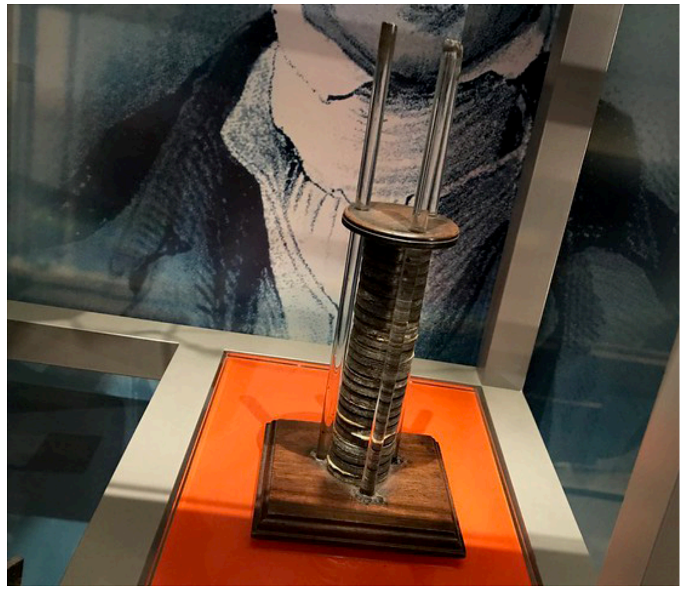
APPLICATION NOTE:
SPECTROELECTROCHEMISTRY

Techniques

- Spectroelectrochemistry

Keywords

- Electrolysis
- Oxidation-reduction reaction
- Reaction Monitoring
- Electron flow



"Alessandro Volta's Battery" by Matt from London via Flickr lic CCby2.0

Introduction

Electrochemistry is an extremely valuable tool for examining the kinetics of a wide range of oxidation-reduction reactions. In these types of reactions, electrons are exchanged between atoms spontaneously, which forms the basic physical principle behind chemical batteries. Just as specific oxidation-reduction reactions can cause electron flow, i.e. current, the same process can also work in reverse. Therefore, one can create a chemical reaction, that would not typically occur by running current through a substance. The most common example of this, known as electrolysis, is demonstrated by using an electrolytic cell to split water into diatomic hydrogen and oxygen. In this case a voltage source is connected to an anode and cathode which are placed in a water bath, and as current flows through the water, electrons are transferred from the oxygen to the hydrogen causing the molecule to separate.

Typical Spectroelectrochemisty Set-Up

Figure 1: A Spectroelectrochemical cell with integrated electrodes

Coupling electrolysis with UV/Vis absorption spectroscopy allows for real-time kinetic measurements of reactions as a function of current and voltage. Similar to how absorption spectroscopy is used in conjunction with titration or plasma process monitoring, but without the need for introducing addtional hazardous chemicals or generating dangerous plasmas. In a typical spectroelectrochemistry measurement, a specialized cuvette, like the one shown in figure 1, is fitted with optically transparent electrodes. Cells such as these along with the required potentiostat controller are offered by a variety of companies such as Metrohm and Pine Research . These electrodes consist of a platinum or gold mesh for most spectroelectrochemical cells, but some more advanced cells are also available with carbon or indium tin oxide electrodes as well. These cells are connected to an adjustable voltage source, which can be programmed to sweep the

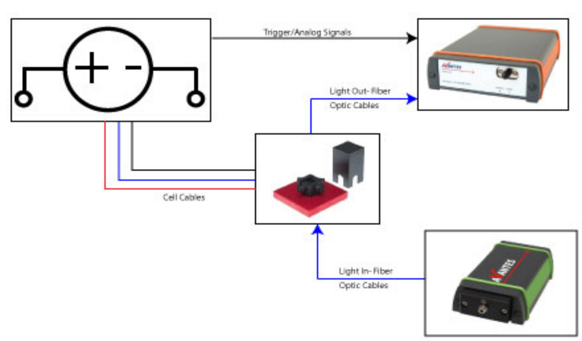


Figure 2 Schematic block diagram of a spectroelectrochemistry experiment showing the AvaSpec-2048 fiber-coupled spectrometer and the Ava-Light-Hal-S fiber-coupled light source from Avantes.

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voltage across the anode and cathode while simultaneously measuring the current which is being generated in the electrochemical cell. Employing this process, known as voltammetry in electrochemistry, in combination with a light source and a spectrometer, forms the basis of the study of spectroelectrochemistry.

