Application Note AN-EC-009

Spectroelectrochemical measurements

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 absorbance. 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 Autolab spectrophotometer was used (see Figure 1). This device is directly integrated in the NOVA software and can be controlled during an electrochemical measurement.
The spectrophotometer is controlled through a USB interface by NOVA. The spectrophotometer can acquire one spectrum in the specified range each time the Autolab sends a TTL pulse to the spectrophotometer, using a dedicated cable.

Figure 1. The Autolab spectrophotometer.

The measurements described in the application note are performed in transmission mode.
The spectrophotometer is connected to a cuvette holder using optical fibers. The cuvette holder is connected to an Autolab light source. 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 ($K_4[Fe(CN)_6]$) solution.

The measurement range of the spectrophotometer is defined in the software, see Figure 2.
The electrochemical measurements were performed using the linear sweep voltammetry. During the electrochemical measurement, a trigger is sent to the spectrophotometer 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).

This solution is pale yellow in color. When the potassium ferrocyanide is oxidized in potassium ferricyanide ($K_3[Fe(CN)_6]$), the solution changes to orange. This electron transfer reaction can therefore be followed by visible light spectroscopy.

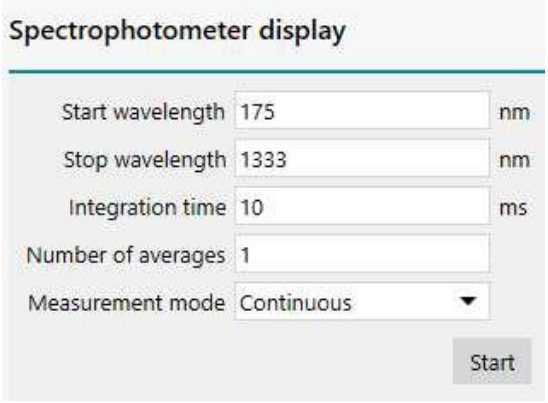


Figure 2. Software settings used to control the spectrophotometer.

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

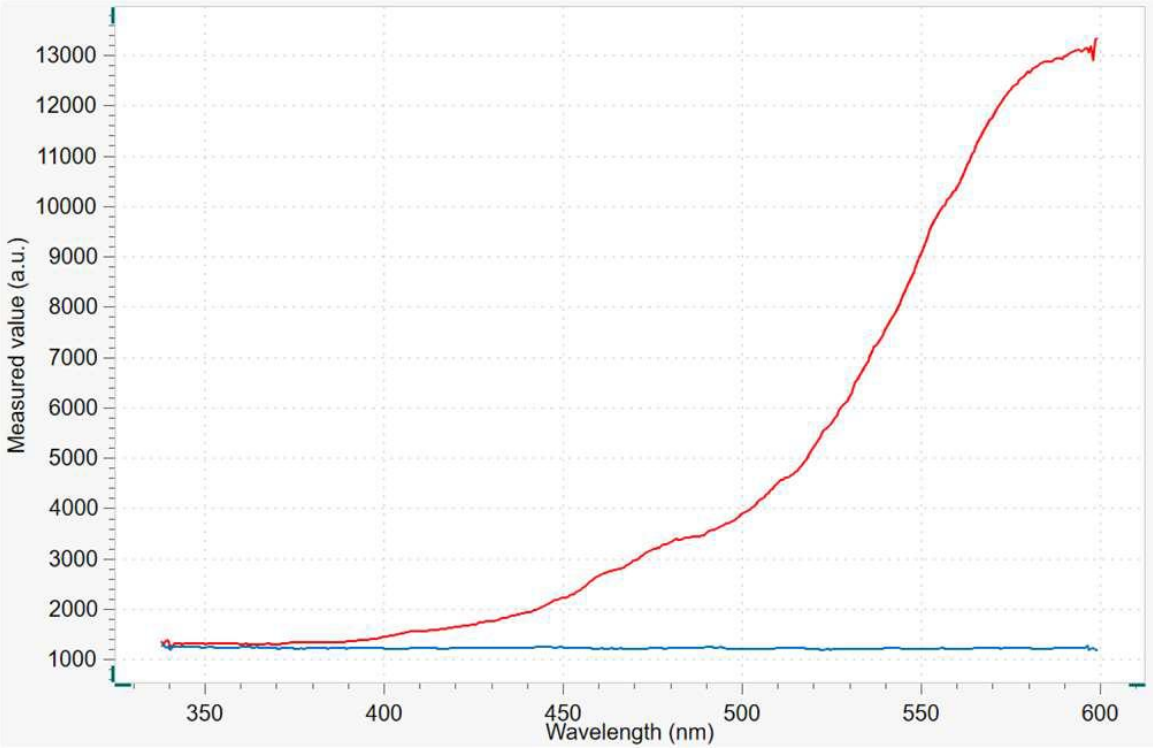


Figure 3. Dark spectrum (blue line) and reference spectrum (red line) recorded at the beginning of the measurement.

