

Autolab Application Note EC07

Comparison between Staircase Cyclic Voltammetry and Cyclic Voltammetry Linear Scan

Keywords

Staircase scan, Analog scan, Current integration

Summary

Digital potentiostats cannot apply a true linear waveform. Instead, a scan is generated by a sequence of discrete steps, resulting in a so-called staircase scan. In many experimental situations this is used as an approximation to a true linear scan. This application note compares the traditional staircase to alternative methods available with the Autolab.

Staircase scan

The staircase method for cyclic voltammetry is widely used in digital instruments, due to the discrete nature of digital electronics. Figure 1 shows an example of a waveform for a staircase potential scan.

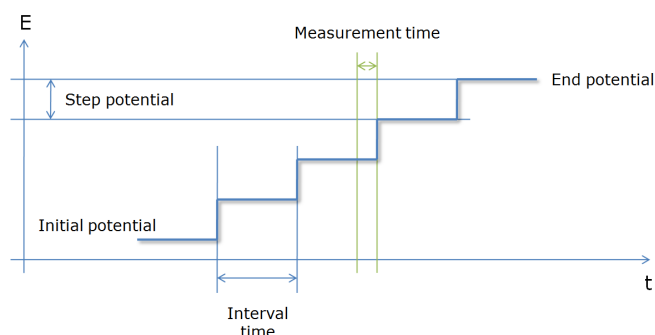


Figure 1 – A typical staircase scan profile

The staircase scan is defined by two parameters, the scan rate, \vec{V} , in V/s and the step potential, E_{step} , in V. These parameters define the interval time, t_{int} , defined in seconds:

$$t_{int} = \frac{E_{step}}{\vec{V}}$$

Each potential step triggers the occurrence of a charging current or capacitive current, which decays exponentially, as:

$$i_C = \frac{E_{step}}{R_u} e^{-\frac{t}{R_u C_{dl}}}$$

Where R_u is the uncompensated resistance and C_{dl} is the double layer capacitance. These values are often combined to express a characteristic time, τ , given by:

$$\tau = R_u C_{dl}$$

With typical values encountered in aqueous solutions, a characteristic time in the range of a few hundred μ s is to be expected. This means that the charging current has all but decayed at the end of the interval time.

In the standard staircase method, the measurement time window is located at the very end of the interval time (see Figure 1). Whenever possible, the duration of this measurement time is set to 20 ms or 16.67 ms, depending on the line frequency, during which the current is sampled and averaged out to suppress the noise.

Since the sampling of the current occurs at the end of the interval time, if this time is sufficiently long, the charging current will be negligible. The resulted data can be treated as originating from faradaic processes only.

True linear scan

The modular Autolab PGSTAT instruments can be fitted with the SCAN250 module. This module is a true analog or linear scan generator. The potential scan is in this case not created by a sequence of small potential steps, but by a linear increase or decrease of the potential between the vertices of the scan. The current is sampled at regular intervals during the scan (see Figure 2).

This linear scan also triggers the occurrence of a charging current or capacitive current, however since the potential variation is now constant, the charging current settles to a constant value given by:

$$i_C = C_{dl} \vec{V}$$

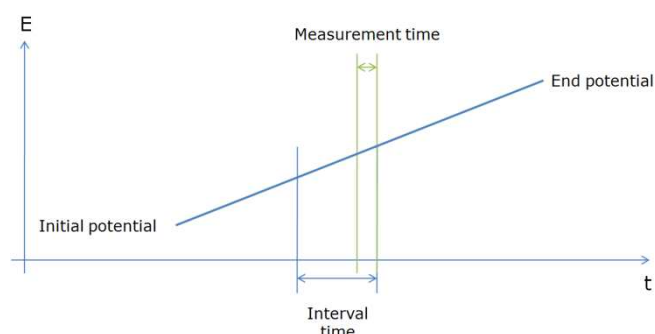


Figure 2 – A typical linear scan generated using the SCAN250

Comparison

The staircase and linear scan methods are intrinsically different and it is obvious that the staircase method can only provide an approximation of a linear scan response. Indeed, since the introduction of digital potentiostats, this comparison has been reviewed and revisited many times in the literature. The conclusion is that the interval time, t_{int} is a critical parameter in the comparison. Since this parameter is defined by the potential step and the scan rate, both parameters will have a significant impact in the comparison. For staircase measurements, the potential step value must be specified carefully. Furthermore, the difference will also be affected by the electrochemical system being investigated.

