Fluorescence spectroelectrochemistry of $[Ru(bpy)_3]^{2+/3+}$ in semi-infinite diffusion regime

Summary

Spectroelectrochemical techniques combine simultaneous electrochemical and spectroscopic data recording, which allow to obtain information about different properties of electroactive species or electrochemical-based processes. The ideal feature of these techniques is the ability to get time-resolved in situ spectroscopic information from the electrochemical processes. Although the most employed thin-layer configurations may be useful for some applications, they also produce a thin-layer electrochemical response, which sometimes is not desirable, and a diffusion-limited regime may be more appropriate to monitor electrochemical reactions.

In this Application Note, the Metrohm DropSens SPELEC instrument is used with the FLUORESCENCE KIT for time-resolved monitoring of electrochemical reactions in a semi-infinite diffusion regime by performing fluorescence spectroelectrochemistry of the $[Ru(bpy)_3]^{2+/3+}$ redox couple.

Configuration

SPELEC - SPELEC UV-VIS Instrument (200-900 nm)
SPELEC is an instrument for performing spectroelectrochemical measurements. It combines in only one box a Lightsource, a Bipotentiostat/Galvanostat and a Spectrometer (UV-VIS wavelength range: 200-900 nm) and includes a dedicated spectroelectrochemical software that allows optical and electrochemical experiments synchronization.

RPROBE-VIS-UV - Reflection probe VIS-UV
Reflection probe VIS-UV designed to perform reflection experiments suitable to work with our Reflection Cell for our Screen-printed electrodes or with any conventional cell.

REFLECELL - Reflection Cell for Screen-Printed Electrodes
Cell in Teflon suitable to perform reflection experiments with standard format Screen-Printed Electrodes with the electrochemical cell in the middle of the strip. Closing system with powerful magnets.

110 - Screen-Printed Carbon Electrode
Screen-Printed Carbon Electrode (Aux.:C; Ref.:Ag). Suitable for working with microvolumes, for decentralized assays or to develop specific sensors.

CAST - µStat Cable connector for Screen-Printed Electrodes
Connects any DropSens equipment with DropSens Screen-Printed Electrodes

Equipment

The versatile, compact and integrated instrument **SPELEC** was used for performing the luminescence spectroelectrochemical experiment. The rest of the setup is composed by a 395 nm LED (ref. LEDVIS395) in combination with the Fluorescence Kit for Screen-Printed Electrodes (ref. FLKITSPE) – including a high-pass and low-pass optical filters, a reflection probe (ref. RPROBE-VIS-UV) in a near-normal position to the electrode surface (epiluminescence mode) and a reflection spectroelectrochemical cell for Screen-Printed REFLECELL).

For the electrochemical reactions, Screen-Printed Carbon Electrodes (ref. 110) were employed.

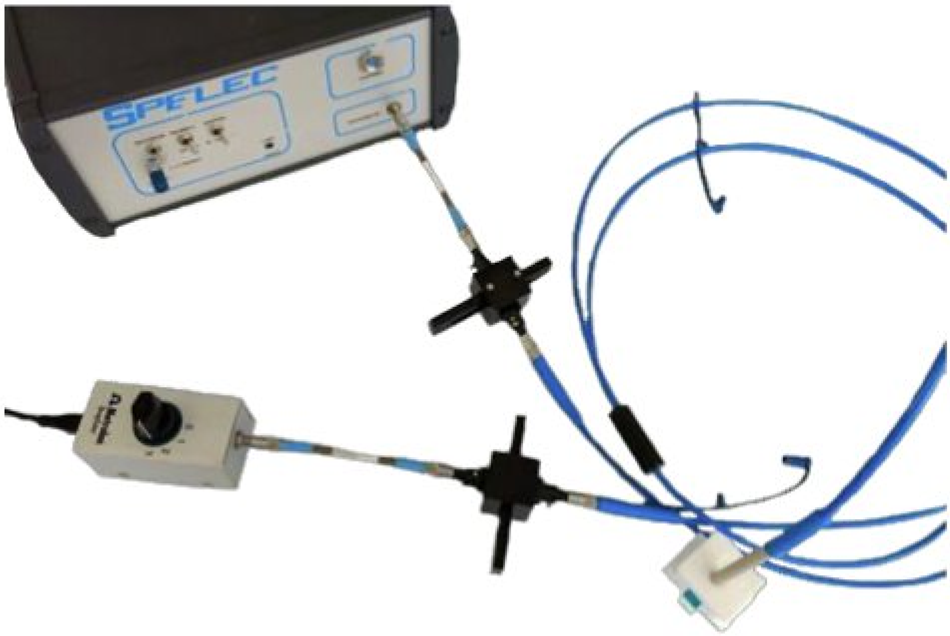

Figure 1. The SPELEC setup used for the fluorescence spectroelectrochemistry measurements

Methods

Screen-Printed Electrodes (ref.DRP-110) were employed for the spectroelectrochemistry experiments using 40 µL of a 2 mM $[Ru(bpy)_3]^{2+}$ solution in 0.1 M KNO_3. Cyclic voltammetry was used to produce the redox processes of the $[Ru(bpy)_3]^{2+/3+}$ couple.

