Application Note AN-RS-042

用 EC-Raman 解决方案揭示电池的秘密

An inner look at how nickel-metal hydride batteries work

The development of rechargeable lead-acid batteries and their use in automobiles has prompted research into new battery chemistries with superior properties. As a result, nickel-metal hydride (NiMH) and lithium-ion batteries were created with higher energy density and longer lifecycles. Energy storage technology contributes to cleaner and more sustainable societies by increasing access to both efficient power sources and renewable energy as well. Substituting internal combustion engines with electric-based alternatives aims to reduce greenhouse gas emissions and air pollution. These shifts towards cleaner technologies are reflected in the strong growth of the battery market, which is projected to quadruple between 2021 and 2030 [1].

Electrochemical Raman (EC-Raman) spectroscopy is a powerful analytical tool that increases understanding of the working of energy storage devices by monitoring physicochemical changes. This Application Note explains EC-Raman insights discovered during simulated charging and discharging of a nickel-metal hydride battery.

INTRODUCTION

Raman spectroscopy is used for in-situ, real-time monitoring of chemical reactions, among other things. When combined with electrochemical techniques (e.g., EC-Raman), this allows researchers to monitor physicochemical changes occurring in electrolytes at different depths, at electrode surfaces, and more. This powerful combination of techniques (otherwise known as spectroelectrochemistry or SEC) provides further insight into the progress of electrochemical reactions.

MATERIALS

All materials used in this study are listed in **Table 1**. The experiment was conducted using an i-Raman Prime 532H and a PGSTAT302N. The Metrohm EC-Raman Starter Solution will achieve comparable results. Experimental design was based on a study by Yeo and Bell [**2**].

Table 1. Instruments, electrodes, and chemicals used herein.

Experimental Materials	
Potentiostat	PGSTAT302N (Metrohm Autolab)
Raman Instrument	i-Raman Prime 532H, BAC151C video microscope system with 50x objective, BAC150B probe holder, BWSpec Software (B&W Tek)
EC-Raman Cell	EC-Raman Flow Cell with gold WE, platinum wire CE, and Silver/Silver chloride RE (Ag/AgCl, 3 mol/L KCl) (RedoxMe)
Electrode	Cable Connector for Screen-Printed Electrode (CAC4MMH) and 220BT Electrode with gold printed WE and CE and silver printed RE (Metrohm DropSens, **Figure 1**)
Chemicals	0.1 mol/L KCl, 0.01 mol/L $Ni(NO_3)_2$, and 0.1 mol/L NaOH (Sigma Aldrich)

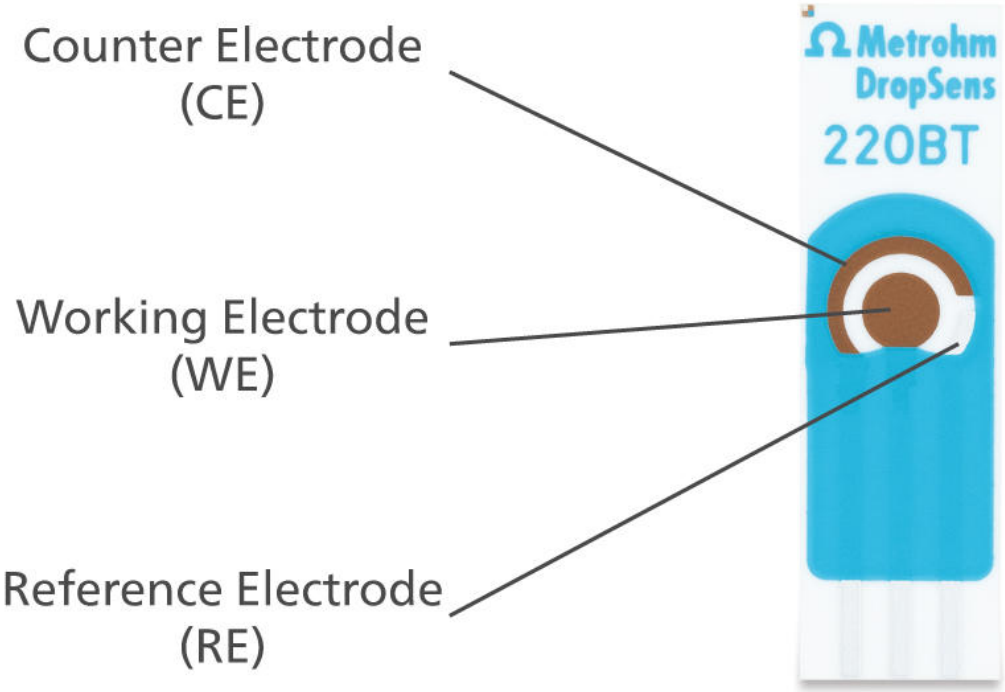


Figure 1. A screen-printed electrode (SPE) from Metrohm Dropsens with the counter, working, and reference electrodes indicated.