When kinetic processes are studied, the difference between the staircase and the linear sweep method is expected not to be very large. Serlathan and Osteryoung have made a theoretical comparison between normal staircase voltammetry and cyclic voltammetry, linear scan. They showed that similar results could be obtained when the current is measured at the right moment during the step; for a reversible system the current should be sampled at one quarter of the total step duration. So, for those involved in the research of electrochemical kinetics, staircase voltammetry is a good alternative for linear scan cyclic voltammetry.

Figure 3 shows a practical comparison of a staircase and a linear scan voltammetry measurement recorded in 0.5 M H₂SO₄ solution. The potential is expressed with respect to a Ag/AgCl (KCl saturated) reference electrode. The two curves are very similar. However, closer inspection of the curves, as shown in Figure 4, reveals that the linear scan voltammetry data is larger than the data recorded by staircase voltammetry by the value of the double layer capacitance. This contribution is partially suppressed in the staircase measurement.

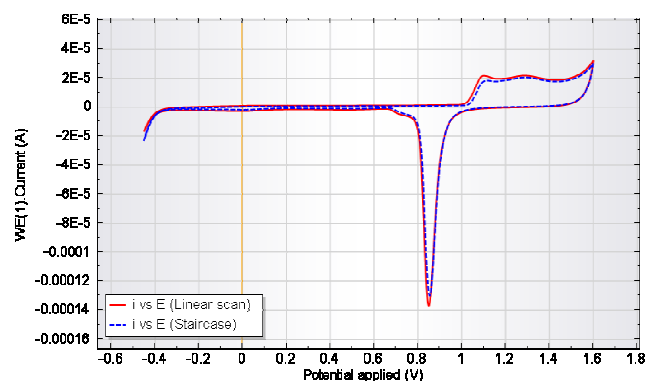


Figure 3 – Comparison of Staircase and Linear scan cyclic voltammetry for polycrystalline gold in sulfuric acid

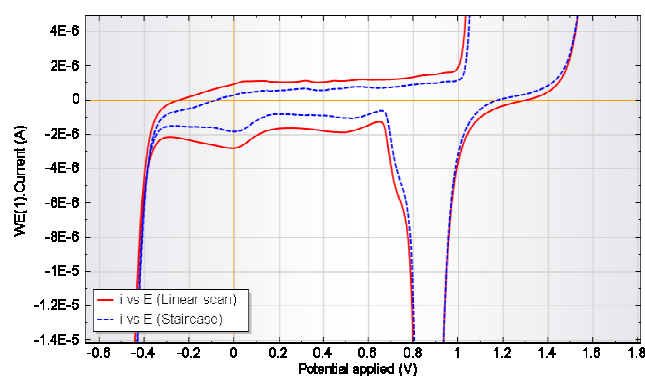


Figure 4 – Detailed view of the double layer region for polycrystalline gold, measured by staircase and linear scan voltammetry

Nevertheless, in the case of time dependent processes, like underpotential deposition (UPD), electrical double layer effects and hydrogen adsorption on Pt, the staircase method is not suitable any longer. In these cases, the above described (normal) staircase method fails because these phenomena take place at the beginning of a step and vanish when the current is sampled.

Figure 5 shows a practical comparison of a staircase and linear scan voltammetry measurement recorded in 0.1 HClO₄ solution. The potential is expressed with respect to a Ag/AgCl (KCl saturated) reference electrode. The two curves are quite similar in the positive end of the curve, displaying similar differences as shown in Figures 3 and 4 which can be ascribed to the suppression of the charging currents. However, on the low potential end of the curves, the currents associated with the H underpotential deposition, H_{upd} , is significantly lower in a staircase scan.

