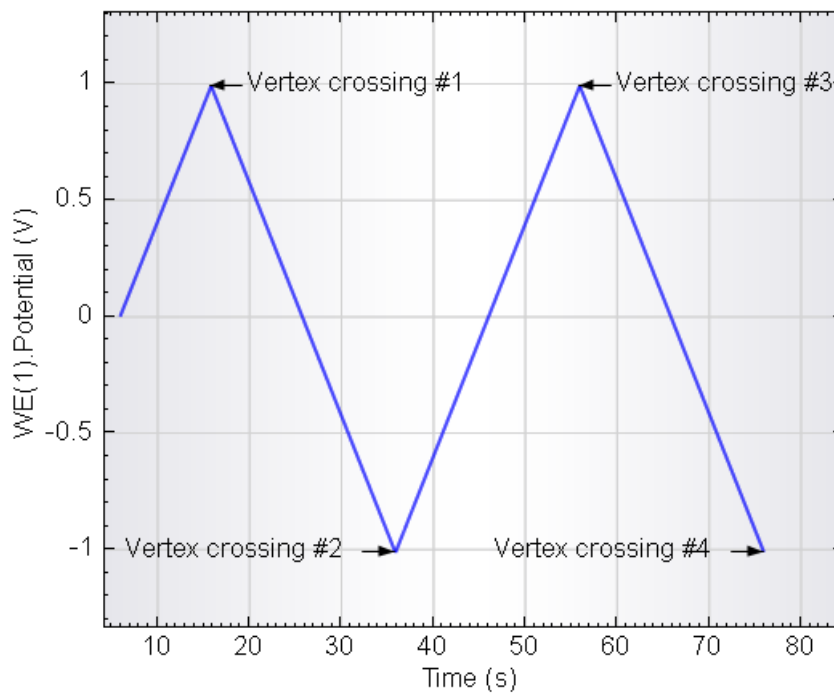


Figure 8 – The potential profile applied with four vertex potential crossings

Note: when the number of crossings is 1 and the linear scan generator module is instructed to stop on a vertex potential, the resulting scan will correspond to a linear sweep voltammetry with linear scan.

4.3 – Using a different stop point

The SCAN250 module allows to stop the scan on the start potential or at one of the vertices⁷. By choosing on which point to stop the scan, additional flexibility can be built into the measurement (see Figure 9).

⁷ The SCANGEN module can only stop on a vertex potential.

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Commands	Parameters	Links
Cyclic voltammetry linear scan		
Remarks	Cyclic voltammetry linear scan: requires SCA...	...
End status Autolab		...
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Instrument		
Instrument description		
Timed procedure		
Autolab control		...
Set potential	0.000	
Set cell	On	...
Wait time (s)	5	
Optimize current range	5	
CV linear scan	[0.000, 1.000, -1.000, Up, 3, 0.100]	
Start potential (V)	0.000	
Upper vertex potential (V)	1.000	
Lower vertex potential (V)	-1.000	
Initial direction	Up	...
Number of start or vertex potential crossings	3	
Stop on start potential or vertex potential	Start value	▼
Potential interval (V)		Vertex
Scan rate (V/s)		Start value
Estimated number of points		...
Interval time (μs)	24400	
Signal sampler	Time, WE(1).Potential, WE(1).Current	...
Options	1 Options	...
Scan	<.array.>	
Time	<.array.> (s)	
WE(1).Potential	<.array.> (V)	
WE(1).Current	<.array.> (A)	
Index	<.array.>	
i vs E		...
Set cell	Off	...
<.>		
<.>		

Figure 9 – Setting the Stop on start potential or vertex potential property for measurements with the SCAN250 module

Note: this option is only available for the SCAN250 module. The SCANGEN module can only be stopped on a vertex potential.

If the stop on vertex potential is used, it is possible to stop the scan on any of the vertices, depending on the number of vertex potential crossings and the scan direction.

