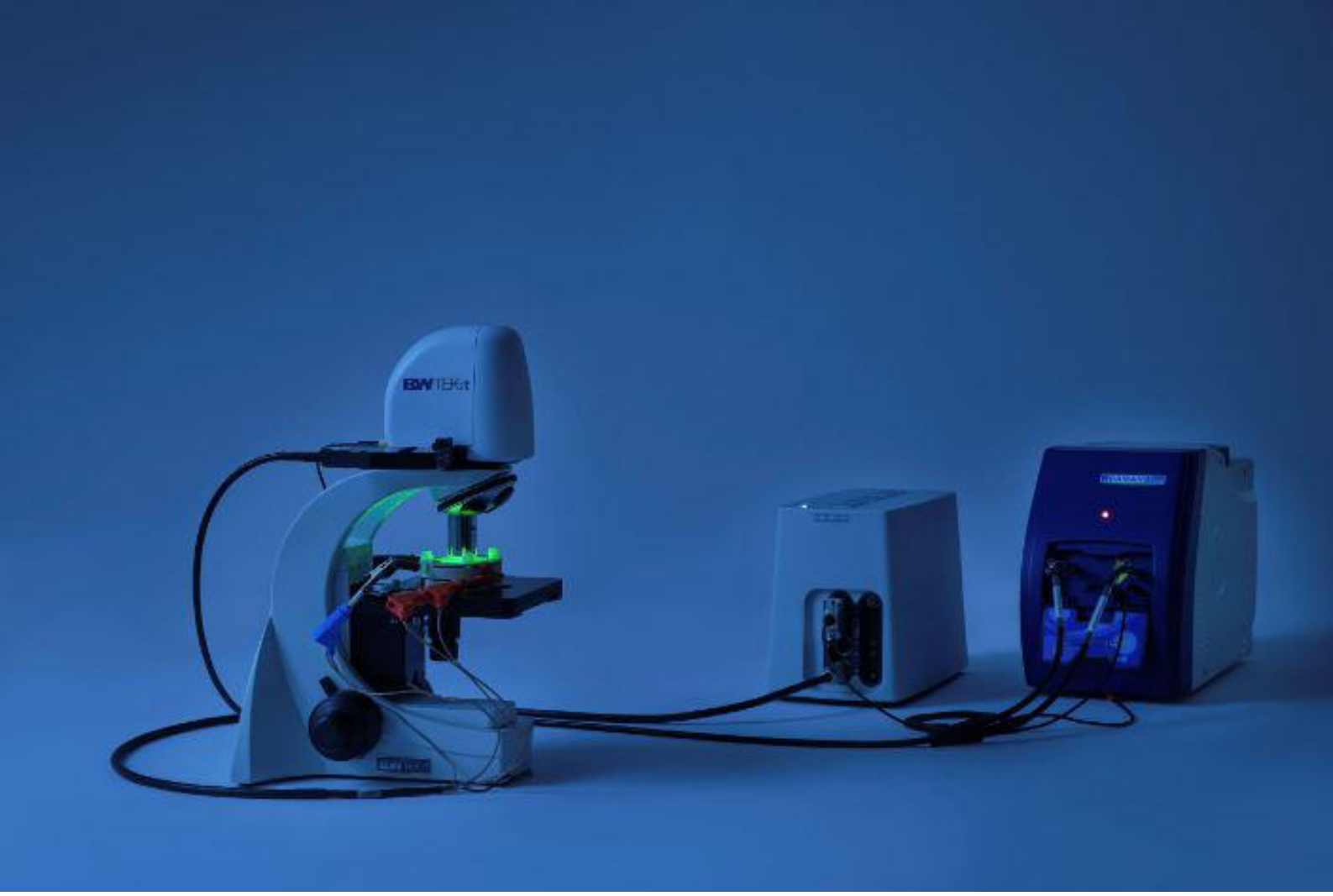


Application Note AN-EC-031

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, andchronoamperometry) 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 (B&W Tek) 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 (B&W Tek) equipped with a 20x objective. Raman spectra were acquired with the i-Raman Plus 532H controlled by BWSpec software. EC-Raman spectra were acquired with a 5 s integration time and 100% laser power with BWSpec Timeline 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 ($[Fe(CN)_6]^{-4}$) and ferricyanide ($[Fe(CN)_6]^{-3}$) were used to acquire reference spectra (Figure 1).

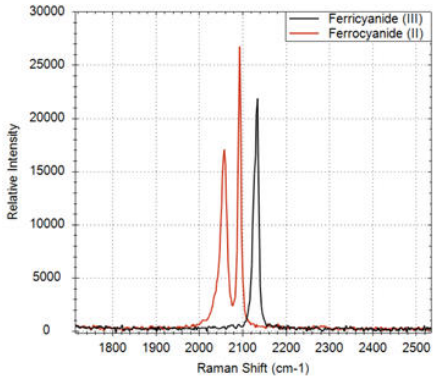


Figure 1. Raman spectra corresponding to solutions of ferricyanide (Fe(III), black) and ferrocyanide (Fe(II), red)

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 (v_{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 ([Fe(CN)6]-4) and ferricyanide ([Fe(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
$[Fe(CN)_6]^{-4}$	2062 (**2056**)	ν_{CN} (E_g)	1
	2098 (**2096**)	ν_{CN} (A_{1g})	2
$[Fe(CN)_6]^{-3}$	2129 (**2134****)	ν_{CN} (E_g)	3
	2135 (**2134****)	ν_{CN} (A_{1g})	

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.

