UFS-SEC:
the SpectroElectrochemical Cell for UV-Vis, NIR and IR measurement

I – INTRODUCTION

The tandem application of spectroscopy to electrochemistry can be carried out either *ex situ* or *in situ*. In some cases the *ex situ* method may be of limited use, in that something could change upon removing the sample from the electrolytic solution under the control of the working potential. This possible drawback can be circumvented by *in situ* spectro-electrochemistry, in which the measurement is carried out simultaneously with the redox change. Conversely, while *ex situ* measurements do not require special spectroscopic apparatus, *in situ* experiments need special cells designed to be the best compromise between the requirements of spectroscopic and electrochemical techniques, which do not always coincide. A reasoned compromise concerning the size of the cell, the electrode geometry, the choice of the supporting electrolyte and the sample concentration is critical. Consequently, many different cell designs and optically transparent electrodes developed for specific spectroscopic methods are described in scientific literature [1].

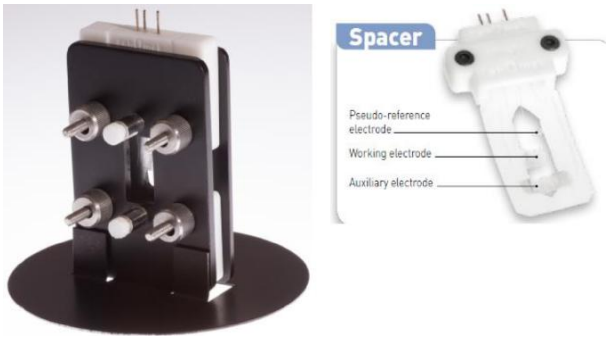

Figure 1: Thin-layer spectro-electrochemical cell (left). Zoom on the Electrode configuration, the so-called "spacer" (right).

In this application note, the use of a thin layer spectro-electrochemical cell is presented (Fig. 1). Firstly, experimental information about the setup is presented. Then, the specificity of the thin layer cell is discussed. Finally, UV-Vis and IR measurements are shown.

II – EXPERIMENTAL CONSIDERATIONS

The electrodes are wired to 2 mm banana plugs so that they can be connected to any Bio-Logic potentiostat (Fig .2).

The colors of the wires are the same as the Bio-Logic standard *i.e.* Red to working electrode, white to the reference electrode (here a pseudo-reference) and blue to counter electrode.

Figure 2: The spacer with the three wires.

The cell can be placed directly in a bench spectrometer. Alternatively, optical fibres can be used to connect the cell to light source and to the spectrometer (Fig.3).

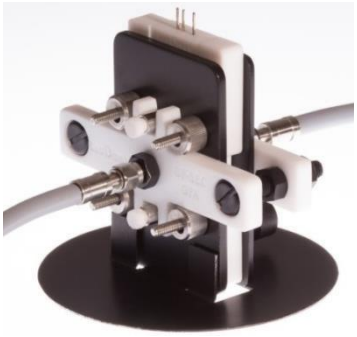

Figure 3: Spectroelectrochemical cell with optical fibres.

Another point that has to be emphasized concerns synchronization. EC-Lab® has a trigger ouput (available in the technique builder section) that allows users to synchronize the spectro (from spectrometer) and electro-chemical (from the potentiostat) acquisition.

III – MEASUREMENT

III - 1 GENERAL CONSIDERATIONS

In such finite-diffusion conditions, a thin solution layer (about 0.2 mm) adjacent to the electrode is confined by the cell walls, so that the cell thickness is smaller than the diffusion layer and the mass transfer can be ignored. The most significant virtue of thin-layer cells is the absence of diffusion and the rapidity with which the electroactive species can be completely electrolyzed. The drop to zero of the current flow following the peak in the current potential plot is a characteristic behavior of thin-layer cells, indicating exhaustive electrolysis of the cell reactant and minimal diffusion effects in thin-layer electrochemical cells.

Small potential sweep rates (2-10 mV/s) are necessary both to ensure the homogeneity of the reactant/product concentrations in the cell and to control the resistive effects.

In fact, one of the main problems with thin layer cells is the *i*R gradient across the electrode surface and between the electrode and the bulk solution. This gradient may affect the shape of an electrochemical response, even if it does not affect quantitative determinations.

The *i*R drop can be also minimized by increasing the supporting electrolyte concentration.

The design of a real thin-layer cell of exactly predetermined and fixed thickness is still problematic. In fact, the narrowness of the thin cavity is, to a limited extent, dependent on the mounting procedure, so exact reproducibility is, in practical terms, very difficult to achieve.

However, this aspect can be easily overcome by using either a colorimetric calibration curve or, by micro-coulometry recorded in the cell to acquire knowledge of the electrode area,

A CV should be registered in your SEC cell to better localize the redox process of your interest: in fact, the UF spacer has an Ag pseudo-reference electrode, which is sensitive to the solution medium (but is expected to remain constant in time in each given experimental condition) Potential drifts can be possibly observed in the presence of irreversible redox reactions, which may severely alter the solution/analyte composition.

Diffusion is limited in thin layer conditions, so you can run your spectra after the stepwise redox change of your sample, choosing the step size (potentials and time) according to your specific needs.

