Application Note AN-SEC-002

Gathering information from spectroelectrochemical experiments

Calculation of electrochemical parameters from data

In-situ spectroelectrochemistry provides dynamic electrochemical and spectroscopic information concurrently with the redox reaction occurring on the electrode surface. Although different spectroelectrochemical configurations can be used, simple equations explain how to relate electrochemistry and spectroscopy for each experimental setup.

This Application Note describes how the quantification of one electrochemical parameter (the diffusion coefficient) is calculated from the spectroscopic data as a proof of this concept.

FUNDAMENTAL CONCEPTS

The Lambert–Beer law relates absorbance (*Abs*) to the molar absorption coefficient (ε), the optical path length (*b*), and the electroactive compound concentration (*C*):

$$Abs = \varepsilon . b . C$$

Taking into account the following electrochemical reaction:

$$A - e^{-} \rightarrow B$$

the spectroscopic monitoring process in a normal transmission configuration means that the light beam passes through each infinitesimal layer (*n*) until it arrives at the electrode surface.

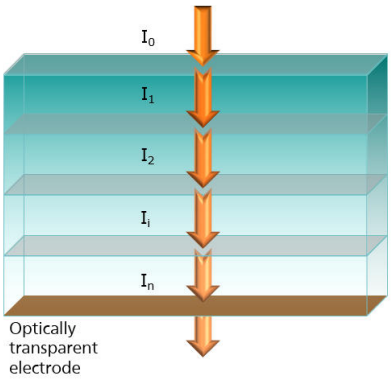


Figure 1. Normal transmission configuration.

Each layer is considered as a homogeneous solution (Figure 1) and the absorbance can be expressed as the sum of the absorbance of these layers.

$$Abs = Abs_1 + Abs_2 + \cdots + Abs_n = \varepsilon bc_1 + \varepsilon bc_2 + \cdots + \varepsilon bc_n$$

$$Abs = \frac{\varepsilon\, b}{n} \sum_{i=1}^{n} c_i$$

Considering also that a segment of solution of thickness *dy* and cross-sectional area *A* is uniformly illuminated and only *B* species absorb light, the differential absorbance registered upon passage of the light though this segment is [1]:

$$dAbs = \varepsilon_B C_B(y,t)dy$$

and then, the total absorbance is given as:

$$Abs = \varepsilon_B \int_0^\infty C_B(y,t)dy$$

If *B* species are stable, the integral is the total amount of *B* species per unit area and is equal to *Q/nFA*. Then, the absorbance is calculated as:

$$Abs = \varepsilon_B \frac{Q}{nFA}$$

Furthermore, considering that the charge *Q* is given by the integrated Cottrell equation:

$$Q = \frac{2nFAD_A^{1/2}C_A t^{1/2}}{\pi^{1/2}}$$

The total absorbance is therefore:

$$Abs = \varepsilon_B C_A \left(\frac{4D_A t}{\pi}\right)^{1/2}$$

The methodology followed is exactly the same when the spectroelectrochemical experiment is carried out in normal reflection configuration (Figure 2), but in this case the light passes though the solution two times: when it goes to the electrode surface and when is reflected back.

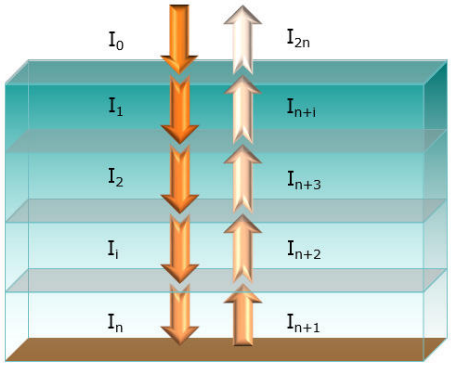


Figure 2. Normal reflection configuration.

For that reason, the absorbance equation is expressed as such:

$$Abs = \varepsilon_B C_A 2 \left(\frac{4D_A t}{\pi}\right)^{1/2}$$

If the light does not arrive completely perpendicular to the electrode surface, the angle of incidence must be taken into consideration:

$$Abs = \varepsilon_B C_A \frac{2}{cos\theta}\left(\frac{4D_A t}{\pi}\right)^{1/2}$$

where θ is the angle of incidence. Therefore, spectroelectrochemical experiments in different configurations allow analysts to calculate electrochemical parameters such as the diffusion coefficient from the spectroscopic data.

APPLICATION: CALCULATION OF THE DIFFUSION COEFFICIENT

An amperometric detection experiment was performed in 0.5 mmol/L ferrocyanide in 0.1 KCl solution, applying +0.80 V for 900 s in order to generate ferricyanide. UV-Vis spectra were simultaneously recorded to the electrochemical reaction, obtaining the absorbance value of 0.045 a.u. at 420 nm at the end of the experiment.

RESULTS

Taking into account that the molar absorption coefficient of ferricyanide is 1040 $L \cdot mol^{-1} \cdot cm^{-1}$ [2], the diffusion coefficient of ferrocyanide can be easily calculated from the spectroscopic information:

$$0.045 = 1040 L \cdot mol^{-1} cm^{-1} \times 5 \cdot 10^{-4} mol \cdot L^{-1} \left(\frac{4\ D\ 900s}{\pi}\right)^{1/2}$$

Then, $D_{ferrocyanide} = 6.5 \times 10^{-6}\ cm^2 \cdot s^{-1}$. This value agrees with literature [3,4]. In case the molar absorption coefficient is an unknown parameter, it can be calculated with the calibration curve of absorbance obtained by working in total electrolysis or thin layer configuration for a different reagent concentration.

CONCLUSION

Spectroelectrochemistry is a multi-response technique which combines both electrochemistry and spectroscopy. However, the techniques are related as the calculation of electrochemical parameters from the optical signal demonstrate. The diffusion coefficient of ferrocyanide has been calculated from UV-Vis spectroelectrochemistry in this study, obtaining the value established already in the literature.

REFERENCES

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2. Sigma Aldrich Product Information Sheet of Potassium hexacyanoferrate (III) reagent. (https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Sigma-Aldrich/Product_Information_ Sheet/244023pis.pdf).
3. O.V. Klymenko, R.G. Evans, C. Hardacre, I.B. Svir, R.G. Compton, J Electroanal. Chem. 2004, 571, 211– 221.
4. N. P. C. Stevens, M. B. Rooney, A. M. Bond, S. W. Feldberg, J. Phys. Chem. A 2001, 105, 9085–9093.

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