On the other hand, if the start potential is used instead of the vertex potentials, it is possible to build a different potential profile. Figure 10 shows the potential profile applied during the linear scan procedure, using the SCAN250 module, when the start potential is used to define the stop condition. In this example, the number of start or vertex potential crossings parameter has been set to two.

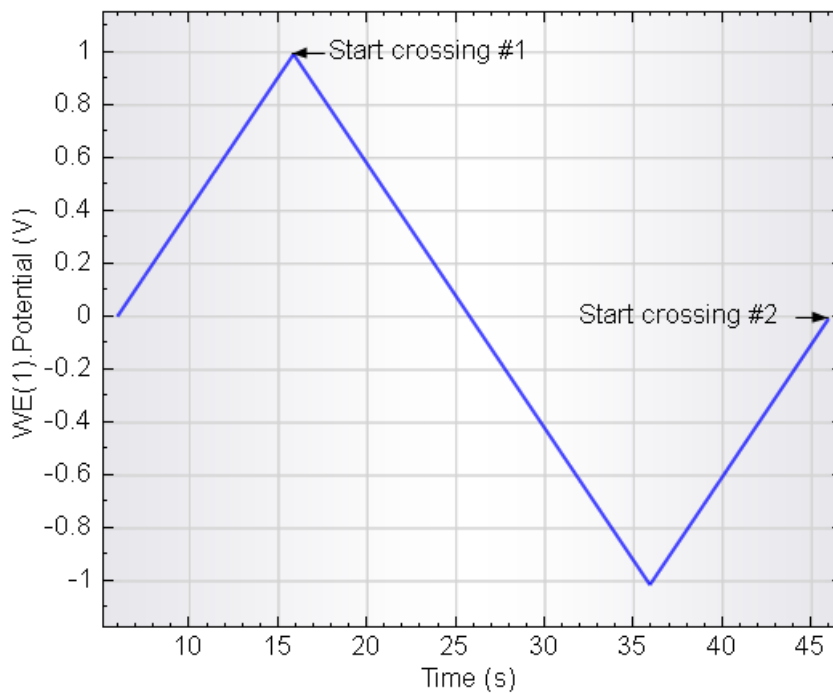


Figure 10 – The potential profile generated by the SCAN250 module during the Autolab linear scan procedure, using the start potential crossings to define the number of scans

5 – Using the *CV linear scan high speed* command

The standard Autolab Cyclic voltammetry linear scan high speed procedure provides a good example of the use of the *CV linear scan high speed* command (see Figure 11).

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Commands	Parameters	Links
Cyclic voltammetry linear scan high speed		
Remarks	Cyclic voltammetry linear scan high speed: re...	...
End status Autolab		...
Signal sampler	No signals.	...
Options	No Options	...
Instrument		
Instrument description		
Timed procedure		
Autolab control		...
Set potential	0.000	
Set cell	On	...
Wait time (s)	5	
CV linear scan high speed	[0.000, 1.000, -1.000, Up, 3, 100.000]	
Start potential (V)	0.000	
Upper vertex potential (V)	1.000	
Lower vertex potential (V)	-1.000	
Initial direction	Up	...
Number of start or vertex potential crossings	3	
Stop on start potential or vertex potential	Vertex	...
Potential interval (V)	5.6E-04	
Scan rate (V/s)	100.000	
Estimated number of points	8930	
Interval time (µs)	5.6	
ADC high speed settings		...
WE(1).Potential	<..array..> (V)	
Scan	<..array..>	
Time	<..array..> (s)	
Channel2	<..array..> (A)	
Index	<..array..>	
i vs E		...
Set cell	Off	...
<..>		
<..>		

Figure 11 – The Autolab High speed linear scan procedure

The standard High speed linear scan procedure performs a single scan, from 0 V to an upper vertex potential of 1 V, then to a lower vertex potential of -1 V and finally stopping at the upper vertex potential, 1 V. The number of vertex potential crossings is three. The scan rate is 100 V/s and the initial scan direction is upwards (i.e. from the start potential to the upper vertex potential). Figure 12 shows the potential profile of this experiment.

