Differences between digital scans, analog scans and signal integration

Keywords

Cyclic voltammetry, CV, staircase voltammetry, Linear scan voltammetry, SCAN250, LSV, signal integration, FI20, resolution, noise, double layer.

Introduction

In this application note, analog and digital staircase potential signals are applied to a platinum working electrode in an acidic solution. The differences in measured currents are highlighted and compared with a similar experiment where the current is being calculated from the measured charge.

Analog and digital signals

The potentiostat or galvanostat (PGSTAT) applies a digital signal, e.g., potential, which is converted into analog form by the digital-to-analog converter (DAC), before being sent to the cell. The analog signal measured from the experiment, e.g., current, is then converted into digital form by the analog-to-digital converter (ADC), in order to be processed by the software. Prior to routine interfacing with personal computers, PGSTATs worked only with analog signals. For this reason, there is a certain degree of confusion and even mistrust when it comes to issues surrounding digital signal handing in electrochemistry.

The terms analog and digital refer to nature of the signals. An analog signal is a continuous, time-varying signal of a quantity. A digital signal, on the other hand, is composed of discrete, non-continuous values of the signals sampled at specific time intervals.

Due to its continuous wave form, an analog signal has virtually infinite resolution, while digital signals have a discrete resolution related to the sampling interval.

In this respect, analog signals, and therefore analog PGSTATs, seem preferable.

However, the processing of analog signals results in noise addition at all processing steps, leading to a severe signal degradation. In contrast, a digitized signal contains only the so-called digital noise due to the resolution of the ADC, and it can be processed in principle without any further degradation.

In the vast majority of the electrochemical experiments, digital signals contain all the information relating to the processes occurring in the electrochemical cell.

Applied and sampled signals

In a closed circuit electrochemical experiment two categories of currents are considered. The potential applied to a cell results in the passage of faradaic current, i_f, related to the electrochemical reaction. Besides, a capacitive current i_C, due to the charging of the double layer, also occurs. The amount and the behavior of the capacitive current changes according to the nature (analog or digital) of the potential applied. The faradaic current, on the other hand, has a decay proportional to the inverse of the square root of time (Cottrell equation), in both cases, as shown in Equation 1.

$$i_f \propto \frac{1}{\sqrt{t}} \qquad\qquad 1$$

True linear scan

The modular Autolab PGSTAT instruments can be equipped with the SCAN250 module, a true analog or true linear scan generator. Here, the potential scan is created by a linear increase or decrease of the potential between the initial and the end potential. The current is sampled at regular intervals, called measurement time, or potential interval, during each interval time, Figure 1.
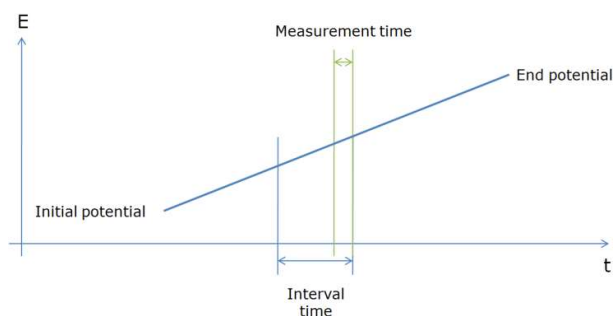

Figure 1 – A typical true linear scan generated using the SCAN250. The interval time and the measurement time are also shown.