PROCEDURE

Electrochemical roughening of WE surface

Add 5 mL of 0.1 mol/L KCl to the EC-Raman cell (adjust volume according to cell specifications). Ensure that there are no bubbles on the WE surface. Drop 100 µL of 0.1 mol/L KCl onto the printed surface of 220BT, ensuring that all electrodes are submerged. WE roughening follows the procedure detailed in Table 2 [3]. During the process, the electrode should change color, as shown in Figure 2. After the roughening process is complete, rinse the substrate with deionized (DI) water. The WE is now ready for electrochemical deposition of $Ni(OH)_2$.

Figure 2. Surface of the WE before (left) and after (right) electrochemical roughening.

Table 2. Operational settings for the simulated discharge/charge of a Ni(OH)2 electrode. Settings may change based on experimental results.

PGSTAT302 Operation Settings	
Task	Autolab Control
Electrochemical Roughening of WE	Repeat 25x*: chronoamperometry (CA) at -0.3 V vs. Ag/AgCl (30 s), Linear sweep voltammetry (LSV) from -0.3 to 1.2 V at 10 mV/s, CA at 1.2 V (60s), LSV from 1.2 to -0.3 V at 10 mV/s.
Electrochemical $Ni(OH)_2$ deposition on WE	Chronopotentiometry (-100 µA, 300 s) in a two-electrode cell (WE = Au disk, CE/RE = Pt)**
Simulated Cycle of $Ni(OH)_2$ electrode	CV between -0.4 and 1.5 V vs. Ag/AgCl (start/stop at 0V, scan rate 10 mV/s) † .

Electrochemical deposition of $Ni(OH)_2$ on WE

Connect all cables to the EC-Raman cell and add 5 mL of 0.01 mol/L $Ni(NO_3)_2$ while checking that there are no bubbles on the surface. Drop 100 µL of 0.01 mol/L $Ni(NO_3)_2$ onto the printed surface of 220BT, ensuring that all electrodes are submerged. $Ni(OH)_2$ deposition on the WE surface is achieved through precipitation of the $Ni(NO_3)_2$ salt by chronoamperometry (CA) according to the settings described in **Table 2**. After deposition, disconnect the EC-Raman cell and 220BT SPE and rinse the substrate with DI water. The electrodes are ready for the electrochemical discharging and charging cycle.

Electrochemical discharging/charging WE

Reconnect the EC-Raman cell, then add 5 mL of 0.1 mol/L NaOH to the EC-Raman cell and ensure that there are no bubbles on the $Ni(OH)_2$ WE surface. Drop 100 µL of 0.1 mol/L NaOH onto the printed surface of 220BT. Check that all electrodes are submerged. Submit the deposited nickel film to cyclic voltammetry (CV) according to details in **Table 2**. Nickel is deposited with a +2 oxidation state as $Ni(OH)_2$ and can be reversibly oxidized to Ni^{+3} (NiOOH) according to the following equation:

$$Ni(OH)_2 + OH^- \quad NiOOH + H_2O + e^-$$

Monitoring WE surface with i-Raman Prime 532

Place the EC-Raman cell or 220BT on a BAC150B probe holder or BAC151C video microscope stage and position the laser on the WE surface. A 50x objective is used for this experiment; adjust magnification to the required depth of focus (**Figure 3**). EC-Raman spectra were acquired with the timeline function of BWSpec: integration time = 5s, laser power = 100%, and average = 1.