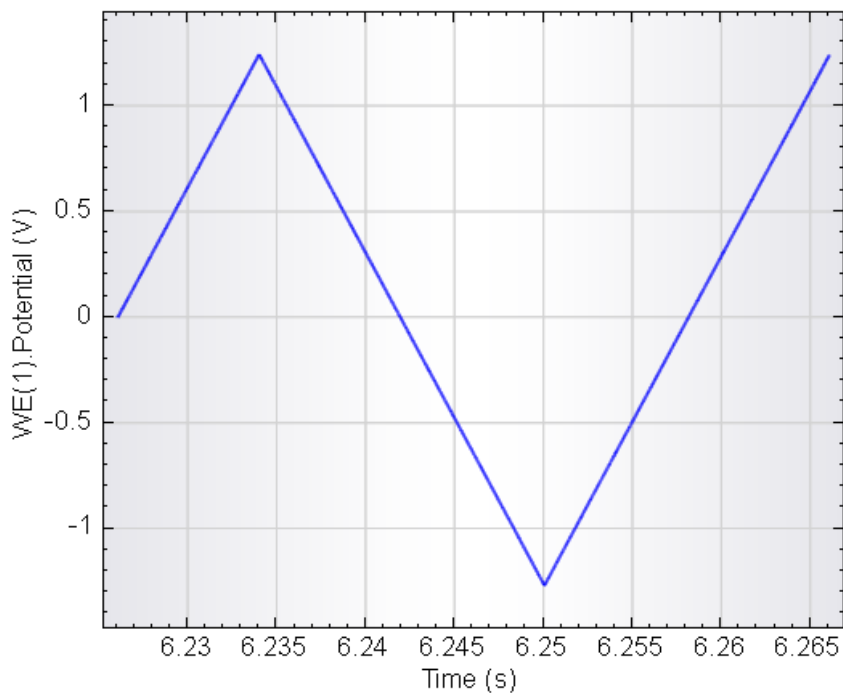


Figure 12 – The potential profile generated during the High speed linear scan procedure

The options available in the *CV linear scan* command are also possible with the *CV linear scan high speed* command. However, in order to use the CV linear scan high speed command, a fast sampling ADC module (ADC750 or ADC10M) must be used.

Note: because of the high sampling rate used during the CV linear scan high speed measurements it is not possible to display the measured data points in real-time. The measurement view will be updated at the end of the experiment.

Hardware specifications

The linear scan generator module can be used to generate an analog triangular waveform which can be used to perform linear scan cyclic voltammetry. The module is capable of generating the waveform with a maximum amplitude of ± 5 V. This waveform is added on to the summation point of the Autolab which means that in practice, the linear scan generator can be used to generate a scan with a ± 5 V amplitude with respect to a ± 5 V offset produced by the Autolab.

Note: please refer to the Getting Started manual for more information about the Autolab PGSTAT and the summation point.

Table 1 provides an overview of the linear scan generator modules.

Module	SCAN250	SCANGEN
Scan range	± 5 V	± 5 V
Vertex resolution	0.15 mV	2.5 mV
Vertex accuracy	2 mV	5 mV
Output offset	± 0.2 mV	± 1 mV
Maximum scan rate	1 MV/s	10 kV/s
Minimum scan rate	10 mV/s	10 mV/s

Table 1 – Overview of the specifications of the linear scan generator modules

Important note: the **SCAN250** module is fitted with a vertex detection circuit which is used to synchronize the reversal of the scan direction with the detection of the vertex. At very high scan rates, this circuit can cause the linear scan generator module to stop the scan at a potential value that does not match the experimental parameters. This potential difference depends on the scan rate. The **SCANGEN** module does not have this circuit and will stop when the vertex is reached. At high scan rates, this will cause the SCANGEN to overshoot the vertex value. The potential difference depends on the scan rate.