Figure 2 shows a schematic block diagram of a typical spectroelectrochemistry instrument. From this diagram it can be seen that the voltage driver is not only connected to the spectroelectrochemical cell, but it is also critical for the voltage driver to be able to directly trigger the spectrometer each time that the voltage is adjusted. Without this capability it is impossible to ensure the acquired absorption spectra are correlated to the proper drive voltage.

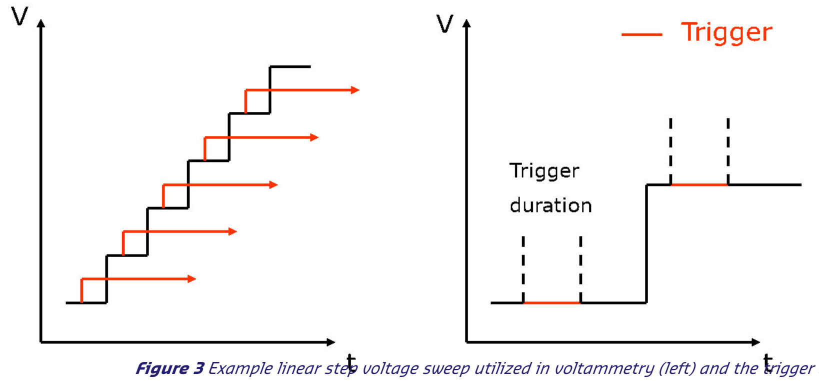

***Figure 3** Example linear step voltage sweep utilized in voltammetry (left) and the trigger duration for the spectrometer acquisition for each step (right).*

Figure 3 goes on to show a typical triggering diagram used in measuring linear sweep voltammetry. It is important to note that sweep rate is going to be limited by both the triggering capabilities and the data transfer rates of the spectrometer. Low-jitter, high-speed triggering is also critical to ensure that there is no latency between each voltage step and the spectrometer acquisition. Avantes AvaSpec-ULS2048CL-EVO is an ideal candidate for this application with a 890 nanosecond external trigger delay minimum and jitter of just 14 nanoseconds.

Once the spectrometer and voltage driver is properly synchronized, then software, such as Avantes' AvaSoft spectrometer acquisition software, can be used to generate a waterfall plot monitoring the changes in the absorption spectrum of the solution, for each step in the applied voltage. Figure 4 shows an example of one such waterfall plot where each dot on the current-voltage (IV) curve is directly correlated to each spectrum in the waterfall plot. For this acquisition, the spectrometer was configured to average two 2-ms integrations, and the trigger was set to initiate a scan every time it was edge-triggered and then autosave the spectrum.

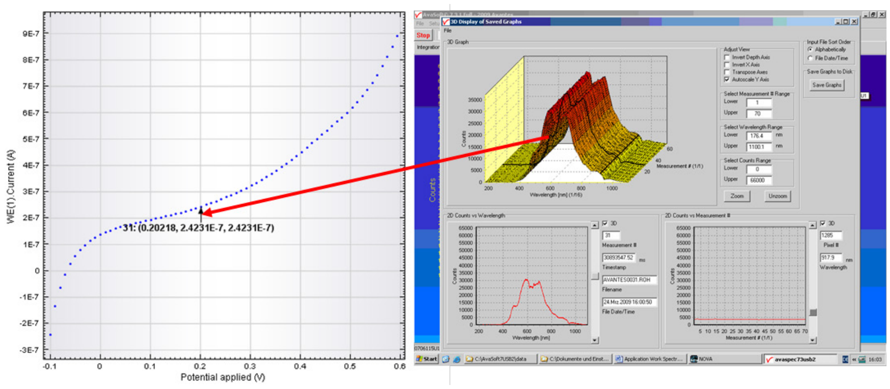

***Figure 4** Screenshot of a kinetic spectroelectrochemistry experiment performed using Avantes' Avasoft, spectrometer acquisition software.*

Application Example

Electrochemistry and by default spectroelectrochemistry, has gained importance in modern times due to its importance to battery technology. In fact, the entire field of electrochemistry was birthed when Alessandro Volta discovered the battery in 1793. He accomplished this by realizing that when he placed silver and zinc on opposite sides of a brine-soaked cloth, it generated a voltage. We now know that this resulted from a spontaneous oxidation-reduction reaction because the zinc ions have a reduction potential of -0.76V and the silver ions have a reduction potential of +0.80V, resulting in electrons spontaneously flowing from the zinc to the silver, thus generating current. Surprisingly, not a lot has changed with regards to battery technology since Volta's original invention, and as a result most modern battery technology relies on designing better and more efficient versions of this same effect.

