



Application Note AN-EC-031

Monitoring ferrocyanide oxidation using hyphenated EC-Raman

Performing Raman spectroscopy at the surface of an electrode during electrochemical measurements (e.g., cyclic or linear sweep voltammetry, and chronoamperometry) can provide additional molecular or structural information about the redox process. Hyphenation of the analytical techniques synchronizes both Raman spectra acquisition and electrochemical measurement, allowing researchers to correlate electrochemical (EC) processes to changes in the Raman spectra. This

EC-Raman hyphenation thus helps identify electron transfer-induced molecular changes.

This Application Note highlights the use of Metrohm Hyphenated EC-Raman Solutions to monitor the reversible oxidation of ferrocyanide at a gold electrode. Variations of the band intensities with the potential can be used to track relative changes in the concentration profile of ferrocyanide and ferricyanide at the surface of the electrode during cyclic voltammetry (CV).

EXPERIMENTAL SETUP

A Metrohm EC-Raman Starter Solution was used comprising an i-Raman Plus 532H system and a PGSTAT204 (Metrohm Autolab). A Raman electrochemical cell (Redox.me) was used with a gold disk as working electrode, platinum wire as counter electrode, and an Ag/AgCl reference electrode. The cell was filled with a 50 mmol/L ferrocyanide solution in 0.1 mol/L NaOH and mounted onto a video microscope sampling

system equipped with a 20x objective. Raman spectra were acquired with the i-Raman Plus 532H controlled by SpecSuite software. EC-Raman spectra were acquired with a 5 s integration time and 100% laser power with SpecSuite during a cyclic voltammogram. The CV was run from -0.2 V to +0.65 V starting at 0 V for one cycle at 10 mV/s.

RESULTS

Solutions of ferrocyanide ($[\text{Fe}(\text{CN})_6]^{-4}$) and ferricyanide ($[\text{Fe}(\text{CN})_6]^{-3}$) were used to acquire

reference spectra (Figure 1).

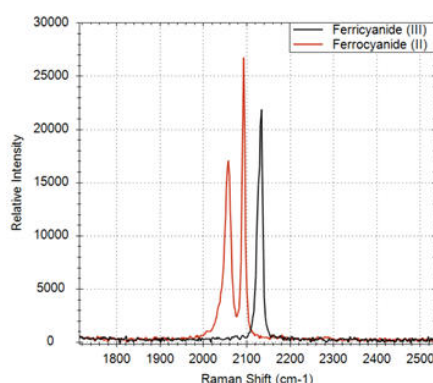


Figure 1. Raman spectra corresponding to solutions of ferricyanide (Fe(III), black) and ferrocyanide (Fe(II), red)

The ferrocyanide spectrum (Figure 1, red) exhibits two Raman bands at 2056 cm^{-1} and 2096 cm^{-1} . The bands are assigned to two different vibration modes of the cyanide ligands (ν_{CN}) with different symmetries (E_g and A_{1g}) [1].

The spectrum of the ferricyanide solution (Figure 1, black) exhibits only one peak at 2134 cm^{-1} which is the combination of both cyanide vibration modes (E_g and A_{1g}). All peaks are reported in Table 1.

Table 1. Raman shift and associated vibration modes of ferrocyanide ($[\text{Fe}(\text{CN})_6]^{4-}$) and ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) ions as reported in ref. [1] and in this Application Note (bold); **: only one band is observed for these two modes.

Compound	Raman shift (cm^{-1})	Vibration mode	Label
$[\text{Fe}(\text{CN})_6]^{4-}$	2062 (2056)	$\nu_{\text{CN}} (\text{E}_g)$	1
	2098 (2096)	$\nu_{\text{CN}} (\text{A}_{1g})$	2
$[\text{Fe}(\text{CN})_6]^{3-}$	2129 (2134**)	$\nu_{\text{CN}} (\text{E}_g)$	3
	2135 (2134**)	$\nu_{\text{CN}} (\text{A}_{1g})$	

RESULTS

The cyclic voltammogram in **Figure 2** shows the typical shape of a reversible diffusion-limited process: the oxidation of ferrocyanide into

ferricyanide on the forward scan, and then the reduction of the formed ferricyanide into ferrocyanide.

