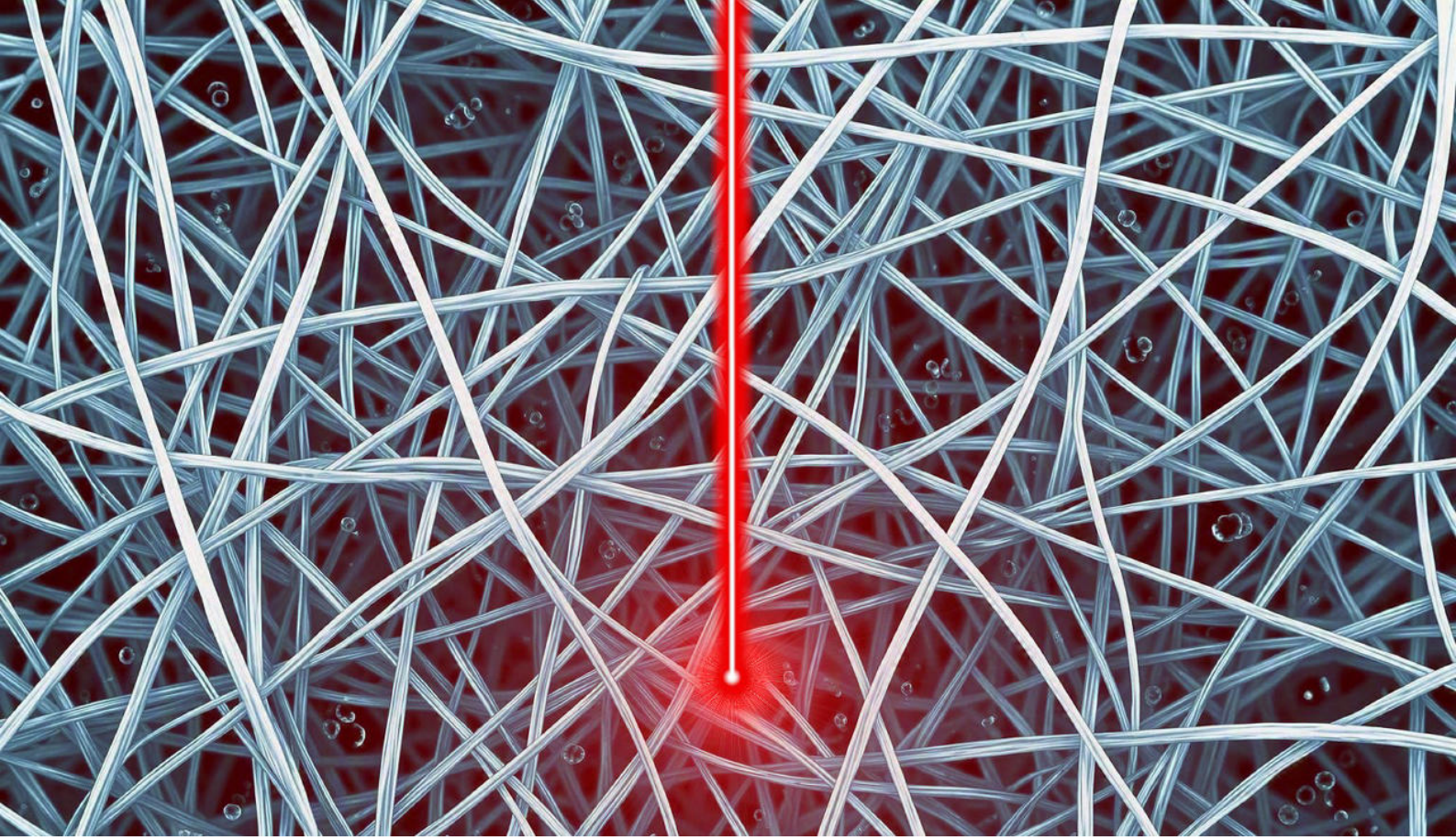


Application Note AN-RA-011

# Operando Raman characterization of oxygen evolution reaction (OER) catalysts

## Gain insight into the electrocatalytic behavior of Ni-based electrocatalysts through Raman spectroelectrochemistry

Operando Raman characterization provides direct insight into the structural evolution of catalysts for the oxygen evolution reaction. Specifically, nickel-based materials undergo potential-dependent transformations that define their catalytic activity. Tracking these changes through Raman spectroelectrochemistry makes it possible to identify the formation of active phases and correlate them with electrochemical performance. By linking vibrational signatures with catalytic behavior, operando Raman studies support the development of efficient Ni-based electrocatalysts.