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

EXPERIMENTAL RESULTS

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

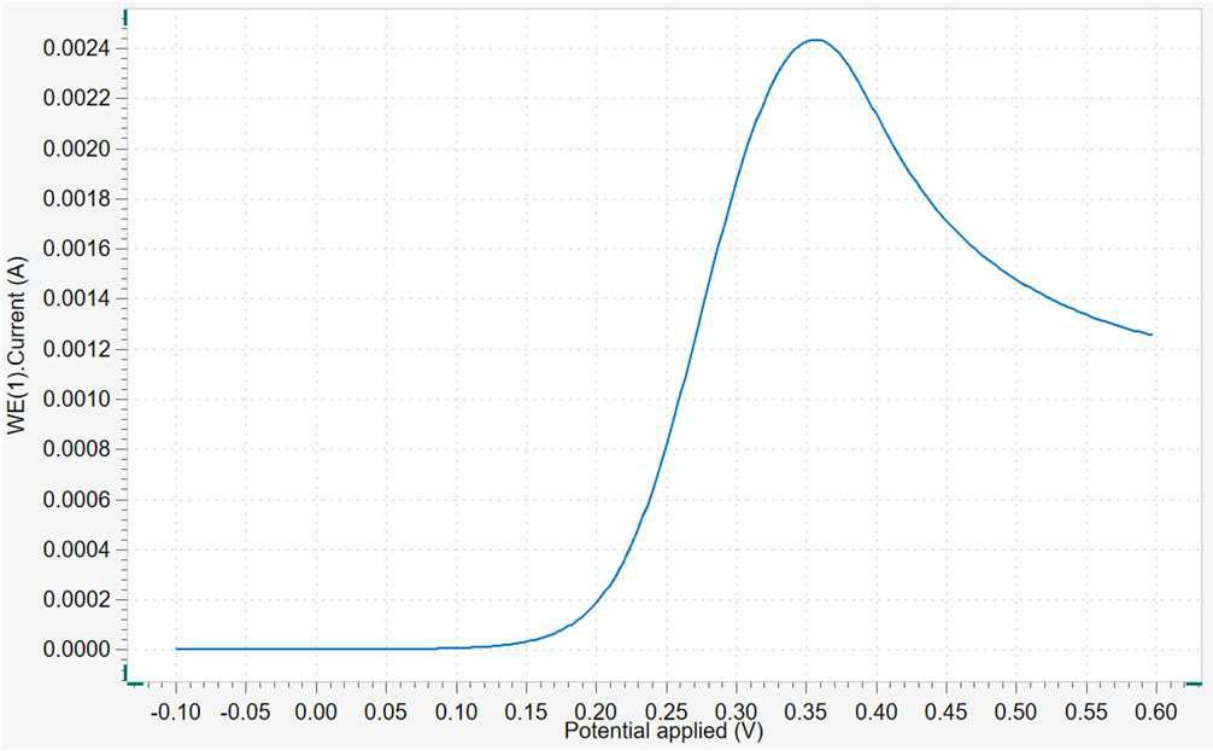


Figure 4. Typical linear sweep voltammogram for the oxidation of ferrocyanide.

At the end of the linear sweep voltammetry measurement, the spectroscopic data is recovered from the spectrophotometer and correlated to the electrochemical data. The measured intensity is converted into absorbance *A*, using the following Equation:

$$A = -\log\left(\frac{I - I_{Dark}}{I_{Reference} - I_{Dark}}\right) \qquad 1$$

Where I (a. u.) is the measured intensity, I_{Dark} (a. u.) is the measured dark intensity and $I_{Reference}$ (a. u.) 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.