In a true linear scan, the variation of potential is constant. Therefore, the capacitive charging current related to a linear scan $i_{C,ls}$ settles to a constant value given by the product of the double layer capacitance C_{dl} and the scan rate dV/dt, Equation 2.

$$i_{C,ls} = C_{dl} \frac{dV}{dt} \qquad\qquad 2$$

Staircase scan

The applied potential vs. time plot of a staircase scan is shown in Figure 2. The "staircase" shape is due to the digitization of the signal. The interval time, t_{int}, defines the duration of each step, while the step potential, E_{step}, defines the potential difference between two consecutive steps. At the end of each step, the measurement time defines the duration of the sampling.
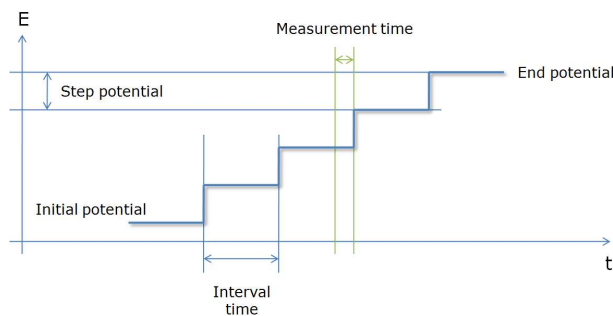

Figure 2 – A typical staircase scan profile. The step potential E_{step} is shown. The interval time and the measurement time are also shown.

The interval time t_{int} (s), is calculated as the ratio between the scan rate dV/dt (V/s) and the step potential, E_{step} (V), Equation 3.

$$t_{int} = \frac{E_{step}}{dV/dt} \qquad\qquad 3$$

The capacitive current resulting from a staircase scan, $i_{C,ss}$, decays exponentially, as shown in Equation 4:

$$i_{C,ss} = \frac{E_{step}}{R_u} EXP\left(-\frac{t}{R_u C_{dl}}\right) \qquad\qquad 4$$

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, or time constant of the cell τ, given by Equation 5:

$$\tau = R_u C_{dl} \qquad\qquad 5$$

After the decay of the capacitive current, the faradaic current i_f is predominant.

In a standard staircase method, the measurement time window is located at the very end of the interval time (Figure 2). Whenever possible, the measurement time is set to 20 ms or 16.67 ms, depending on the frequency of the electrical grid (50 Hz or 60 Hz, respectively), during which the current is sampled and averaged to suppress the noise. Typical interval times used in staircase CV experiments are in the order of 50 ms. Therefore, the charging current $i_{C,ss}$, which has a characteristic time of approximately 100 µs (aqueous solutions), is completely decayed before the current is sampled. Figure 3 shows the duration of different events, during a potential step.
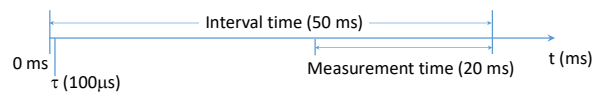

Figure 3 - Visual comparison between the characteristic time τ of the $i_{C,ss}$ decay (100 µs), the measurement time (20 ms) and the interval time (50 ms).

The resulted data can be treated as originating from faradaic processes only, as highlighted in Figure 4.
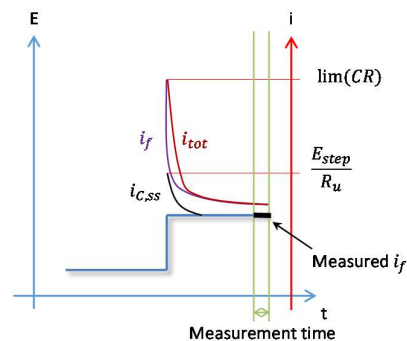

Figure 4 - Potential (blue lines) and current (red lines) profiles for a staircase scan. The current profile is divided into capacitive current $i_{C,ss}$ and faradaic current i_f. The measurement (sampling) time is also shown. For clarity, the decay of the capacitive current and the decay of the faradaic current are not in scale.

In Figure 4, the current decay profile (red line) due to the potential step (blue line), is shown as sum of the capacitive current (black line) and faradaic current (purple line). The position of the measurement time shows that the measured current can be attributed solely at the faradaic current i_f.

However, some electrochemical processes can have a characteristic time comparable to the charging of the double layer. Therefore, the current from the beginning of the step should not be neglected.