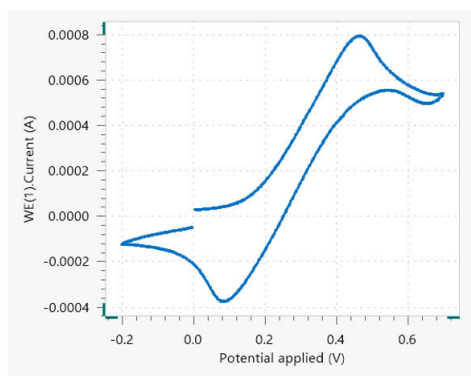


Figure 2. Hyphenated EC-Raman cyclic voltammetry: cyclic voltammogram of a ferrocyanide solution at 10 mV/s.

The 17 individual spectra acquired every 100 mV are displayed in **Figure 3**. The first three spectra (cv_01 to cv_03) display only the two peaks assigned to the ferrocyanide ion. From spectrum

cv_04 onward (0.3V vs. Ag/AgCl), peak 3 appears at 2134 cm^{-1} and its intensity decreases until the end of the CV measurement (cv_17).

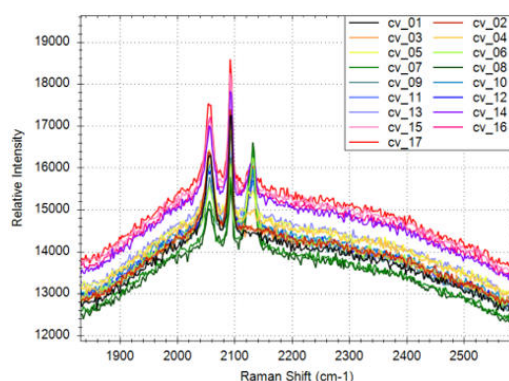


Figure 3. Hyphenated EC-Raman cyclic voltammetry: series of Raman spectra acquired approximately every 100 mV during the CV (Figure 2). The number in the name of the spectrum in the legend is the index of the spectrum.

For Raman spectra, the peak area is directly related to the concentration of analytes present. The peaks in **Figure 3** were integrated using analytics tools in the SpecSuite software and plotted versus potential (**Figure 4**). This plot qualitatively reflects the relative amounts of analytes in the sample volume investigated by the laser near the electrode surface also probed by the laser. In **Figure 4**, the areas of peak 1 at 2056 cm^{-1} (P1, red) and of peak 2 at 2096 cm^{-1} (P2, dark red) are indicative of the ferrocyanide concentration at the interface of electrode and electrolyte. The area of peak 3 (P3, black) indicates the presence of ferricyanide at the electrode/electrolyte interface. The areas of P1 and P2 decrease during the anodic scan and increase again during the cathodic scan

suggesting that the concentration of ferrocyanide in the diffusion layer decreases during its oxidation and is restored to its initial level at the end of the CV. The change in P3 area suggests that the concentration of ferricyanide follows the opposite trend. The maximum concentration of ferricyanide in this experiment is observed around 0.6 V during the forward scan while the ferrocyanide concentration reaches its minimum at the same potential, after the anodic peak in the CV, before the scan is reversed. This part of the CV corresponds to the diffusion-limited region where the concentration of reactant is minimal and the concentration of products reaches a maximum in the diffusion layer [2].