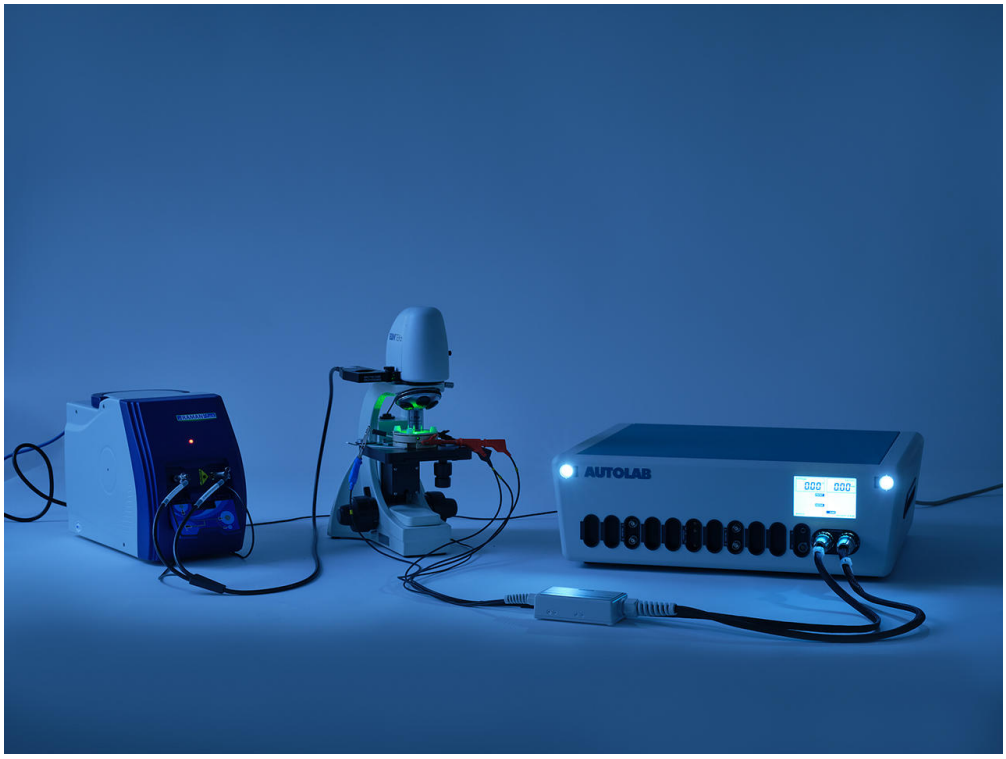


Figure 3. Example of a hyphenated EC-Raman setup from Metrohm.

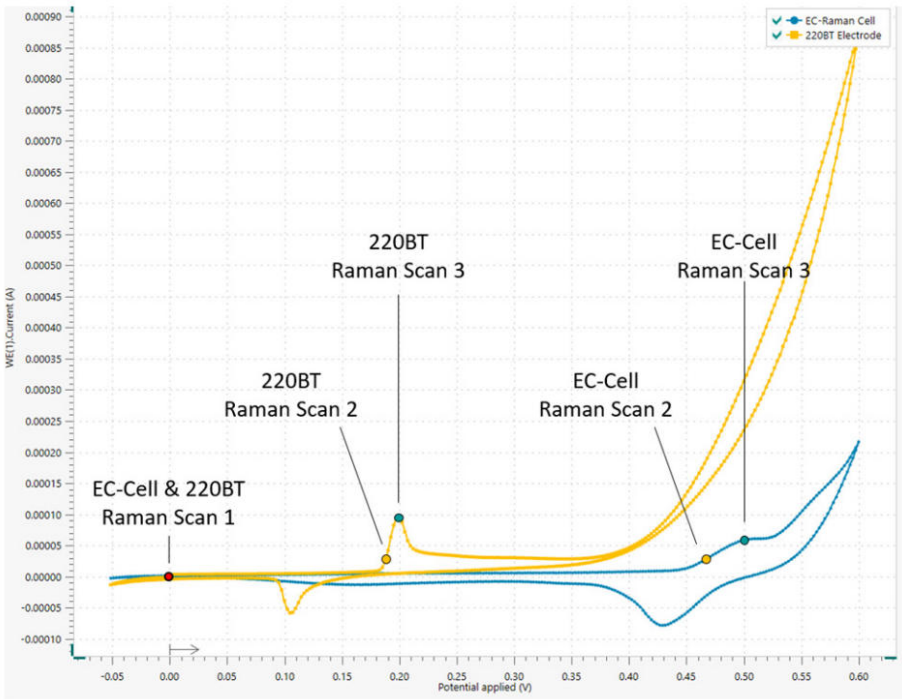
RESULTS

Electrochemical characterization of the nickel oxide film was performed with cyclic voltammetry. A typical voltammogram is displayed in **Figure 4a** with a pair of reversible peaks, characteristic of the reversible oxidation of $Ni(OH)_2$ to NiOOH, observed around 0.50 V vs. Ag/AgCl. During the forward (anodic) scan, the main species present is $Ni(OH)_2$ until the potential reaches 0.45 V vs. Ag/AgCl. After this potential, the film is mainly composed of NiOOH until the potential reaches approximately 0.35 V vs. Ag/AgCl on the reverse (cathodic) scan.

Note: The EC-Raman cell uses a true Ag/AgCl (3 mol/L KCl) reference electrode with a stable reference potential, while the 220BT SPE has an Ag pseudo-reference. The potential will shift with oxygen concentration in this cell: the O_2 that is generated at high potentials saturates the electrolyte and defines a new reference potential for the Ag pseudo-reference.

