

WHITE PAPER

Seamless electrochemical measurements with VIONIC powered by INTELLO

Electrochemical experiments generally consist of observing properties of the electrode in response to an applied perturbation, e.g., the current in response to an applied potential. The applied perturbation can be simple (e.g., a potential step) or complex (e.g., multiple steps in sequence, a ramp, a unique waveform, etc.).

It is expected that sequences are applied to the electrochemical cell as they are visualized and programmed in sequences of commands, and that the response of the cell is recorded without missing any possible details. Electrochemists expect a continuous, uninterrupted, and precisely timed applied waveform along with continuous, uninterrupted, and true-to-nature response signals. With respect to sequences or unique waveforms, it is often the case that interesting properties of the system are revealed at the instance when a new part of the sequence is executed, i.e., at the transition between two measurement commands and/or when the applied perturbation changes, for example, at the beginning of a pulse or the reversal of a ramp [1].

Modern potentiostats offer the flexibility to program sequences and unique waveforms, and the ability to sample the responses with precision, accuracy, and high sampling rates. These impressive specifications allow electrochemical systems to be explored in unprecedented depth.



DO THE EXPECTATIONS MEET REALITY?

Sequences and waveforms are programmed and edited in software using the available tools and options to communicate the details of an experiment to a procedure that the instrumentation can execute. A sequence is trusted to be executed as programmed. However, the instruments use digital and analog electronics, programmed events, conversions, and more, which work together to run the measurement. These variables can affect how a sequence is implemented by the software, sometimes adding small gaps and delays.

This White Paper presents VIONIC powered by INTELLO's unique combination of electronics and software which delivers on the expectations of electrochemists: continuous, uninterrupted, precisely timed true-to-nature measurements. In a word: **Seamless**.

WHAT IS «SEAMLESS?»

Seamless is a concept related to the time in which a signal is applied or measured; it is related to commands and transition between commands. It refers to the possibility to apply a desired waveform **without delays** between parts of the sequence, and the ability to acquire the resulting signal without temporal gaps in the measured data.

Between two consecutive commands, if there is no delay in applying the perturbation and no gap in measuring the response signals from the cell, the transition is called a Seamless transition. A Seamless transition is possible between Seamless commands. The Seamless commands include Linear Sweep and Cyclic Voltammetry (linear and staircase), chrono methods, apply and record signal, and others.



BENEFITS OF SEAMLESS

The perturbation signal is applied exactly as programmed by the user in the software. Thanks to the following two factors, the accuracy of the measurement is increased.

1. DON'T MISS A SINGLE DATA POINT

As an example, a step potential was applied to a cell (Figure 1a) and the corresponding current response was plotted in the case of non-seamless (Figure 1b) and Seamless (Figure 1c) situations. The current response is shown with red lines in the graphs, while gray shaded areas show the calculated charge.



Figure 1. Benefits of Seamless on a simple step potential. a) The applied potential vs. time; b) the measured current vs. time plot (red line) and the calculated charge (gray area) in a non-seamless measurement; c) the measured current vs. time plot (red line) and the calculated charge (gray area) in a Seamless measurement.

If the measurement is not Seamless (**Figure 1b**), there will be a certain delay $(t + \Delta t)$ and uncertainty between the initial and final applied potential and a resulting gap in the recorded current response. The early points of the current decay cannot be recorded. During a Seamless transition (**Figure 1c**), there is no delay between the initial and final potential, and the current response is measured concurrently with the potential step. In addition, in the case of charge calculation (the gray areas in **Figure 1b and c**), the plot clearly shows that Seamless measurements give more accurate and complete results.

An example of the consequences of missing data points in the case of a non-seamless measurement at a potential step is shown below in **Figure 2**.

On the left side of the figure, the applied step potential is shown (black line) together with the theoretical behavior of the current transient for different types of electrochemical processes: diffusion-controlled processes (black dots), kinetic-controlled processes (blue dots), and mixed diffusion- and kinetic-controlled processes (red dots) [**2**].

The right side of **Figure 2** shows the results between the use of a Seamless command and a non-Seamless command. If a Seamless command is used, no gap between the applied potential and the measured current will be present. As a result, the information will be complete, and it can be concluded that the process is diffusion-controlled (black line). If a non-seamless command is used, a gap between the applied potential and the measured current will occur. As a result, the information will not be complete, potentially leading to erroneous conclusions about the system under scrutiny.



Figure 2. On the left, the applied step potential (top), and the three types of current response, given by diffusion control (black dots), mixed kinetic and diffusion control (red dots) and kinetic control (blue dots). On the right are the three types of current responses in the case of Seamless and non-seamless measurements.