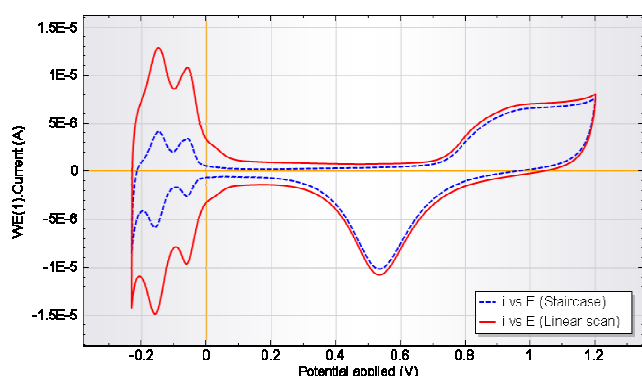


Figure 5 – Comparison of Staircase and Linear scan cyclic voltammetry for polycrystalline platinum in perchloric acid

In the case of the staircase voltammetry, the peaks associated with the adsorption and desorption of hydrogen are almost completely suppressed.

Furthermore, the staircase method is greatly affected by the interval time used in the measurement. Figure 6 shows a comparison of two staircase voltammetry measurements recorded in the same conditions of Figure 5, with a potential step of 2 mV and 1 mV. As shown in this comparison, the total current changes, across the whole cyclic voltammetry, especially in the H_{upd} region, as the interval time decreased (by decrease the potential step).

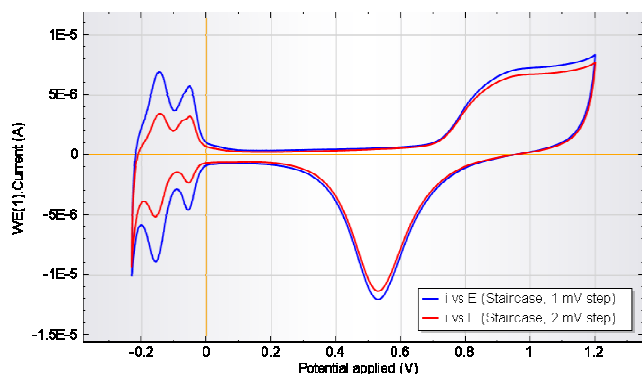


Figure 6 – Comparison of staircase voltammetry of polycrystalline platinum in perchloric acid with different potential step values

Alternative

There is an option available in the software offered with the Autolab instruments fitted with an analog integrator module (FI20 or on-board integrator) which allows the total current to be sampled during the whole potential step. The analog integrator is used to determine the charge accumulated during the potential step, Q_{step} . At the end of the step, the total charge is divided by the duration of the step, t_{step} . This yields a current, i_Q , referred to as integrated current. This

special method is known as cyclic voltammetry current integration. While still being a staircase method, it allows to measure also the current contributions from the beginning of the step.

When applied to the case of polycrystalline platinum, a response very close to the response obtained from the linear scan cyclic voltammetry measurement can be observed, as shown in Figure 7.

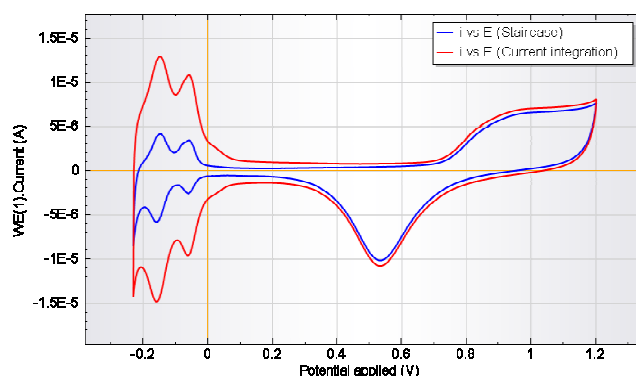


Figure 7 – Comparison of staircase voltammetry and current integration staircase voltammetry for polycrystalline platinum in perchloric acid

Conclusions

The differences illustrated for the case of platinum in this application have significant practical importance, since the peaks associated with the H_{upd} are commonly used to determine the surface area of platinum electrodes or platinum dispersions. Using the staircase method can lead to lower values, therefore leading to higher specific electrocatalytic activities.

When comparing the surface area derived from the integration of the peaks associated with the H_{upd} , significant differences can be observed. These are reported in Table 1. The surface area was estimated by using the charge associated with the formation of the H_{upd} ($220 \mu C/cm^2$).

	Surface area (cm^2)	Ratio
Linear scan	0.0894	1
Current integration	0.0874	0.98
Staircase (1 mV)	0.0379	0.65
Staircase (2 mV)	0.0202	0.47

Table 1 – Comparison of surface areas determined from current integration of the H_{upd} region and ratio with respect to the surface area determined from the Linear scan measurements

References

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