

Application Note AN-EC-037

Differential electrochemical mass spectrometry

Integrating Metrohm Autolab potentiostats with Hiden mass spectrometers

Differential electrochemical mass spectrometry (DEMS) is an advanced analytical technique that integrates an electrochemical experiment with mass spectrometry. This method enables real-time, *in situ* analysis of gaseous and volatile electrochemical reactants, intermediates, and products. DEMS is particularly valuable for studying reaction mechanisms and kinetics in energy conversion and storage applications, such as fuel cells, batteries, and electrocatalytic processes.

This Application Note highlights both the DEMS technique itself and the combination of a Hiden mass spectrometer with a VIONIC used to detect and quantify hydrogen production during a cyclic voltammogram (CV).

INTRODUCTION

Energy conversion and storage has emerged as the leading application of electrochemistry. Its application is broad and includes branches of electrocatalysis, fuel cells, and electrolysis.

In electrocatalysis, when benchmarking new electrocatalysts for CO_2 reduction, it is important to quantify parameters such as the turnover rate – or how much material is produced in a given amount of time. There are many approaches to determine the turnover rate. Differential electrochemical mass spectrometry (DEMS) offers an easy, *in situ* method to do this. DEMS can also be extended to OEMS (online electrochemical mass spectrometry).

A typical DEMS setup includes a half-cell, a nanoporous membrane, and a quadrupole mass spectrometer. In materials science (particularly in cathode studies), electrochemical half-cells, which use a single electrode in an electrolyte solution, are common and are convenient for quickly screening new materials. However, they provide limited *in situ* reaction information. DEMS enhances this by analyzing the half-cell experiment with mass spectrometry, quantitatively identifying gaseous or volatile products, including reactants and intermediates. Like other hyphenated techniques (e.g., spectroelectrochemistry), DEMS correlates a second signal (in this case mass ion currents of the electrolyte flow) with the faradaic current of the electrode, offering reliable, mass-resolved observations of electrochemical reactions.

EXPERIMENTAL

The setup consists of a DEMS cell, a peristaltic pump, and an electrolyte reservoir. The electrolyte is 1 mol/L NaOH. The CE is platinum, the WE is gold sputtered onto a PTFE membrane, and the reference electrode is Ag/AgCl. More can be read about the cell and the setup in the reference provided [1]. The mass spectrometry analysis is conducted with the HPR-40 OEMS system for online mass spectrometry. The electrochemistry is handled by VIONIC powered by INTELLO. The procedure used in INTELLO is shown in Figure 1.

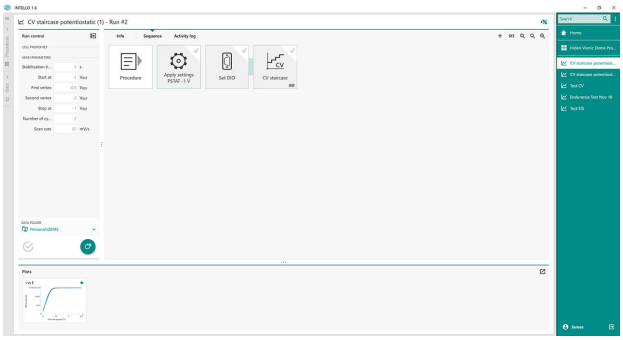


Figure 1. Procedure written in INTELLO.

The voltage and current signals measured by VIONIC are sent to the software of the mass spectrometer using the I- and E- monitor functionality in INTELLO (Figure 2). The current signal is fed to the Hiden software by connecting the iout of the Hiden cable to the A-OUT1 port of the VIONIC. The potential signal is provided to the software by connecting the Eout of the Hiden cable to the A-OUT2 port of the VIONIC. The auxiliary inputs of the Hiden software must be configured according to the Hiden document HA-131-524.

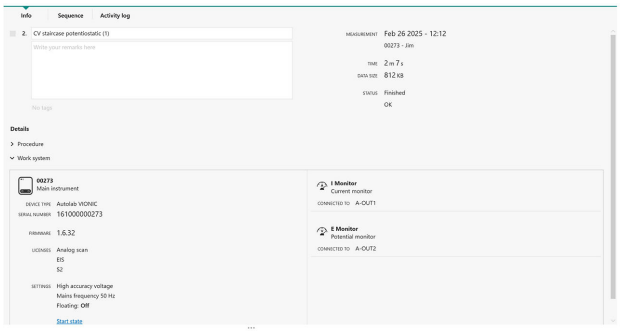


Figure 2. Work system view in INTELLO, showing the I- and E-monitor functionality.