Results

Evaluation of semi-infinite diffusion behaviour

Cyclic voltammetry experiments were initially performed to verify that the electrochemical response of the $[Ru(bpy)_3]^{2+/3+}$ redox couple follows the semi-infinite diffusion regime. The figure shows the cyclic voltammograms at several scan rates and the linear relationship between the anodic peak current and the square root of the scan rate. As the system follows the Randles-Sevcik equation (eq. 1) for a planar electrode and reversible processes, this confirms the semi-infinite diffusion regime under the experimental conditions.

$$i_p = (2.69x10^5)\, n^{3/2}\, A\, C\, D^{1/2}\, v^{1/2} \quad (1)$$

where i_p is the peak current intensity, n is the number of electrons, A is the electroactive electrode area, C is the bulk concentration of the species, D is the diffusion coefficient and v is the scan rate.

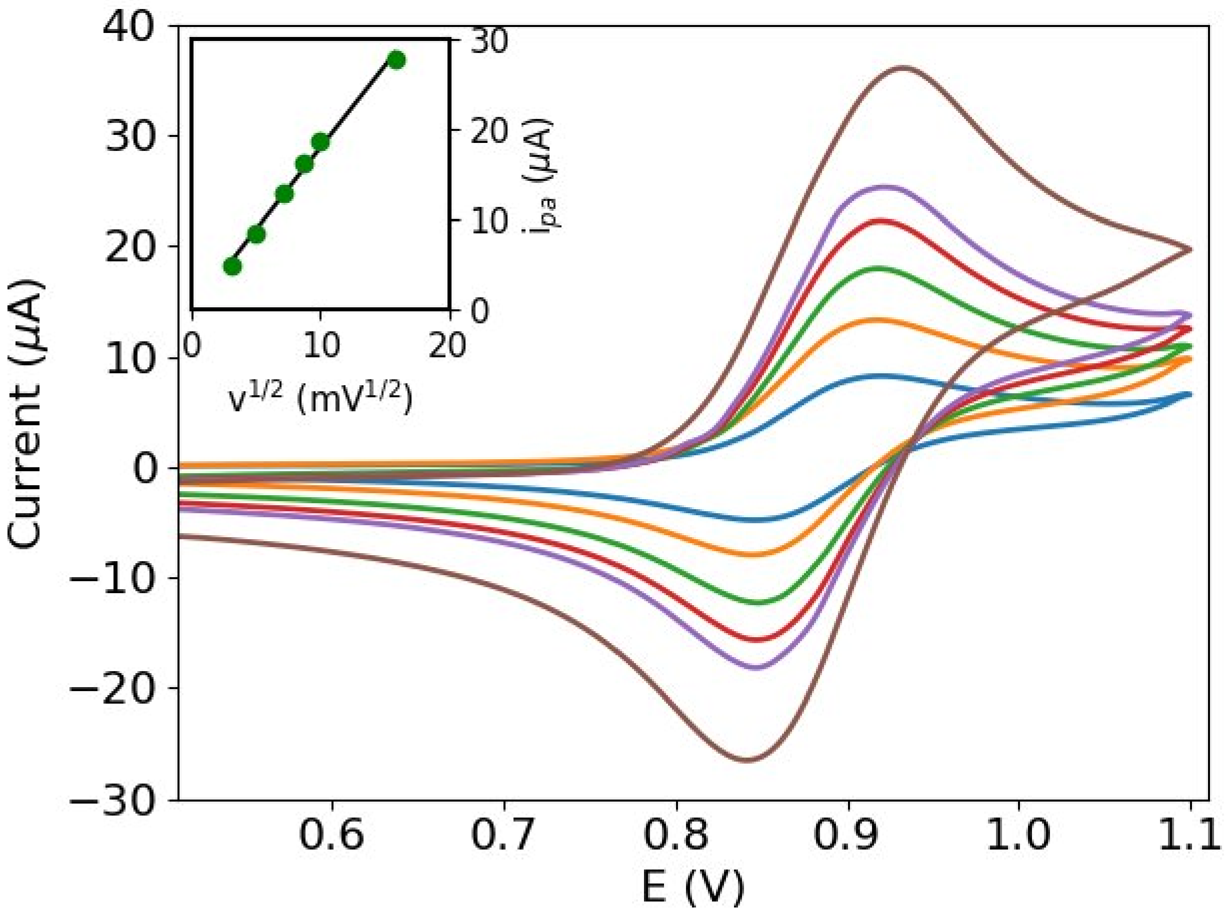

Figure 2. Cyclic voltammograms at different scan rates.