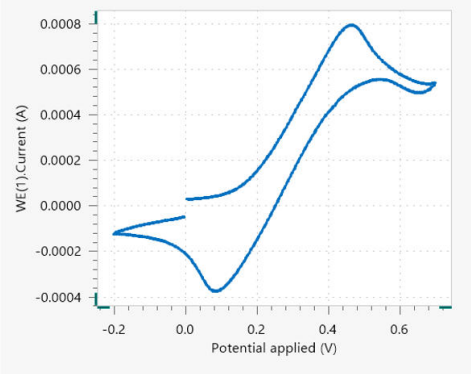


Figure 2. Hyphenated EC-Raman cyclic voltammetry: cyclic voltammogram of a ferrocyanide solution at 10 mV/s.

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).

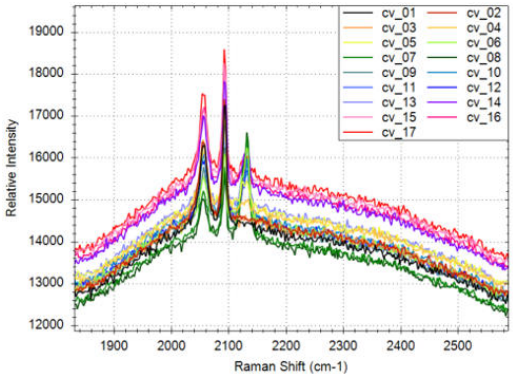


Figure 3. Hyphenated EC-Raman cyclic voltammetry: series of Raman spectra acquired approximately every 100 mV during the CV (Figure 2). The number in the name of the spectrum in the legend is the index of the spectrum.

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 BWSpec 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].

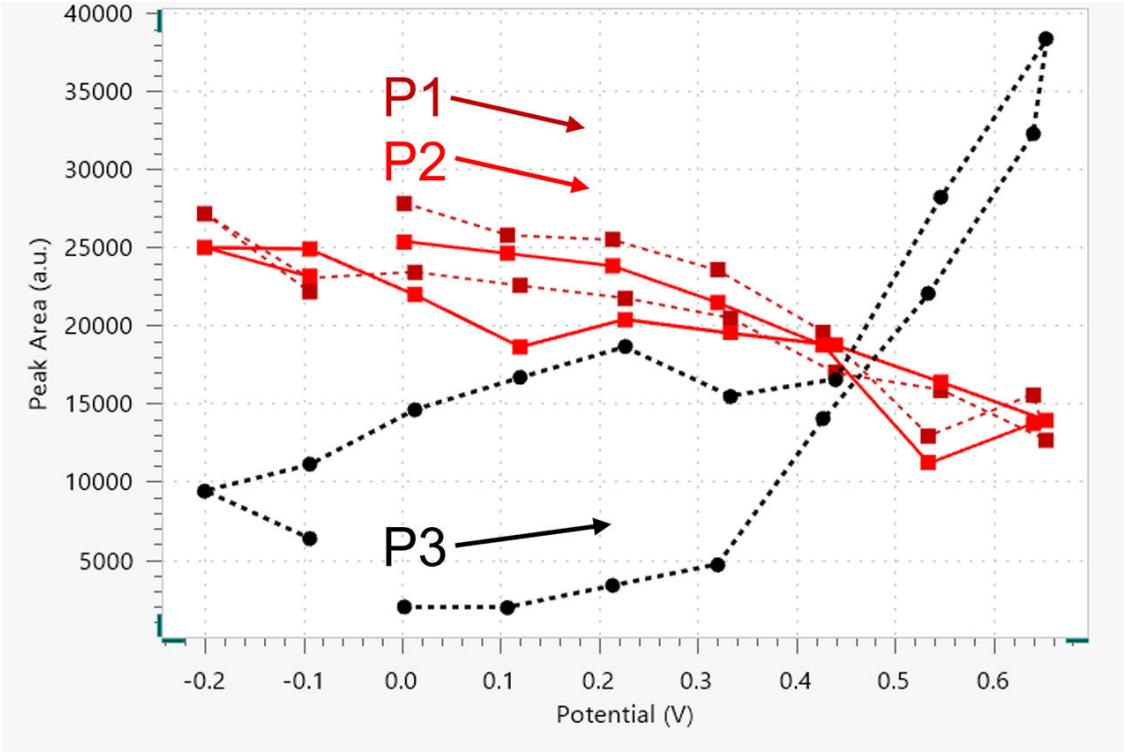


Figure 4. Raman peak areas reported vs. E (V vs. Ag/AgCl) during a CV for ferrocyanide (P1, dark red; P2, red) and ferricyanide (P3, black). The corresponding spectra are visible in Figure 3. The arrows indicate the direction of the scan during the CV.

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, β-Palladium Hydride and Platinum Electrodes. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *182* (1), 12. https://doi.org/10.1016/0368-1874(85)85442-3.
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