One example is the electrochemical behavior of platinum in aqueous solution of sulfuric acid. The cyclic voltammogram of such system is shown in Figure 5.
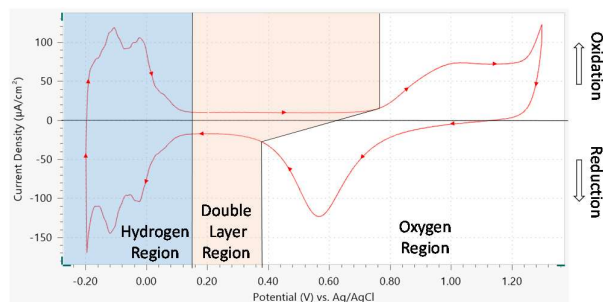

Figure 5 - The cyclic voltammogram of a Pt working electrode immersed in a 0.5 M H_2SO_4 aqueous solution. The reference electrode is a Ag/AgCl 3M KCl, while the counter electrode is a Pt electrode.

Here, the positive current densities are generated by oxidation, while the negative ones by reduction. The cyclic voltammogram is divided in three regions, namely

- Hydrogen region; the hydrogen undergoes anodic desorption (positive current densities) and cathodic adsorption (negative current densities);
- Double layer region; the anodic double layer is charged (positive current densities) and the cathodic double layer is discharged (negative current densities);
- Oxygen region; the platinum surface is oxidized (positive current densities) and reduced (negative current densities).

For a more detailed description of the processes occurring in such systems, please refer to [1].

Hydrogen adsorption and desorption occur in a time scale comparable to that of the buildup of the double layer. Therefore, in order to have insights of the hydrogen region, the current at the beginning of the potential step cannot be neglected.

Current integration

A possible alternative to the true linear scan voltammetry is to measure the charge during a staircase scan. This can be accomplished with a capacitor, which converts the current into the respective amount of charge. The current coming from the working electrode is converted *before* the sampling;

therefore, all the current generated during the potential step is integrated. Afterwards, the derivative of the charge C with respect to the integration time dt_{FI20} results in the so-called integrated current i_{FI20}.

$$i_{FI20} = dC / dt_{FI20} \qquad\qquad 6$$

A typical schematic of the integrator is shown in Figure 6.
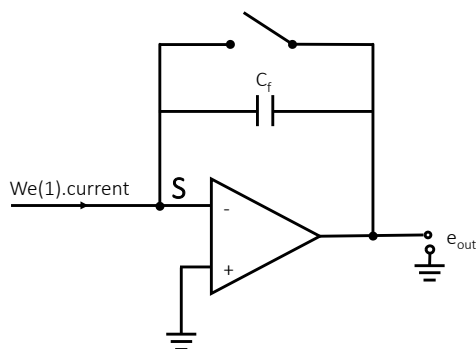

Figure 6 - The schematics of the integrator present is the PGSTATs.

The current coming from the working electrode is fed back to the summation point S, through the capacitor C_f. The switch on top is used to discharge the capacitor before a new measurement [2]. The Metrohm Autolab PGSTAT302N and PGSTAT128N can perform charge measurement with the optional FI20 module; while the Metrohm Autolab PGSTAT101 and PGSTAT204, in single or multichannel configuration, have the integrator as standard feature.

Experimental Setup

A Metrohm Autolab PGSTAT302N, equipped with linear scan generator (SCAN250), and filter and integrator (FI20) modules is used, together with the Metrohm Autolab RRDE cell. A 3 mm diameter platinum disk working electrode is used, with a 1 cm^2 Metrohm platinum counter electrode and a Metrohm Ag/AgCl 3M KCl reference electrode. The disk shape of the electrode is not necessary, clean sheet or wire electrode is also appropriate.

An aqueous solution of 0.5 M sulfuric acid is prepared, by diluting a 0.5 mol/L Titrisol sulfuric acid solution (Sigma-Aldrich) in 1 L of ultra-pure Millipore water.

