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.

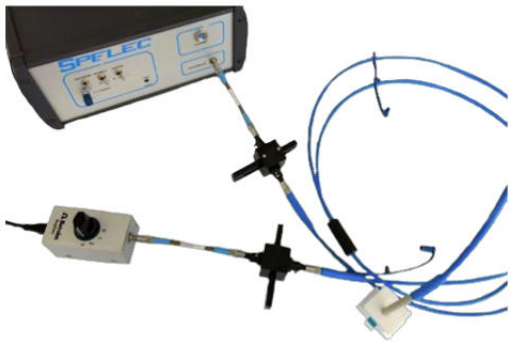

Figure 1. The SPELEC setup used for the fluorescence spectroelectrochemistry measurements

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.

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.

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

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.

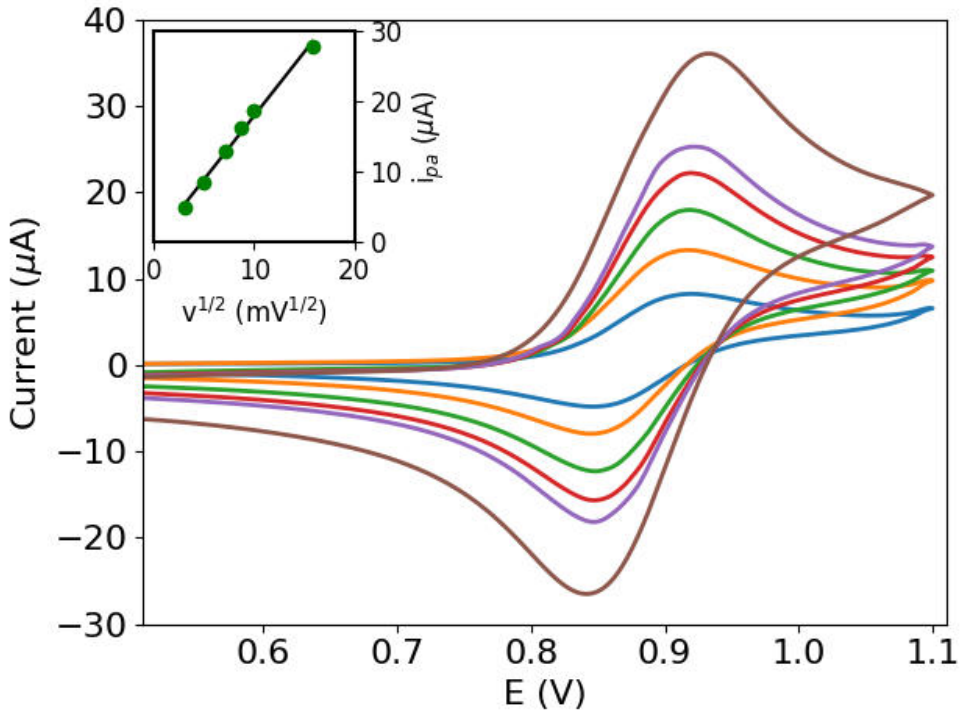

Figure 2. Cyclic voltammograms at different scan rates.

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.

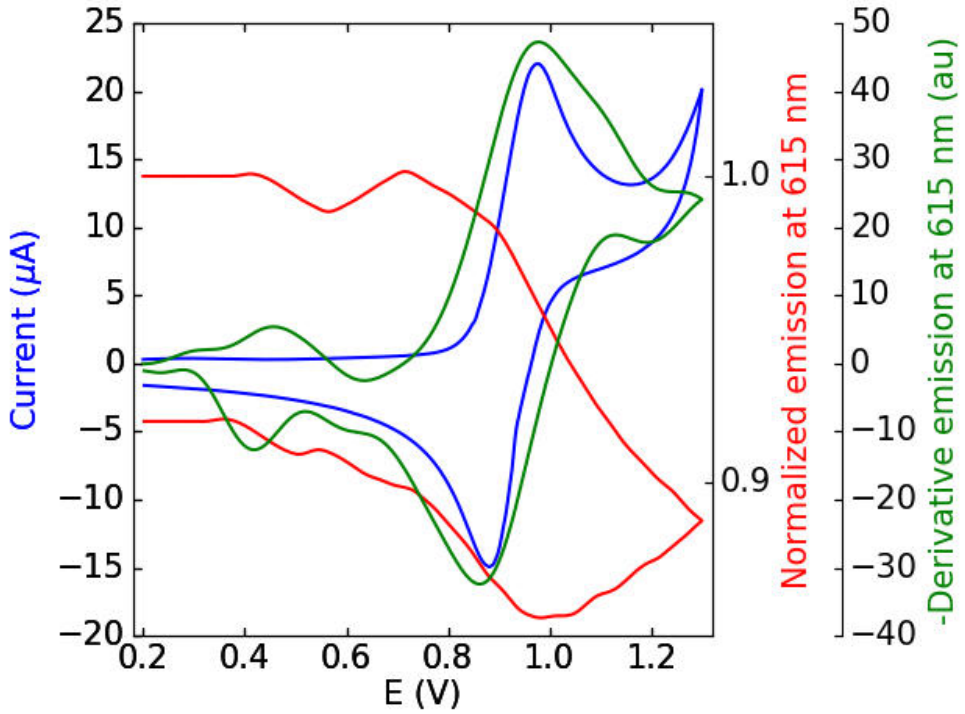

Figure 3. Overlayed cyclic voltammogram (blue), voltabsorptogram (green) and derivated voltabsorptogram (red).

FURTHER READING

Related documents

Brochure on LEDVIS395 and FLKITSPE

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CONFIGURATION

SPELEC UV-VIS 200-900 nm

SPELEC 是一种进行光谱电化学测量的仪器。SPELEC 将一个光源、一个双恒电位仪/恒电流仪和一个光谱仪(UV/VIS 波长范围:200-900 nm)结合在一个箱子中,并配有专用的光谱电化学软件,可同步进行光学和电化学实验。

用于进行荧光实验的试剂盒由 2 个短的光导体(600 µm)组成,末端为 SMA 905 接头,2 个光过滤器(其中一个为 230-500 nm,另一个为 300-750 nm 波长)以及 2 个
过滤器支架。
根据关注的范围(参考 LEDUV275、LEDVIS395 或 LEDRGB)增添所需的激发光,从而完成设置。
为了用丝网印刷电极(SPE)进行与光谱电化学相结合的荧光光谱实验(参考SPELEC),获得适当的反射探针(RPROBE)和反射池(REFLECELL)。

LED - 395 nm

波长为 395 nm 的 LED 灯

该套件专为有兴趣使用丝网印刷电极进行荧光光谱实验的研究人员设计(包含 2 个 SMA 905 接口光导体(600 µm)、2 个滤光片(230-500 nm 和 300-750 nm)、2 个支架、1 个 RPROBE-VIS-UV 探头及 1 个 REFLECELL)。

丝网印刷碳电极(辅助电极:C;参比电极:Ag)。 宜结合微体积进行分散测定或研发特定传感器。