

Electrochemical Impedance Spectroscopy (EIS)

EIS probes electrochemical systems with a small-signal AC excitation to extract frequency-dependent impedance, separating resistive and reactive contributions to quantify kinetics, interfacial processes, diffusion, and degradation.

Introduction

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive frequency-domain analytical method used to evaluate electrochemical systems, including batteries and supercapacitors. It works by applying a small sinusoidal signal to the system and measuring its response across a broad frequency range. This technique reveals valuable information about internal resistance, charge-transfer reactions, double-layer behavior, ion-diffusion processes, and various forms of battery degradation. EIS reveals both resistive and reactive (capacitive or inductive) components of the system.

EIS Test Condition

To obtain high-quality battery EIS data, typical conditions include:

- AC amplitude: 5–10 mV (ensures linearity)
- Temperature control: ± 0.1 °C stability recommended
- State of charge (SOC): Often measured at 0%, 25%, 50%, 75%, and 100%

Frequency range:

- High-frequency: ~100 kHz – 10 kHz (charge transfer, solution resistance)
- Mid-frequency: 10 kHz – 1 Hz (interfacial behavior, double layer)
- Low-frequency: 1 Hz – 10 mHz (diffusion, Warburg element)

EIS results are most visualized using Nyquist and Bode plots. In a Nyquist plot, the real component of

impedance (Z') is plotted along the x-axis, while the negative imaginary component ($-Z''$) is plotted on the y-axis. This representation effectively highlights the characteristic time constants associated with different electrochemical processes within the system.

The Bode plot, on the other hand, presents both the impedance magnitude and the phase angle as functions of frequency. This format is useful for analyzing frequency-dependent behavior, evaluating system stability, and identifying performance-limiting processes in electrochemical and electronic systems.

The following figures show a Nyquist plot and Bode plot.

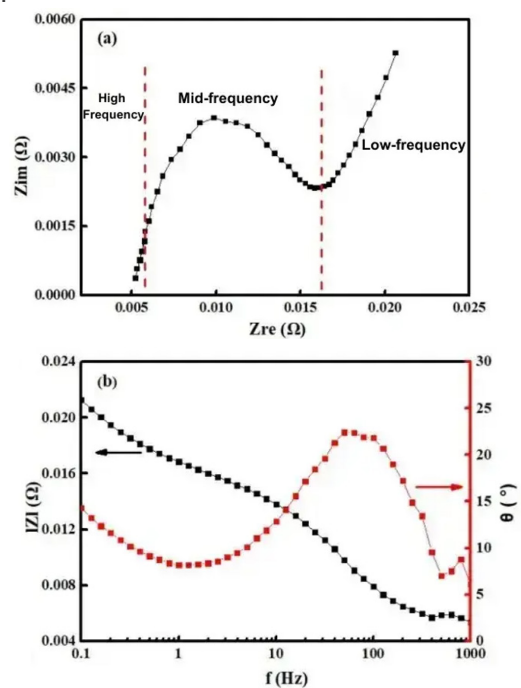


Figure 1. (above) Nyquist plot and (below) Bode plot.

Modes of Electrochemical Impedance Spectroscopy

Potentiostatic EIS (Voltage-controlled EIS): You apply a small AC voltage (like 10 mV) to the electrochemical system and measure the resulting AC current.

- Used for high-impedance materials (coatings, corrosion films).
- Safe because the applied voltage produces only very small currents.

Galvanostatic EIS (Current-controlled EIS): You apply a small AC current and measure the resulting AC voltage.

- Used for low-impedance systems (large batteries, supercapacitors).
- Prevents the large currents that would occur if voltage were applied instead.

At Eurofins EAG we use Gamry Interface 5000E which is a high-performance potentiostat/galvanostat designed for advanced electrochemical testing—especially batteries (cylindrical, pouch cell, coin cell).

Its main specification:

- Dual Electrometer
- Maximum Applied Potential - ± 6 V
- Maximum Current - ± 5 A
- EIS - 10 μ Hz - 1 MHz

Case Study: Application of EIS in Lithium Ion Battery Diagnostics

Electrochemical impedance spectroscopy (EIS) was conducted on four pouch cells maintained at 50% state of charge (SOC) to ensure that impedance differences were not influenced by SOC-dependent electrochemical behavior. Each cell represented a distinct aging or abuse condition: (i) pristine (reference), (ii) high-rate cycled, (iii) overdischarged, and (iv) overcharged leading to visible swelling.

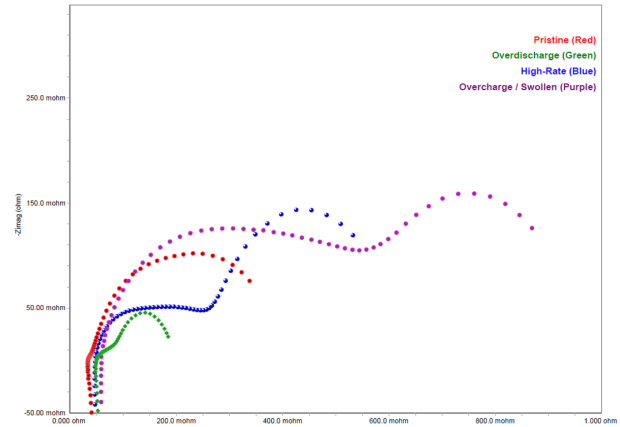


Figure 2. Nyquist plots of (i) pristine (reference) cell, (ii) high-rate cycled cell, (iii) overdischarged cell, and (iv) overcharged cell

By fixing the SOC at 50%, the comparison isolates structural and interfacial degradation effects from lithiation-state variations. The Nyquist plots were analyzed qualitatively without equivalent circuit fitting to evaluate the capability of EIS in distinguishing degradation modes based solely on impedance signatures. The results are summarized in the following table.

Table 1: Summary of EIS Results

| Cell Condition | Color | Ohmic Resistance (R_s) | Semicircle Size (R_{ct}) | Low-Frequency Behavior | Main Interpretation |
|----------------------|--------|----------------------------|------------------------------|---------------------------------|--|
| Pristine | Red | Lowest | Small | Normal diffusion tail | Healthy SEI and charge-transfer kinetics |
| Overdischarge | Green | Slightly increased | Slight distortion | Slight diffusion limitation | SEI alteration, possible Cu dissolution, increased interfacial resistance |
| High-Rate Cycling | Blue | Moderate increase | Larger semicircle | Noticeable diffusion limitation | Increased polarization, thicker SEI, higher R_{ct} |
| Overcharge (Swollen) | Purple | Highest | Very large / multiple arcs | Strong diffusion tail | Severe interfacial degradation, electrolyte decomposition, structural damage |

Conclusion

Electrochemical Impedance Spectroscopy (EIS) is a powerful, non-destructive diagnostic tool for monitoring the "vital signs" of lithium-ion batteries. Unlike traditional methods that only measure voltage or current, EIS provides a detailed map of internal electrochemical processes, such as ion migration, charge transfer, and diffusion, by analyzing frequency-dependent responses.

Contact us today to learn how we can help you with your next project.