Before starting the experiments, all the parts in contact with the solution have been cleaned with the following protocol

- Immerse the necessary part into a solution of potassium permanganate with sulfuric acid for 24 h;
- Rinse the parts with a mixture of sulfuric acid/hydrogen peroxide and water;

- Rinse the parts with water once at room temperature, and twice in boiling water;
- The parts can be stored in a 50:50 sulfuric acid:water solution, and rinsed with water before the use.

Warning: This cleaning protocol involves handling of corrosive substances and management of exothermic process that should only be performed following proper training and with protective equipment. A more detailed description of the cleaning protocol can be delivered on request.

The procedures

For all three experiments, the potential is scanned between -0.2 V to 1.3 V vs Ag/AgCl. The scan rate is set at 0.1 V/s, and the potential interval at 4.44 mV for the true linear scan. For both staircase and current integration scans, the potential step is set to 4.44 mV. In all cases, the interval time results in 44.4 ms. For the current integration procedure, a 10 ms integration time is chosen, and the current range is fixed at 10 μA.

Results and Discussion

In Figure 7, the cyclic voltammograms collected with the three different procedures is shown.
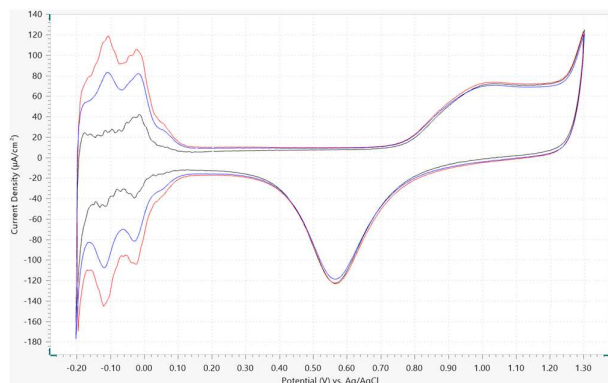

Figure 7 – The red line shows the cyclic voltammogram collected with the SCAN250; the black line shows the cyclic voltammogram collected with the staircase scan; the blue line shows the cyclic voltammogam collected with the current integration.

The main differences among the scans occur in the hydrogen region, from -0.2 V to 0.16 V vs. Ag/AgCl.

The cyclic voltammogram showing the highest amount of current in the hydrogen region is the result of the true linear scan (red line). When a staircase scan is employed, the resulting cyclic voltammogram (black line), show a lower

current in the hydrogen region. However, if the charge is measured with the current integrator, the resulting cyclic voltammogram (blue line) shows a significantly higher current in the hydrogen region. This demonstrates that the current integration method can be a valid alternative for a true linear scan, while the staircase scan is not a suitable method to investigate the hydrogen adsorption and desorption processes.

However, while the voltammogram obtained with a true linear always quantitatively represents the electrochemical processes, the voltammogram obtained with the current integration will depend on the choice of the instrumental setting, such as current range and integration time.

Conclusions

In this application note, the difference between the cyclic voltammograms collected with a true linear scan, a staircase scan is shown. In addition, the current calculated by the measured charge is also compared. A platinum working electrode immersed in an aqueous solution of sulfuric acid is used, together with a reference and a counter electrode.

The true linear scan results in a cyclic voltammogram with all the electrochemical processes represented. The staircase scan, on the other end, under samples processes which decay before the sampling of the current. However, if the charge is measured, the resulting integrated current contains similar information of the current from a true linear scan. Therefore measuring the charge and the following integrated current can be considered as a valid alternative to a true linear scan.

Bibliography

[1]   L. Xing, M. A. Hossain, M. Tian, D. Beauchemin, K. T. Adjemian, and G. Jerkiewicz, "Platinum Electro-dissolution in Acidic Media upon Potential Cycling," *Electrocatalysis*, vol. 5, no. 1, pp. 96–112, 2014.

[2]   A. J. Bard and L. R. Faulkner, *Electrochemical Methods - Fundamentals and Applications 2nd edition*, 2nd editio. John Wiley & Sons, Inc., 2001.

Date

March 2019   AN-EC-007

For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.