Automatic current ranging should also be disabled in order to ensure that the current passed to the Hiden software is correct. Using a trigger cable, INTELLO is able to trigger the mass spectrometer to begin scanning. The Hiden software utilizes a falling edge trigger. The initial/end state of the DIO port on the potentiostat (Figure 3) prior to the measurement should therefore be set to high (1). Pin 5 is used for this.

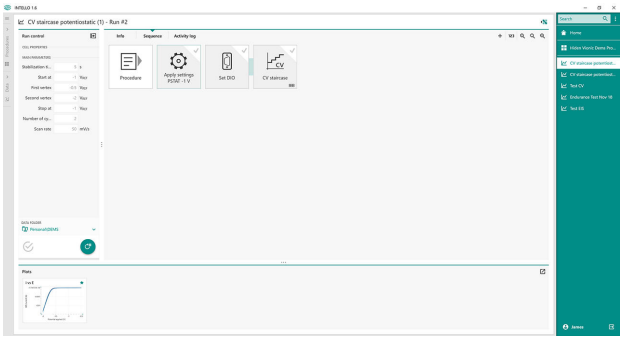


Figure 3. End-state of the instrument in INTELLO.

The bespoke cable used in these experiments is shown in Figure 4. The 25-pin side connects to the HPR-40 system. The 15-pin side is for the VIONIC, and there are two BNC connectors for the *I* and *E* signals, respectively.

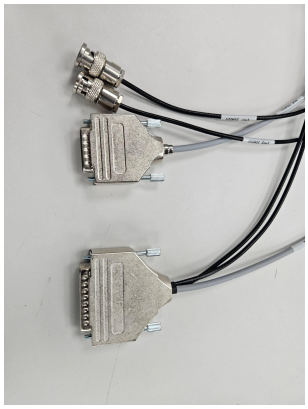


Figure 4. DIO trigger and BNC cable used in this system.

At the beginning of the procedure, the state of pin 5 should be changed to low (0). This is done with a Set DIO command (Figure 5).
All Hiden software has the ability to accept triggers either as a Start/Stop automation event (MASsoft) or in the triggering window (QGA 2). When the trigger signal is received the currently selected setup file will start automatically.

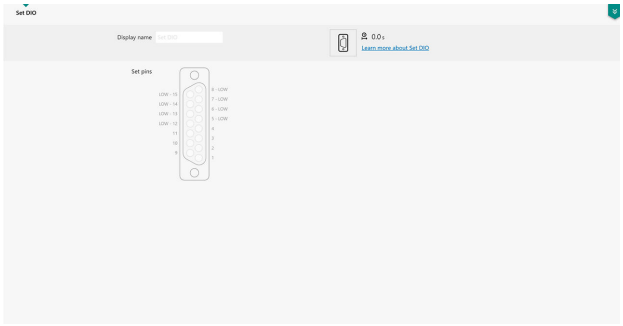


Figure 5. Set DIO command detailed view.

RESULTS AND DISCUSSION

Cyclic voltammetry (Figure 6) was conducted in the region of -0.5 to -2 V, with a start/stop voltage of -1 V vs AgCl. The scan rate was 50 mV/s. There are no discernable features in the CV until about -1.3 V, where the production of hydrogen is triggered via the reduction of the aqueous electrolyte.

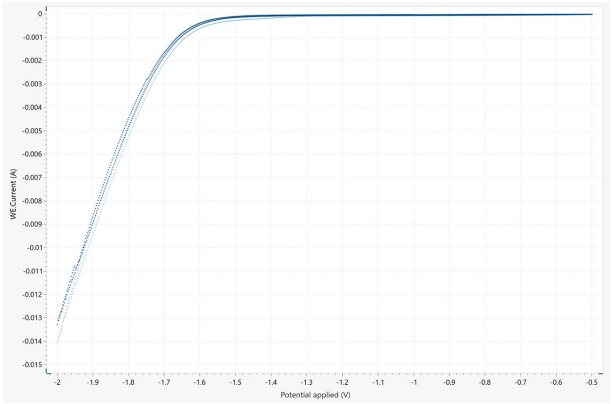


Figure 6. Cyclic voltammogram of 1 mol/L NaOH on an Au-sputtered electrode.

The synchronized mass, current, and potential vs time signals are shown in Figure 7. No discernable change in the mass signal is observed until -1.3 V is reached. The rise in signal corresponds with (and also confirms) the production of hydrogen at the very negative potentials.