Spectroelectrochemical monitoring of $[Ru(bpy)_3]^{2+/3+}$ redox reaction

The electrochemical reaction of the $[Ru(bpy)_3]^{2+/3+}$ redox couple can be monitored by luminescence spectroelectrochemistry because the reduced species is luminescent and the oxidised species is non-luminescent (it is an electroluminochromic species).

$$[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{3+} + 1e^-$$

As shown in the figure, the initial luminescent emission decreased after the oxidation reaction, and increased back with the subsequent reduction reaction. The evolution of the emission is more clearly observed by representing the variation of the derivative luminescent emission with the potential. These results demonstrate the good correlation between the electrochemical reactions and the luminescent response during the experiments.

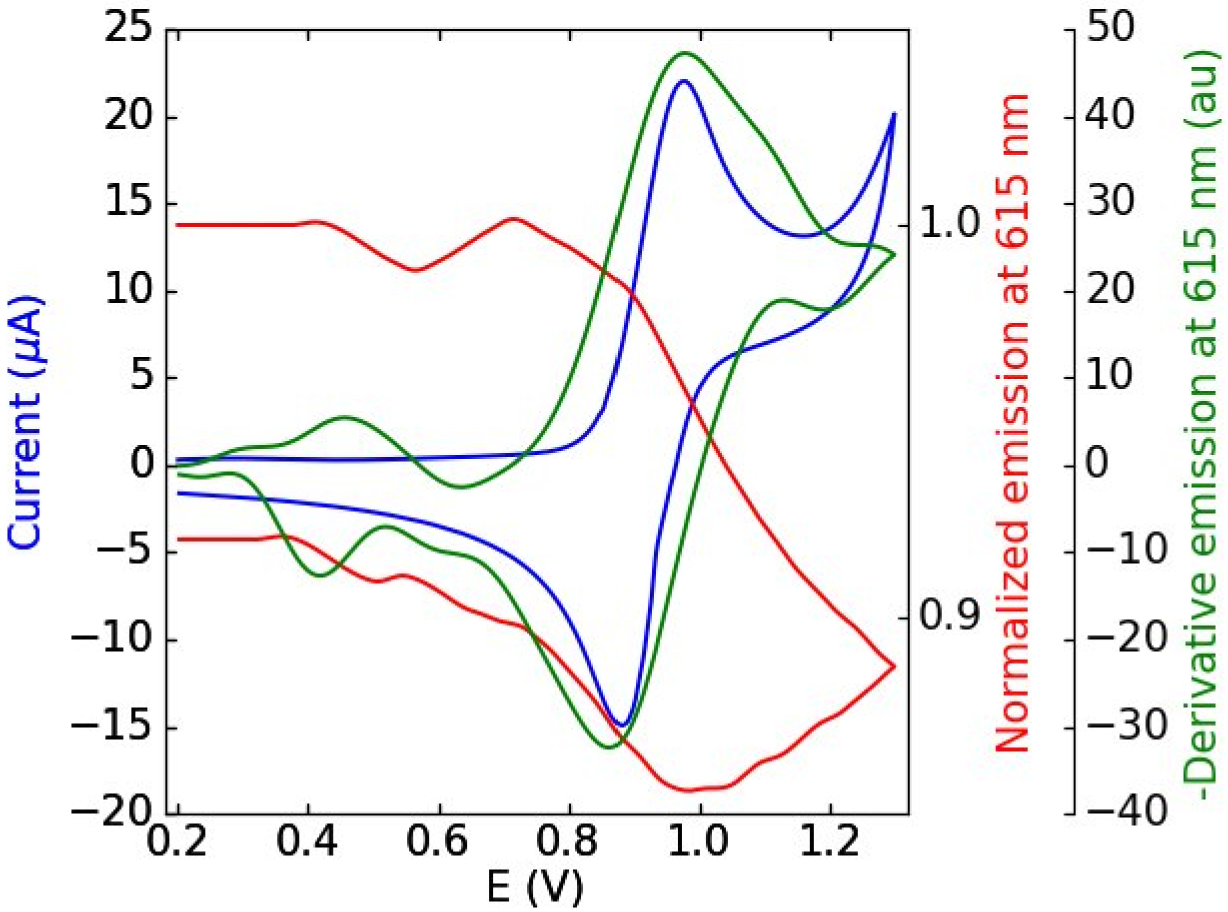

Figure 3. Overlayed cyclic voltammogram (blue), voltabsorptogram (green) and derivated voltabsorptogram (red).

Further reading

Related documents

Brochure on LEDVIS395 and FLKITSPE

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