Application Note AN-EC-009

光谱电化学测量

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. 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.

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).

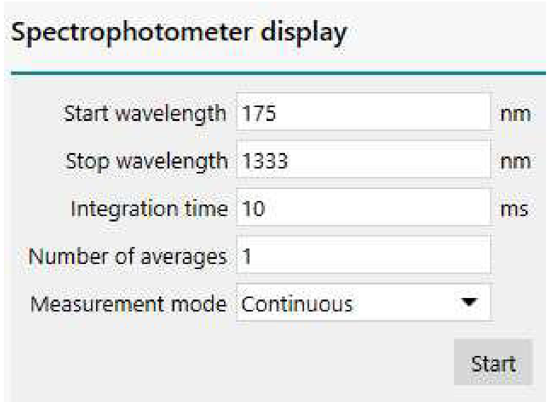

Figure 2. Software settings used to control the spectrophotometer.

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).

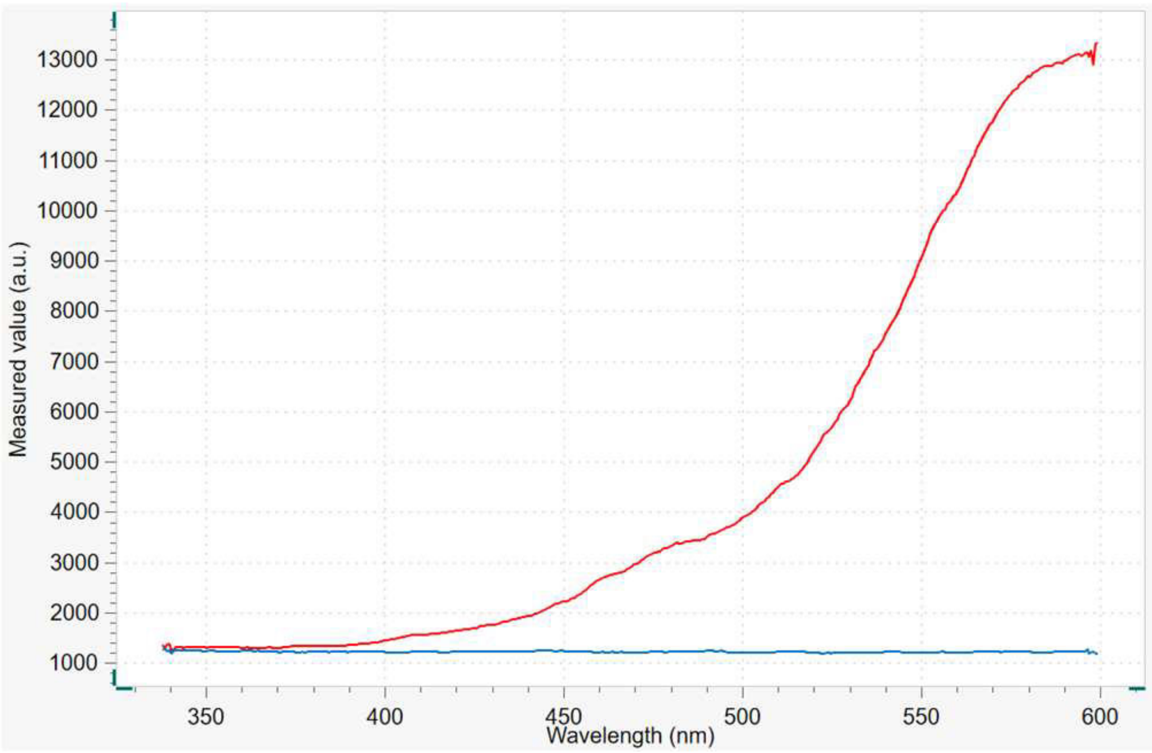

Figure 3. Dark spectrum (blue line) and reference spectrum (red line) recorded at the beginning of the measurement.

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.