## INSTRUMENTATION AND SOFTWARE

Raman spectroelectrochemistry was performed using a SPELEC RAMAN instrument (Figure 1). This portable equipment integrates a 785 nm laser, a spectrometer, and a (bi)potentiostat/galvanostat, ensuring the perfect synchronization between optical and electrochemical signals.

SPELEC RAMAN was controlled with DropView SPELEC, a dedicated software that allows the simultaneous collection of the electrochemical and Raman signals. Furthermore, it includes tools to perform the treatment and analysis of the collected data. All hardware and software used for this study are compiled in Table 1.




**Figure 1.** SPELEC RAMAN instrument.

The experimental setup was completed with a Raman probe corresponding to the laser wavelength, and a spectroelectrochemical cell. Furthermore, Toray Carbon Paper (TCP) modified with 0.5 mg/cm$^2$ of $Ni(OH)_2$ was used as WE (working electrode), Ag/AgCl as RE (reference electrode), and a Pt wire as CE (counter electrode).

**Table 1**. Hardware and software equipment overview.

| Equipment | Article number |
|---|---|
| Instrument | SPELECRAMAN |
| Cell | RAMANCELL-M |
| Connection cable | CABSTAT |
| Software | DropView SPELEC |

## RAMAN CHARACTERIZATION OF NI-BASED ELECTROCATALYSTS

Analytical grade potassium hydroxide (sourced from VWR) was used as received. An aqueous solution was prepared using ultrapure water (Direct-Q® 5 system, Millipore).

Initially, the sample was pretreated by applying 15 conditioning cycles to improve the contact between the TCP surface and the electrolyte. The potential was scanned from 0.00 V to +0.70 V at a scan rate of 0.01 V/s in 1 mol/L KOH. Raman spectroelectrochemical measurements were performed afterwards to obtain deeper insight into the catalytic behavior of the material. During these experiments, amperometric pulses at different potentials were applied while Raman spectra were concurrently recorded. Multipulsed Amperometric Detection (MAD) protocol was configured to apply 600 s steps from 0.00 V to +0.60 V in increments of +0.10 V (Figure 2a). Raman spectra were simultaneously obtained using an integration time of 30 s (Figure 2b). As the electrochemical pulses and spectral acquisition are perfectly synchronized, the spectra corresponding to each applied potential can be clearly distinguished.

