Spectroelectrochemical measurements

Keywords
UV/Visible spectroscopy, Electrochemical methods, Avantes spectrometer

Summary
Spectroelectrochemistry is an experimental method that combines an electrochemical measurement coupled to an in-situ spectroscopical measurement. The spectroscopical measurement can be performed either in transmittance or in reflectance. The light is used to probe the immediate vicinity of the working electrode located in the cell. The spectroscopic measurement provides useful complementary information during an electrochemical measurement. It can be used to identify reaction intermediates or product structures, during an electrochemical measurement.

Choice of spectrophotometer
For this application note, the USB 2.0 Avantes AvaSpec 2048 spectrometer was used (see Figure 1). This device is directly integrated in the NOVA software and can be controlled during an electrochemical measurement.

The spectrometer is connected to a cuvette holder using optical fibers. The cuvette holder is connected to a AvaLight light source (AvaLight-DH-S-BAL). This light source covers a range from 200 nm to 2500 nm. The light source can be connected to the Autolab using a dedicated cable, allowing the shutter of the light source to be operated remotely by using a TTL pulse.

Experimental conditions
The electrochemical cuvette is fitted with a Pt mesh working electrode and a Pt counter electrode. The reference electrode is a small Ag/AgCl 3 M KCl electrode that can be fitted in the lid of the cuvette. The optical path is 1 mm.

The cuvette is filled with a few mL of a 0.05 M potassium ferrocyanide (K₄[Fe(CN)₆]) solution. This solution is pale yellow in color. When the potassium ferrocyanide is oxidized in potassium ferricyanide (K₃[Fe(CN)₆]), the solution changes to orange. This electron transfer reaction can therefore be followed by visible light spectroscopy.

The measurement range of the spectrometer is defined in the software, between 375 and 600 nm (see Figure 2).

Figure 1 – A typical Avantes spectrometer

Figure 2 – Software settings used to control the spectrometer
The electrochemical measurements were performed using the staircase cyclic voltammetry. During the electrochemical measurement, a trigger is sent to the spectrometer every 10 points. For every 10 data points in the electrochemical measurement, one spectrum is acquired, using the settings defined in the software (see Figure 2).

At the beginning of the measurement, two additional measurements are taken in order to determine the reference spectrum and the dark spectrum (see Figure 3).

A single dark and reference spectrum is recorded for the whole experiment. These spectra are recorded at the start potential of the cyclic voltammetry measurement.

**Experimental results**

Figure 4 shows a typical linear sweep voltammetry recorded for the ferrocyanide/ferricyanide system.

At the end of the cyclic voltammetry measurement, the spectroscopic data is recovered from the spectrometer and correlated to the electrochemical data. The measured intensity is converted into absorbance, $A$, using the formula:

$$A = -\log \left( \frac{I - I_{dark}}{I_{reference} - I_{dark}} \right)$$

Where $I$ is the measured intensity, $I_{dark}$ is the measured dark intensity and $I_{reference}$ is the measured reference intensity.

Figure 5 shows an overlay of spectra recorded during the positive going potential scan. The spectra show an increase in absorbance at 425 nm, corresponding to the formation of the oxidized form of ferrocyanide.
The increase in absorbance at 425 nm is consistent with the yellow shift observed during the oxidation of the Fe(II) to Fe(III) complex.

**Conclusions**

NOVA provides direct integration of Avantes spectrophotometers and light sources. Combined with a suitable electrochemical cuvette, the combination of these instruments together with any Autolab potentiostat/galvanostat provides the means to perform any spectroelectrochemical measurement from one convenient software.

The spectroscopic data obtained during the measurement can be directly correlated to the electrochemical data, thus providing the means to create 3D plots combining the spectroscopic data with the electrochemical data.

**Date**

1 July 2012