To confirm the main species at the surface of the electrode, Raman spectra were collected throughout one full discharge/charge cycle of the EC-Raman cell. The Raman profile for three different voltages is presented in **Figure 4b**. At 0.0V vs Ag/AgCl, no Raman band associated with $Ni(OH)_2$ was detected – a possible result of low Raman cross-section or deposit layer depth [2]. As the potential reaches the reversible $NiOOH/Ni(OH)_2$ point, NiOOH-related bands at 476 and 556 cm^{-1} appear, allowing for clear identification of NiOOH in the thin film. These bands disappear again when voltage is reduced to 0.0V.

a)



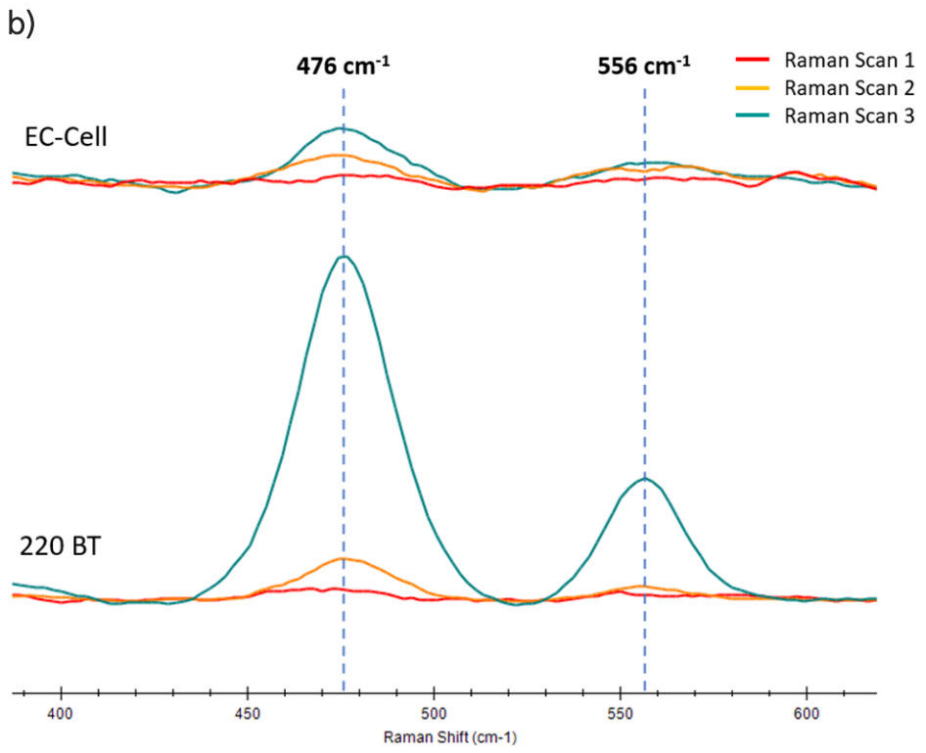


Figure 4. (a) Cyclic voltammogram of the nickel oxide films in two different cells, recorded at 10 mV/s. The arrow next to the x-axis indicates the direction of the scan. (b) Raman measurement of the EC-Raman cell and 220BT electrode at different phases of the reaction.

The Raman profile for the 220BT SPE was comparable to that of the EC-Raman cell, but with stronger peak intensity and lower redox potential. This is possibly caused by the experiment setup, e.g., electrode specification, laser focus/depth of electrolyte, glass window, dimension of the WE, RE type, etc. There are pros and cons of each configuration:

- The EC-Raman cell is a closed system which provides a controlled environment and can accommodate continuous flow reactions. The intensity of Raman peaks is lower for a closed cell and the Raman signal may be compromised by bubbles that form during the reaction.
- The 220BT screen-printed electrode is a more affordable open system that is less susceptible to interference from bubbles, but the sample is vulnerable to contamination and spilling. Moreover, the CV peak position may change due to the influence of oxygen at the working electrode or the reference electrode.

FIELD TEST NOTE

- i-Raman Plus 532 yields comparable results to i-Raman Prime.
- The EC-Raman cell and 220BT SPE can be stored for a few days after roughening.
- Bubbles can interfere with Raman measurement of an EC-Raman cell.
- CV can change depending on experiment parameters when using the 220BT.
- Optimal results are achieved by increasing electrochemical etching and $Ni(OH)_2$ deposition on WE surface.

CONCLUSION

The physicochemical properties of $Ni(OH)_2$ deposits on an electrode during a simulated discharge/charge cycle were monitored using a Metrohm hyphenated EC-Raman system. The changes in the intensity of Raman bands were indicative of oxidation and reduction of nickel during CV, confirming the system's ability to monitor changes in energy storage materials by hyphenated EC-Raman.

REFERENCES

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3. Tian, Z.-Q.; Ren, B.; Wu, D.-Y. Surface-Enhanced Raman Scattering: From Noble to Transition Metals and from Rough Surfaces to Ordered Nanostructures. *J. Phys. Chem. B* **2002**, *106* (37), 9463–9483. https://doi.org/10.1021/jp0257449.

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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。