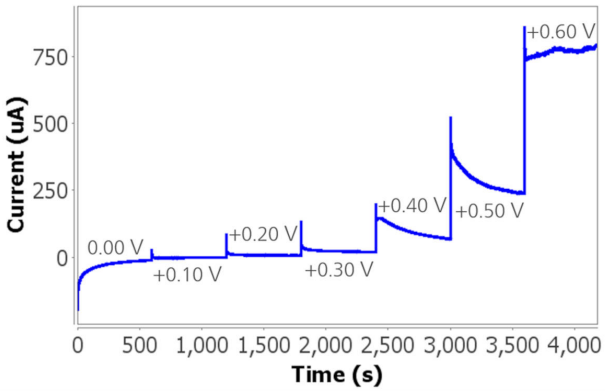



**Figure 2a.** Multipulsed Amperometric Detection in 1 mol/L KOH.

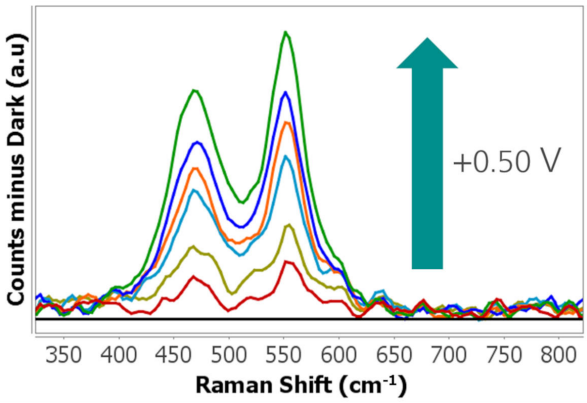



**Figure 2b.** Raman spectra recorded simultaneously (int. time 30 s).

As shown in Figure 2b, two new Raman bands are observed at 475 and 550 cm−1 during the experiment. These bands emerge from +0.50 V onward and are characteristic of NiOOH [1,2]. Specifically, they correspond to the $E_g$ bending vibration and the $A_{1g}$ stretching vibration modes of the Ni–O bonds in NiOOH. The formation of this active oxyhydroxide phase is a key step in nickel-based electrocatalysts since it is directly involved in promoting the oxygen evolution reaction (OER).

## CONCLUSION

In-situ Raman spectroelectrochemistry is an excellent technique to detect the real-time species evolution of Ni-based catalysts in the OER. For instance, the electrochemical conversion of $Ni(OH)_2$ into NiOOH is demonstrated by the detection of the characteristic bands at 475 and 550 $cm^{-1}$. Monitoring these vibrational signatures provides detailed information about the formation and stability of the active oxyhydroxide phase, which is essential for understanding how nickel-based catalysts work.

Beyond clarifying the mechanistic steps involved in oxygen evolution, this methodology also offers valuable information for the design of new electrocatalysts. The correlation of potential-dependent structural changes with catalytic performance can be extended to other important oxidation processes, including the urea oxidation reaction, ammonia oxidation, and related electrochemical transformations where nickel-based catalysts may also play a central role.

## AUTHORS

This Application Note was developed in collaboration with Composite Materials Group (María González-Ingelmo, Zoraida González Arias, and Victoria García Rocha) of Instituto de Ciencia y Tecnología del Carbono INCAR-CSIC (Oviedo, Spain).

## REFERENCES

1. Yang, X.; Zhang, H.; Yu, B.; et al. An Unveiled Electrocatalysis Essence of NiCo Hydroxides through in Situ Raman Spectroscopy for Urea Oxidation. *Energy Tech* 2022, *10* (5), 2101010. DOI:10.1002/ente.202101010
2. Yan, Z.; Sun, H.; Chen, X.; et al. Anion Insertion Enhanced Electrodeposition of Robust Metal Hydroxide/Oxide Electrodes for Oxygen Evolution. *Nat Commun* 2018, *9* (1), 2373. DOI:10.1038/s41467-018-04788-3

## RELATED APPLICATION NOTES

- AN-RA-006 New strategies for obtaining the SERS effect in organic solvents
- AN-RA-007 Enhancement of Raman intensity for the detection of fentanyl
- AN-RA-008 Easy detection of enzymes with the electrochemical-SERS effect
- AN-RA-009 Comparison of SPELEC RAMAN and standard Raman microscopes
- AN-RA-010 SERS detection of pesticides using screen-printed electrodes

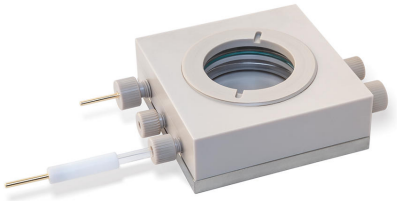
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### Spectroelectrochemical Raman instrument (785 nm laser)

SPELECRAMAN is an instrument for performing spectroelectrochemical Raman measurements. It combines in only one box a laser class 3B (785 nm ± 0.5), a bipotentiostat/galvanostat and a spectrometer (wavelength range 787 – 1027 nm and Raman shift 35 - 3000 $cm^{-1}$) and includes a dedicated spectroelectrochemical software that allows optical and electrochemical experiments synchronization.



### Raman Cell for microscope

Cell for spectroelectrochemical applications in combination with a microscope, allowing the laser focus onto the surface of the working electrode, obtaining valuable information while the electrochemical process takes place.



### mStat Cable connector (2WE) for conventional electrodes

Flexible cable connector that acts as an interface between DropSens bipotentiostats and conventional electrodes