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EXPERIMENTAL RESULTS

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

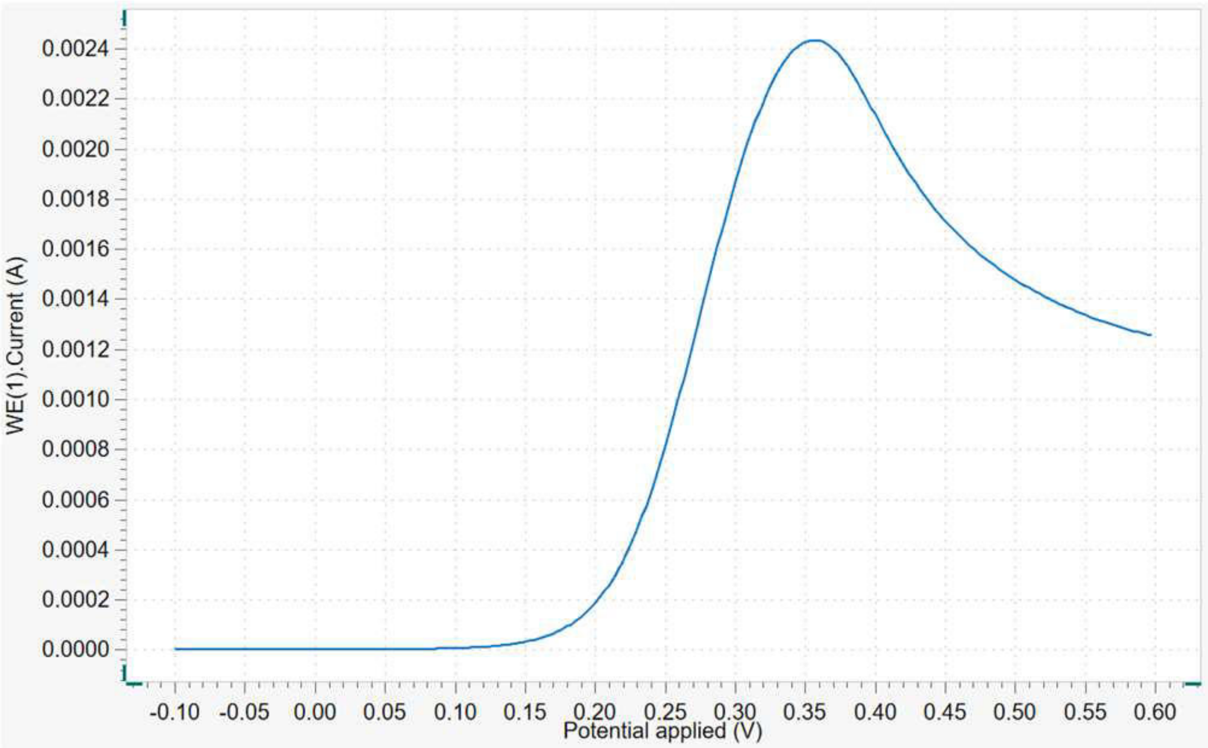

Figure 4. Typical linear sweep voltammogram for the oxidation of ferrocyanide.

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.