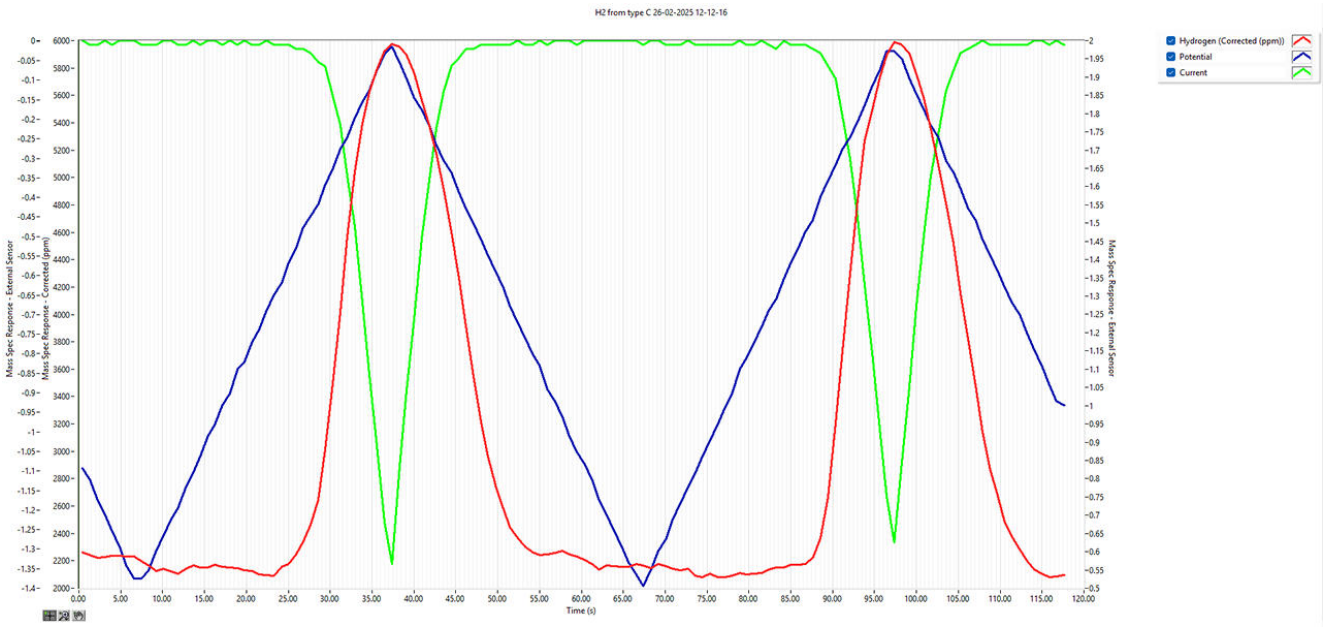


Figure 7. Synchronized, mass (red), potential (blue), and current (green) signals from the Hiden software.

REFERENCE

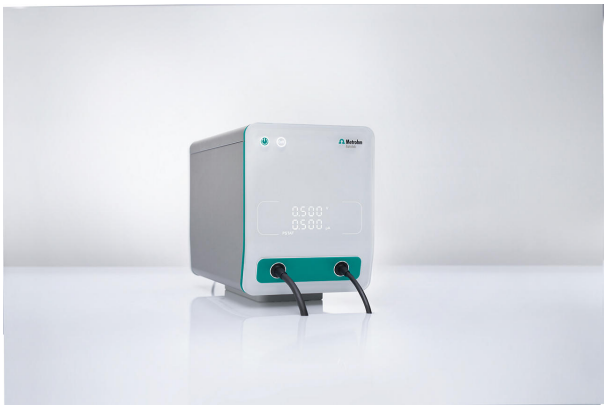
1. Clark, E. L.; Bell, A. T. Direct Observation of the Local Reaction Environment during the Electrochemical Reduction of CO_2. *J. Am. Chem. Soc.* **2018**, *140* (22), 7012–7020. https://doi.org/10.1021/jacs.8b04058.

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CONFIGURATION



VIONIC

VIONIC is our new-generation potentiostat/galvanostat that is powered by Autolab's new INTELLO software.

VIONIC offers the **most versatile combined specifications of any single instrument** currently on the market.

- Compliance voltage: ± 50 V
- Standard current ± 6 A
- EIS frequency: up to 10 MHz
- Sampling interval: down to 1 µs

Also included in VIONIC's price are features that would usually carry an additional cost with most other instruments such as:

- Electrochemical Impedance Spectroscopy (EIS)
- Selectable Floating
- Second Sense (S2)
- Analog Scan