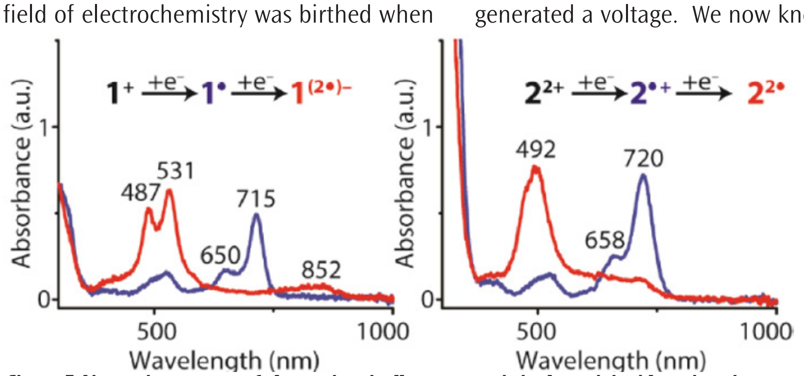

***Figure 5** Absorption spectra of electrochemically generated singly and doubly reduced states of 1+ and 22+ recorded in dimethylformamide, measured using the AvaSpec-ULS2048-USB2-50 from Avantes. [1].*

Recently teams from the chemistry departments of Macalester College and Saint Catherine University, both in Saint Paul Minnesota, working in conjunction, demonstrated how spectroelectrochemistry is utilized in battery research when they published a paper in ACS Omega [1] showing how they were capable of creating a shift of +0.57V to the reduction potential of pyromellitic diimides, by modifying its chemical structure. Since aromatic diimides, like these, are known to have attractive energy storage properties desireable in the photovoltaic industry, increasing their reduction potential could increase the voltage of batteries made from such molecules.

In this experiment, the teams utilized a Pine Research WaveNow potentiostat (current monitoring adjustable voltage source) with a platinum coil electrode, a Pine Research Spectroelectrochemical Cell Kit, and an AvaSpec-ULS2048-USB2-50 for their experiment. Example spectra for both singly and doubly reduced reactions, measured with this setup are shown in figure 5 and figure 6 demonstrating the differences in both the reduction potential and the absorption spectra.

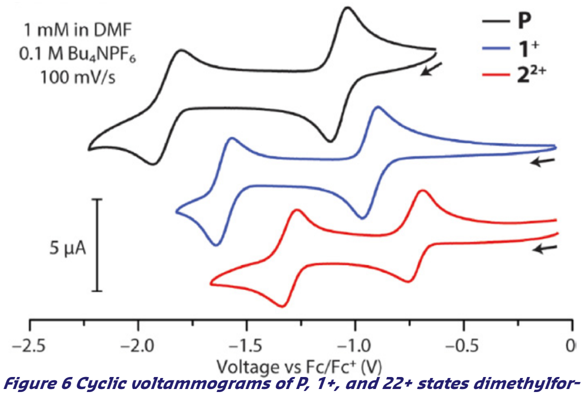

Figure 6 Cyclic voltammograms of P, 1+, and 22+ states dimethylformamide recorded using the WaeNow potentiostat by Pine Research. [1]

Final Thoughts

The above example is just one of many applications where spectroelectrochemistry is being used in the development of new battery technologies. While the examples shown above are all utilizing modular fiber-coupled set-ups, it should be stated that the nature of miniature spectrometer technology makes them ideal for integration into OEM systems. Avantes' Avaspec instruments are ideally suited to high speed triggered or continuous measurements such as those required in this application. All of the spectrometers discussed above are also available as OEM modules and can be integrated into turnkey laboratory spectroelectrochemistry devices, in addition to function as an add-on to existing laboratory equipment. These units can communicate via USB, Ethernet, and the native digital & analog input/output capabilities of the Avantes AS7010 electronics board which provides for a superior interface with other devices. Additionally, the Avantes AvaSpec DLL software development package, with sample programs in Delphi, Visual Basic, C#, C++, LabView, MatLab, and other programming environments, enables users to develop code for their own applications.

For more information about the full range of laboratory and OEM spectrometer options available from Avantes, please feel free to visit the website at www.avantesusa.com or give us a call at +1 (303)-410-8668 where our knowledgeable applications specialists are standing by to help.

Test Drive Instruments for Spectroelectrochemistry

AvaSpec-ULS2048CL-EVO

AvaSpec-NIR256/512-2.5-HSC-EVO

AvaSpec-ULS2048CL-EVO

References

- [1] A. J. Greenlee, Et al., "Pyridinium-Functionalized Pyromellitic Diimides with Stabilized" Radical Anion States ," ACS Omega 2018 3 (1), 240-245.