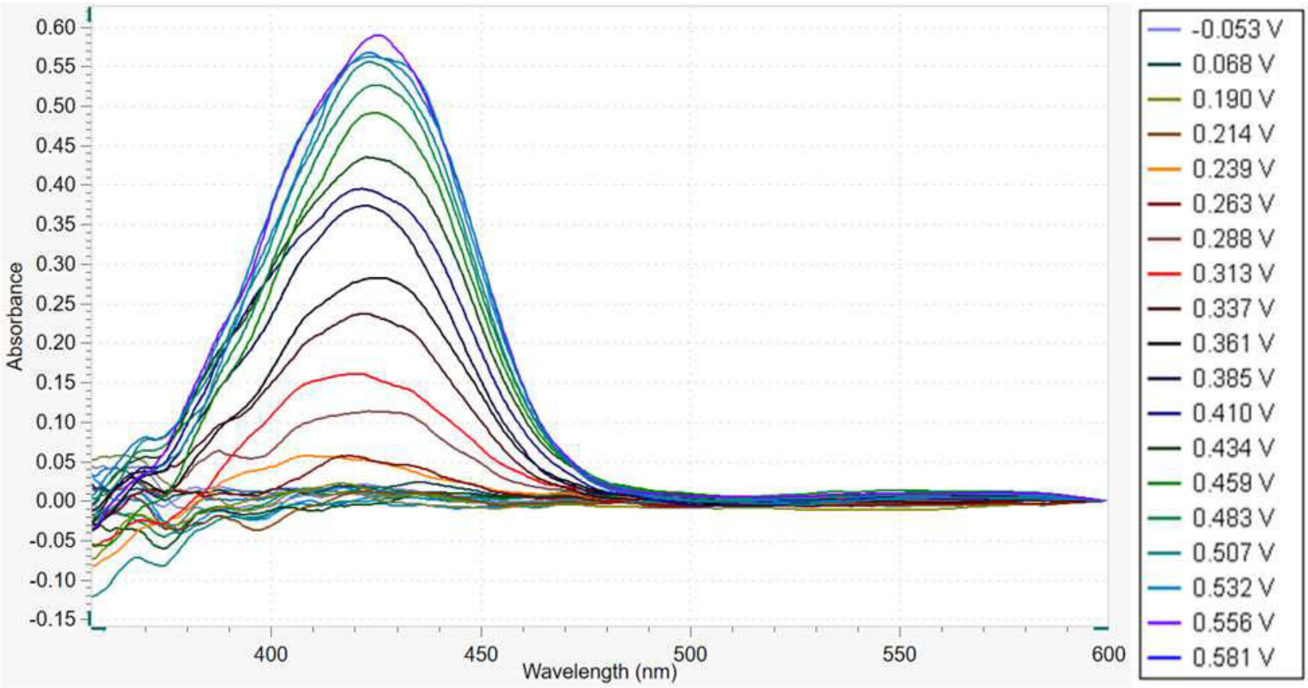

Figure 5. Overlay of spectra recorded between 360 nm and 600 nm for increasing potential values.

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.

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CONFIGURATION

Autolab PGSTAT204

PGSTAT204 结合了小巧规格和模块化设计。该仪器包括基本恒电位仪/恒电流仪,其顺从电压为 20 V,最大电流为 400 mA 或 10 A,与 BOOSTER10A 组合使用。此恒电位仪可随时用附加模块进行扩展,例如 FRA32M 电化学阻抗谱(EIS)模块。

PGSTAT204 是一款经济实惠的仪器,可置于实验室的任何位置。具有模拟和数字输入/输出,可控制 Autolab 附件和外部设备。PGSTAT204 包括内置模拟积分器。与高性能的 NOVA 软件联用,可用于大多数标准电化学技术。

Autolab PGSTAT302N

该恒电位仪/恒电流仪,具有 30 V 顺从电压,带宽为 1 MHz,可与我们的 FRA32M 模块联用,专门针对电化学阻抗谱而设计。

PGSTAT302N 是流行的 PGSTAT30 的后继款型。最大电流为 2 A,借助 BOOSTER20A 电流范围可扩展至 20 A,当电流范围为 10 nA 时电流分辨率为 30 fA。

Autolab Spectrophotometer UA

Autolab Spectrophotometer UA 是用于UV/VIS/NIR波长范围(200nm至1100nm)的紧凑型设备。该仪器被设计可与所有Autolab恒电位仪/恒电流仪器结合使用,并得到NOVA软件的支持,分光光度计可以手动控制或与电化学测量同步。这样可以准确掌握时机,并可使电化学数据和光谱数据直接相关。

Autolab Spectrophotometer UB

Autolab Spectrophotometer UB 是用于 UV/VIS 波长范围(200nm 至 850nm)的紧凑型设备。该仪器被设计可与所有 Autolab 恒电位仪/恒电流仪器结合使用,并得到 NOVA 软件的支持。分光光度计可以手动控制或与电化学测量同步。这样可以准确掌握时机,并可使电化学数据和光谱数据直接相关。

Autolab UV/VIS/NIR

Autolab UV/VIS/NIR分光光度计套件包括:UA分光光度计,光源,光纤电缆和两种DIO触发电缆

Autolab UV/VIS

Autolab UV/VIS分光光度计套件包括:UB分光光度计,光源,光纤电缆和两种DIO触发电缆。

NOVA 是设计为通过 USB 接口控制所有 Autolab 仪器的软件包。

由电化学家针对电化学而设计,集成了超过二十余年的用户体验和最新的 .NET 软件技术,NOVA 使您的 Autolab 恒电位仪/恒电流仪拥有更强性能和灵活性。

NOVA 提供了以下的独特功能:

- 功能强大且灵活的程序编辑器
- 重要实时数据一目了然
- 强大的数据分析和绘图工具
- 集成化控制外围仪器,诸如万通 LQH 液体处理设备

下载最新版本的 NOVA