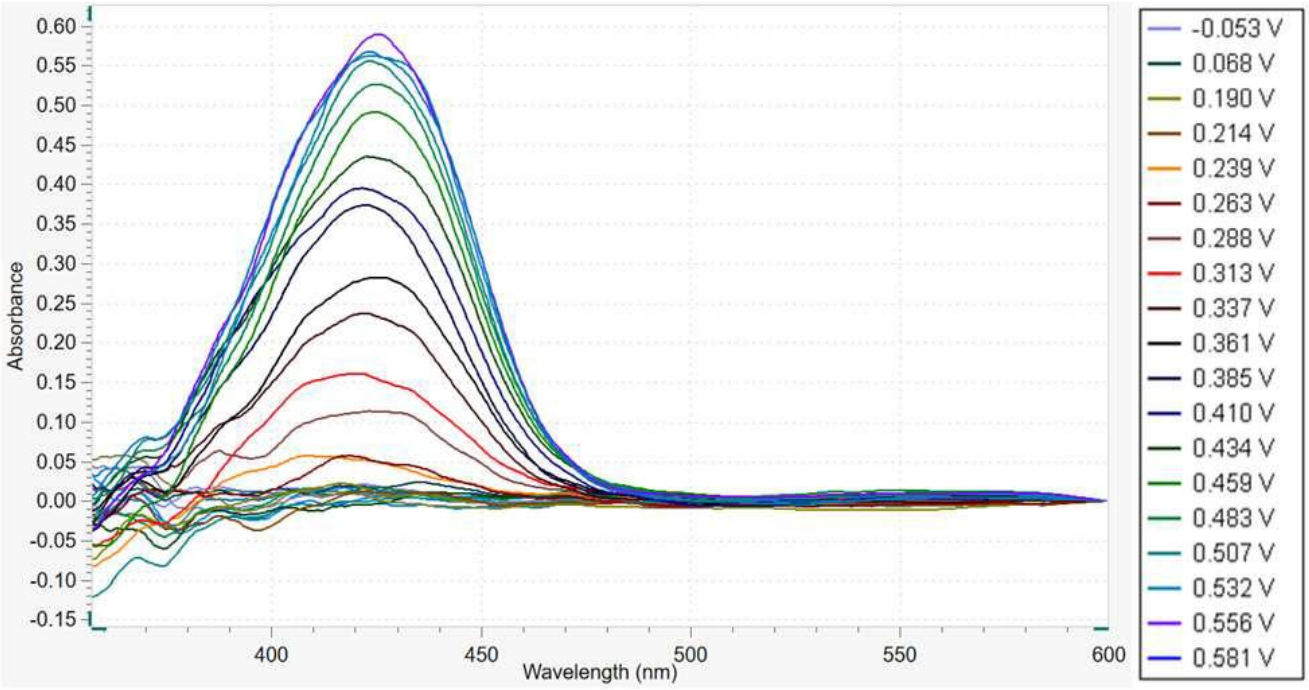


Figure 5. Overlay of spectra recorded between 360 nm and 600 nm for increasing potential values.

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

The Autolab NOVA software provides direct integration of Autolab 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.

CONTACT

瑞士万通中国
北京市海淀区上地路1号院
1号楼7702
100085 北京
marketing@metrohm.com.cn

CONFIGURATION

Autolab PGSTAT204

PGSTAT204 合了小巧格和模化。器包括基本恒位/恒流,其从 20 V,最大流 400 mA 或 10 A,与 BOOSTER10A 合使用。此恒位可随用附加模行展,例如 FRA32M 化学阻抗(EIS)模。

PGSTAT204 是一款惠的器,可置于室的任何位置。具有模和数字入/出,可控制 Autolab 附件和外部。PGSTAT204 包括内置模分器。与高性能的 NOVA 件用,可用于大多数准化学技。

Autolab PGSTAT302N

高端高流恒位/恒流,具有 30 V 从, 1 MHz,可与我的 FRA32M 模用,化学阻抗而。

PGSTAT302N 是流行的 PGSTAT30 的后款型。最大流 2 A,借助 BOOSTER20A 流范可展至 20 A,当流范 10 nA 流分辨率 30 fA。

Autolab Spectrophotometer UA

Autolab Spectrophotometer UA 是用于 UV/VIS/NIR波范(200nm至1100nm)的型。器被可与所有Autolab恒位/恒流器合使用,并得到NOVA件的支持,分光光度可以手控制或与化学量同步。可以保量期精掌握机,并可使化学数据和光数据直接相。

Autolab Spectrophotometer UB

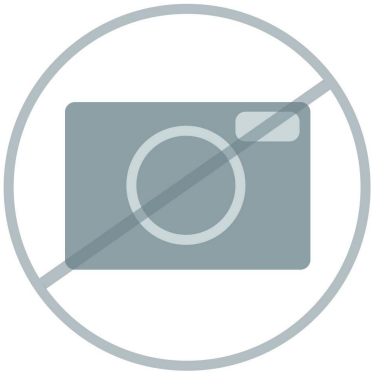
Autolab Spectrophotometer UB 是用于 UV/VIS 波范(200nm 至 850nm)的型。器被可与所有 Autolab 恒位/恒流器合使用,并得到 NOVA 件的支持。分光光度可以手控制或与化学量同步。可以保量期精掌握机,并可使化学数据和光数据直接相。

Autolab UV/VIS/NIR

Autolab UV/VIS/NIR分光光度套件包括:UA分光光度,光源,光和DIO触

Autolab UV/VIS

Autolab UV/VIS分光光度套件包括:UB分光光度,光源,光和DIO触。



NOVA 是通 USB 接口控制所有 Autolab 器的件包。由化学家化学而,集成了超二十余年的用体和最新的 .NET 件技,NOVA 使的 Autolab 恒位/恒流有更性能和活性。

NOVA 提供了以下的独特功能:

- 功能大且活的程序器
- 重要数据一目了然
- 大的数据分析和工具
- 集成化控制外器,如万通 LQH 液体理