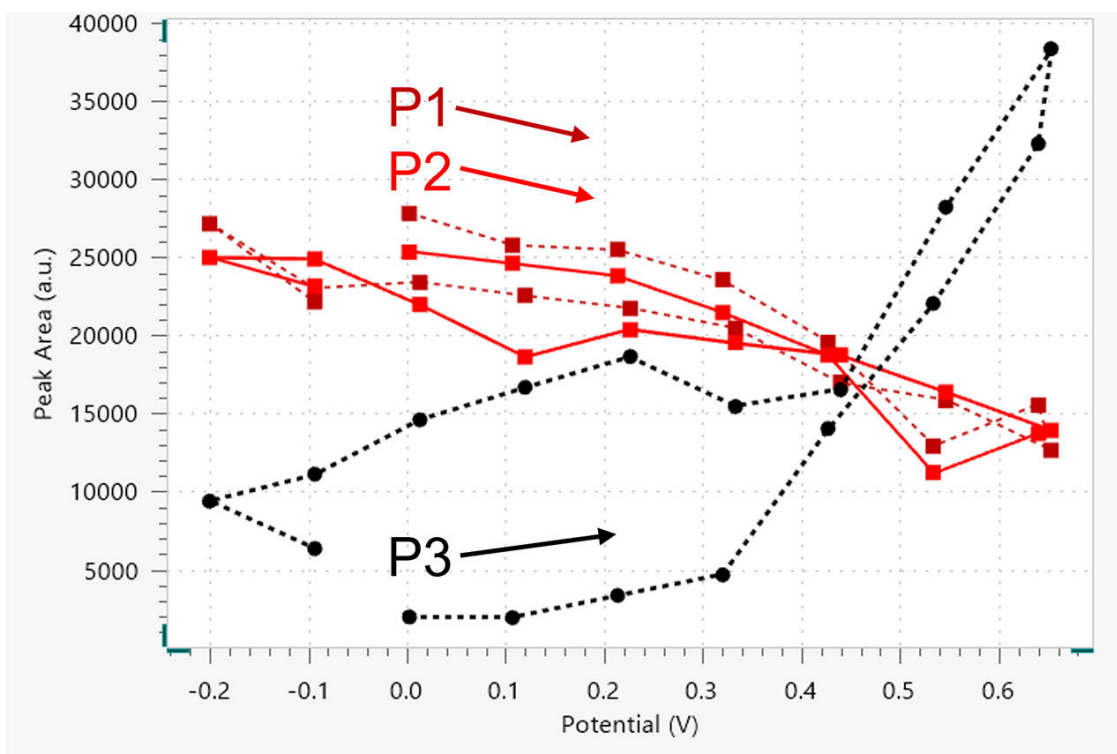


Figure 4. Raman peak areas reported vs. E (V vs. Ag/AgCl) during a CV for ferrocyanide (P1, dark red; P2, red) and ferricyanide (P3, black). The corresponding spectra are visible in Figure 3. The arrows indicate the direction of the scan during the CV.

CONCLUSION

Hyphenated EC-Raman spectroscopy was used in this Application Note to monitor concentration changes in the diffusion layer during the reversible oxidation of a ferrocyanide solution. The change in

the intensity of Raman bands could be correlated to the concentration variations occurring at the working electrode during a cyclic voltammogram of a species in solution.

REFERENCES

1. Robinson, J.; Fleischmann, M.; Graves, P. R. The Raman Spectroscopy of the Ferricyanide/Ferrocyanide System at Gold, - Palladium Hydride and Platinum Electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, 182 (1), 12.
[https://doi.org/10.1016/0368-1874\(85\)85442-3](https://doi.org/10.1016/0368-1874(85)85442-3).
2. Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; et al. A Practical Beginner's Guide to Cyclic Voltammetry. *J. Chem. Educ.* **2018**, 95 (2), 197–206.
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CONFIGURATION



i-Raman Plus 532H

该 i-Raman® Plus 532H 是我们屡获殊荣的 i-Raman 便携式拉曼光谱仪系列的一部分,其采用我们创新的智能光谱仪技术。这款便携式拉曼光谱仪使用了具有高量子效率、TE 冷却功能和高动态范围的 CCD 阵列检测器,即使集成时间长达 30 分钟,也能提供出色的低噪声性能。因此,还可以测量较弱的拉曼信号。

i-Raman Plus 532H 具有宽光谱范围和高分辨率的独特组合,其配置允许在 65 cm^{-1} 至 3400 cm^{-1} 之间进行测量。该系统基础面积小,结构形式轻巧并且能耗低,故此可随时随地进行研究级别的拉曼分析。该 i-Raman Plus 配备有便于采样的光纤探头,并可以与一个比色皿支架、一个视频显微镜、一个带探头支架的 XYZ 平移台、我们公司内部的 BWIQ® 多变量分析软件和鉴定软件 BWID® 搭配使用。有了 i-Raman Plus,您始终可以使用高精度拉曼解决方案进行定性和定量分析。



Autolab PGSTAT204

PGSTAT204 结合了小巧规格和模块化设计。该仪器包括基本恒电位仪/恒电流仪,其顺从电压为 20 V,最大电流为 400 mA 或 10 A,与 BOOSTER10A 组合使用。此恒电位仪可随时用附加模块进行扩展,例如 FRA32M 电化学阻抗谱(EIS)模块。

PGSTAT204 是一款经济实惠的仪器,可置于实验室的任何位置。具有模拟和数字输入/输出,可控制 Autolab 附件和外部设备。PGSTAT204 包括内置模拟积分器。与高性能的 NOVA 软件联用,可用于大多数标准电化学技术。