As discussed, in order to keep the *i*R drop as low as possible, the current should also be kept low, this means that low scan rates *and* low sample concentrations may be preferred. However, in some cases, due to the narrowness of the optical path, the use of a relatively high concentration of the sample may be required to study the changes of bands with a low molar extinction coefficient. You should adjust the best experimental conditions for every specific experiment, even if, as a general rule, a millimolar concentration appears to be a reasonable compromise in many cases.

III - 2 UV-VISIBLE

A CV of the Ferrocen in Dichloromethane with $TBAPF_6$ as supporting salt (0.2 M) is shown in Fig. 4.

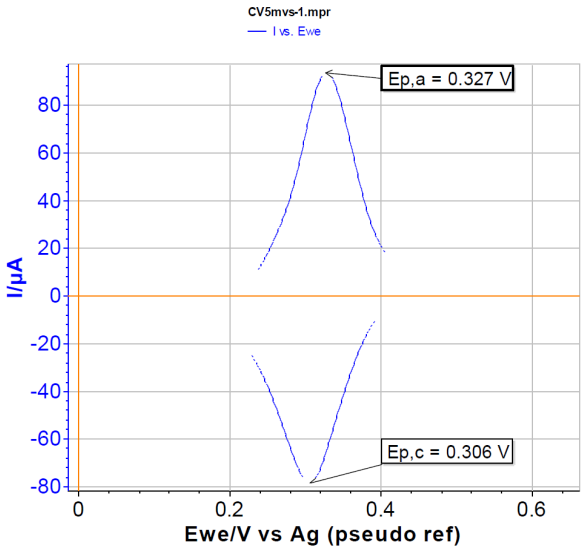

Figure 4: CV of Ferrocene in CH_2Cl_2/TBAPF$_6$ (0.2M) at 5 mV/s.

During the potential sweep spectrometer data was collected every 50 mV. The starting potential is +150 mV. The resulting spectra are shown in Fig. 5.

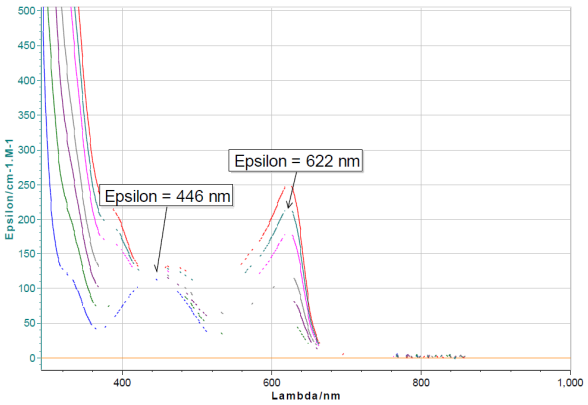

Figure 5: UV-Vis spectra acquired during the potential Sweep of ferrocene in CH_2Cl_2/TBAPF$_6$ (0.2M) at 5 mV/s. Initial potential: 150 mV. A spectra is measured every 50 mV.

III - 3 INFRARED

Due to the high Infra-Red absorbance of more common solvents and electrolytes, a very carefully measured background should be obtained before every IR spectro-electro-chemical experiment. For the same reason, in these experiments it is also important to avoid changing the tightening of the cell screws during the experiment itself, to avoid changes of the optical path.

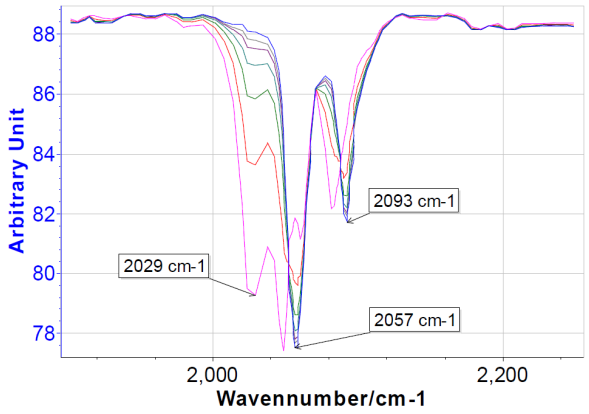

Figure 6: IR spectra acquired during the potential sweep of $[Pt_6(\mu\text{-}PtBu_2)_4(CO)_6]^{2+}$ (9 mM in CH_2Cl_2/TBAPF$_6$ (0.2M). Initial potential: 150 mV. A spectra is measured every 50 mV.

IV – CONCLUSIONS

In this application note, we have shown how to set up a spectro-electrochemical investigation. In the last paragraph, spectro-electrochemical measurements (UV-Vis and IR) are shown.

Data files can be found in :
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Fundamental Electrochemistry\ AN52_spectroEchem_IR_DCM2

REFERENCES

1) M. Krejčik, M. Daněk and F. Hartl, J. Electroanal. Chem., 317 (1991) 179.
2) P. Leoni, F. Marchetti, C. Bonaccorsi, F. Fabrizi de Biani, L. Marchetti, P. Zanello, Chem. Eur. J., 14 (2008) 847.

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