Application Note AN-FLU-001

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

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.

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.

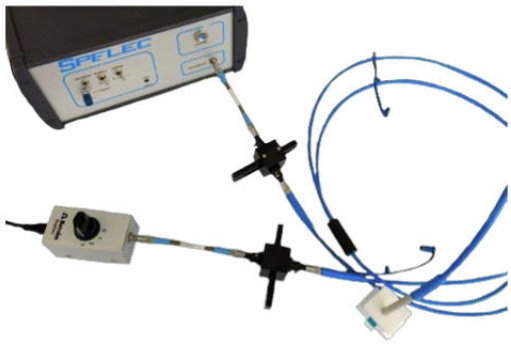

Figure 1. The SPELEC setup used for the fluorescence spectroelectrochemistry measurements

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.

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.

$$i_p = (2.69 \times 10^5)\, n^{3/2}\, A\, C\, D^{1/2}\, v^{1/2} \quad (1)$$

RESULTS

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.

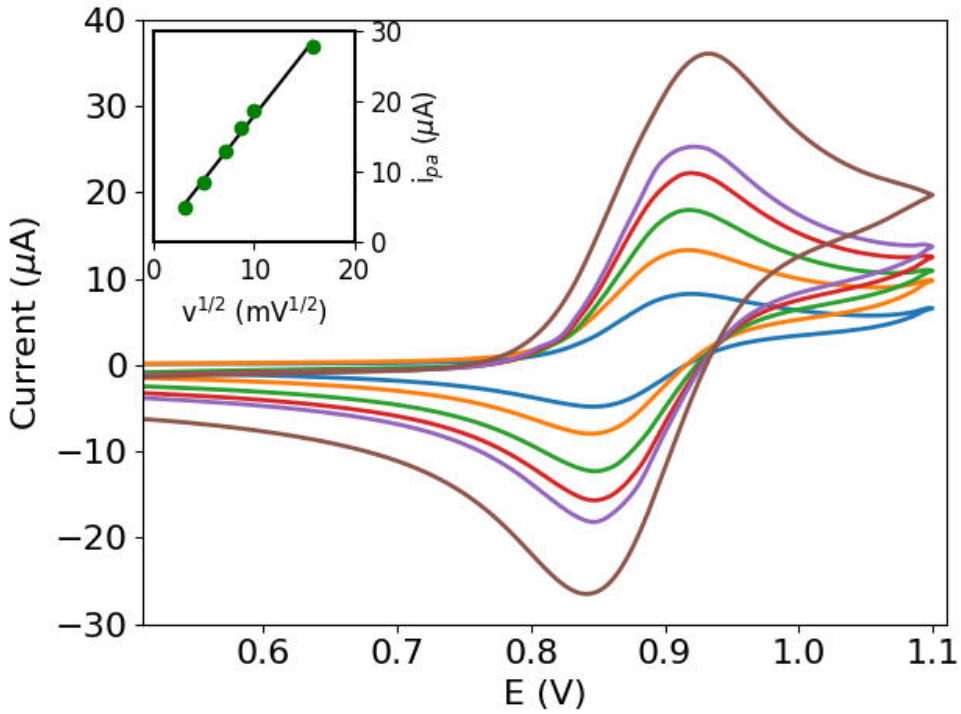

Figure 2. Cyclic voltammograms at different scan rates.

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.

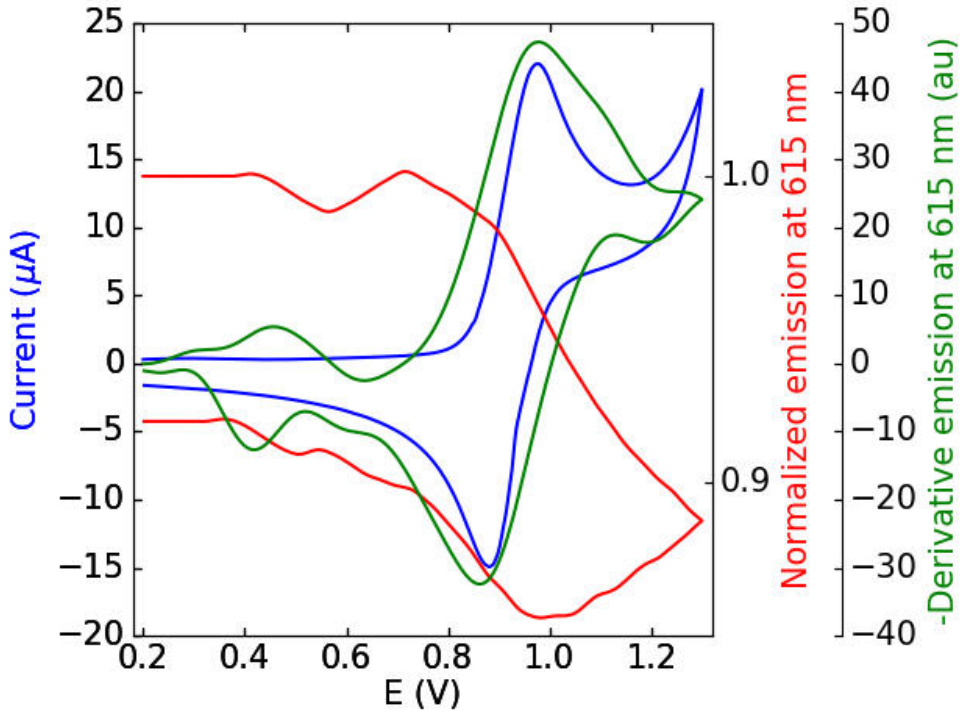

Figure 3. Overlayed cyclic voltammogram (blue), voltabsorptogram (green) and derivated voltabsorptogram (red).

FURTHER READING

Related documents

Brochure on LEDVIS395 and FLKITSPE

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CONFIGURATION

SPELEC UV-VIS 200-900 nm

SPELEC 是一行光化学量的器。SPELEC 将一个光源、一个双恒位/恒流和一个光(UV/VIS 波范:200-900 nm)合在一个箱子中,并配有用的光化学件,可同步行光学和化学。

用于行光的盒由 2 个短的光体(600 µm)成,末端 SMA 905 接,2 个光器(其中一个 230-500 nm,一个 300-750 nm 波)以及 2 个
器支架。
根据注的范(参考 LEDUV275、LEDVIS395 或 LEDRGB)增添所需的激光,从而完成置。
了用网印刷(SPE)行与光化学相合的光光(参考 SPELEC),得当的反射探(RPROBE)和反射池(REFLECELL)。

LED - 395 nm

波 395 nm 的 LED 灯

"Fluorescence Kit for screen-printed electrodes (Includes 2 x optical fibers (600 um) ended in SMA 905 connections, 2 x optical filters 230-500 and 300-750 nm 2 x holders, 1 x RPROBE-VIS-UV and 1 x REFLECELL)"

Kit designed for those researchers interested in performing fluorescence spectroscopy experiments with screen-printed electrodes

网印刷(助:C;参比:Ag)。 宜合微体行分散定或研特定感器。