2. ELECTRODE EXPERIENCES THAT YOU WANT – AND ONLY WHAT YOU WANT

In a Seamless transition, the applied signal is continuous between the two commands. In a non-seamless sequence, what happens during the gap is unknown not only as previously demonstrated on the recorded signal, but also on the applied signal. For more details about the different responses to potential steps refer to reference [**2**] (specifically, chapter 5). The example in **Figure 3** shows what happens between two linear sweeps at two different scan rates. The system used here is the diffusion-limited oxidation of a redox species. The scan rate is increased from 0.1 to 0.5 V/s which corresponds to two successive LSV (linear sweep voltammetry) commands. When increasing the scan rate during the oxidation peak, the current is expected to increase instantaneously as shown in **Figure 3**.



Figure 3. Benefits of Seamless on the applied potential. The scan rate was changed from 0.1 to 0.5 V/s in linear sweep voltammetry (LSV). With a Seamless transition (left), the applied potential (blue curve) instantaneously changes to adjust to the new scan rate and the measured current (green line). For a non-seamless transition (right) the applied potential differs from the programmed waveform due to the introduction of a delay (gray zone) affecting the nature of the process occurring and the recorded signal (green line).

NOTE: To reproduce the effect of a non-seamless transition, the procedure was stopped for 20 ms at the transition and the signals (E and i) were recorded. At a non-seamless transition, the last applied potential is held until the following command can be processed. Most electrochemical systems have different responses to a linear sweep vs. a constant potential: this can be observed here as the current decays during the transition and then increases when the second potential sweep starts.

In the non-seamless case, the current at the beginning of the second sweep is lower than the one at the end which cannot be explained without knowing that there is a gap between the two commands.

For this situation, not only would some data be missing, but the applied waveform is also not exactly what would be expected in the programmed sequence. As for the previous example, the Seamless measurement delivers results that are both true to nature and to expectations.



SEAMLESS APPLICATIONS

In principle, all measurements benefit from Seamless since no data is lost due to delays in the application of a command and gaps in recording of a signal. However, Seamless is a highly beneficial feature specifically for applications such as:

- chronoamperometry or chronopotentiometry for pulsed electrodeposition

 chronoamperometry stripping with steps and sweeps for the determination of the electrode surface area

- study of fast processes with the Cottrell equation in interfacial electrochemistry

- time-resolved adsorption/desorption and reaction mechanism studies

All of these measurements benefit from Seamless since the processes under investigation occur very close in time during the application of the signal, so no delay in measuring is allowed.

HOW SHORT IS A SEAMLESS TRANSITION?

By definition, a Seamless transition has no duration. For the applied perturbation to the cell, the time delay between two consecutive Seamless commands is limited by the time resolution of the processor used in VIONIC (i.e., 10 ns). For the measured response from the electrochemical cell, the duration of the transition is dictated by the sampling interval of the seamless commands, which can be as low as 1 μ s.

When these commands have the same sampling interval, no difference in time will be present in the data over the transition in a Seamless measurement. If two consecutive Seamless commands have different sampling intervals, the gap between the signals between the two Seamless commands will be dictated by the largest sampling interval.

HOW LONG IS A NON-SEAMLESS TRANSTION?

The real question to ask would be: what makes a transition non-seamless? The answer lies in how the instrument and the software communicate, and what is necessary for a command to be started after another command is applied. This can involve changes in the instrument settings such as a switch between galvanostatic and potentiostatic modes, data transfer from the instrument to the computer, or sending the information of the new waveform to be applied.

Without the Seamless feature, the shortest possible transition is on the order of magnitude of tens of milliseconds. With increasing complexity of the procedure and actions taken in between two commands, the time delay can increase up to seconds.

The Seamless feature, i.e., the disappearance of this variable time gap, is made possible by the new design of the architecture of VIONIC and INTELLO with the control and sampling occurring via two parallel paths, independent of any other hardware or software actions that usually induce a gap between commands. The only non-seamless commands are therefore ones requiring physical changes in the hardware (e.g., switching relays). In this case, the delay between commands is the time required to apply these changes to the instrument.

CONCLUSION

This White Paper introduced Seamless as a new concept and feature unique to VIONIC powered by INTELLO. It eliminates delays in applying a perturbation signal and gaps in signal acquisition, within and between Seamless commands. Comparisons between results with and without Seamless demonstrate that Seamless commands can change the way the system is observed and understood, allowing electrochemists to apply the exact signal they have in mind when designing their experiments with INTELLO. Seamless can be applied to applications involving pulsed electrodeposition, determination of the electrode surface area, and interfacial electrochemistry.



References

[1] McMath, A.A.; Van Drunen, J.; Kim, J.; et al. Identification and Analysis of Electrochemical Instrumentation Limitations through the Study of Platinum Surface Oxide Formation and Reduction. *Anal. Chem.* **2016**, *88* (6), 3136–3143. DOI:10.1021/acs.analchem.5b04239

[2] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001.

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