Electrochemical Impedance Spectroscopy (EIS) for Advanced Battery Diagnostics

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Admiral Instruments

Test the potential™

Electrochemical Impedance Spectroscopy

Electrochemistry

AC Resistance

Range of Frequency

$$\mathbf{Z} = \frac{V_{AC}}{i_{AC}}$$

IN OTHER WORDS,

EIS is a **non-invasive**, typically **rapid** measurement technique that reveals a wealth of information about conditions inside a battery

Three Most Common EIS Applications for Batteries

- Battery Testing
- Battery Management
- Battery R&D

Raw Information → **Useful Applications**

Raw Information

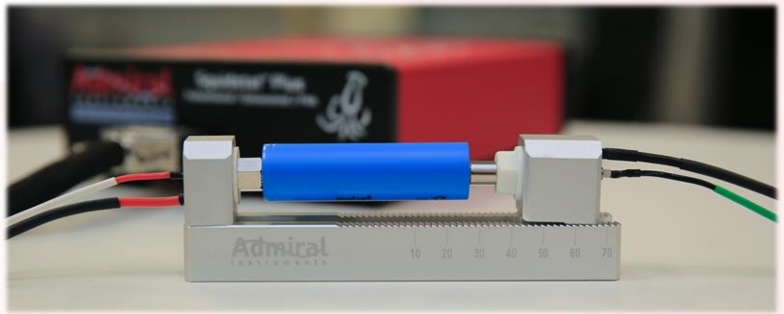
- Internal Resistance
- Charge-transfer Resistance
- Mass-transfer Resistance
- Interfacial Resistance
- State of Charge (SOC)
- State of Health (SOH)

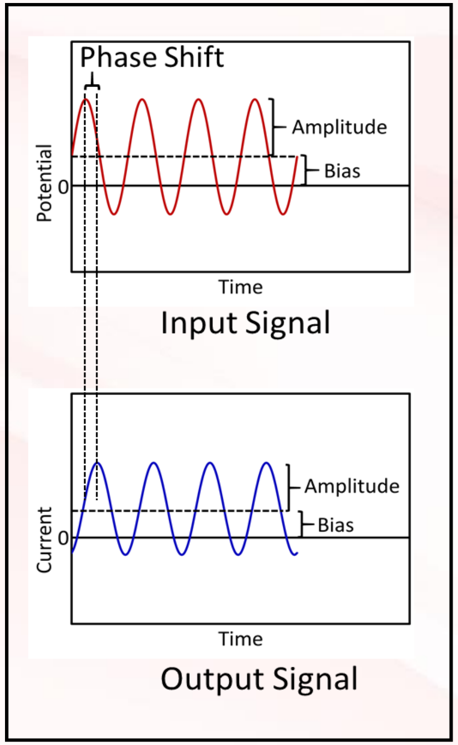
Useful Applications

- Battery Characterization
- Battery Management System
- New Battery Development
- Failure Diagnosis

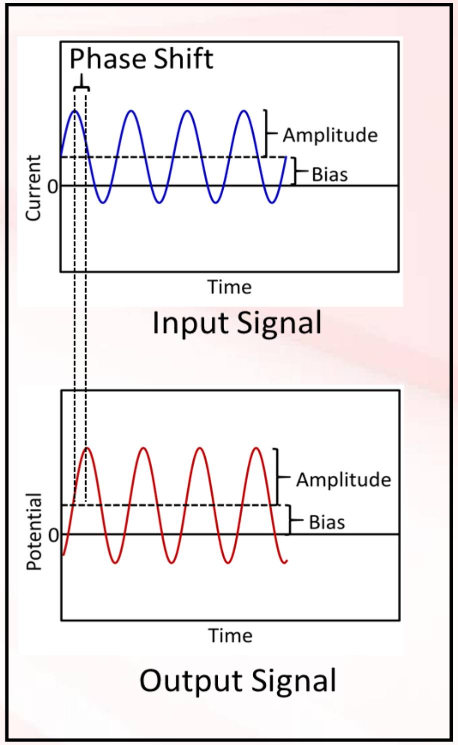
Steps to run a standard EIS experiment

1. Find an EIS-capable instrument, typically a potentiostat, and connect it to the battery being tested
2. Decide to use Potentiostatic EIS or Galvanostatic EIS on the battery. *Pot. = Voltage input, Galv. = Current input*
3. Configure input AC signal the potentiostat will apply to the battery (frequency range, amplitude, DC bias, etc.)
4. The potentiostat applies the AC input signal and records the resulting AC output signal for internal processing
5. Internal processing calculates: Frequency, Impedance Modulus (real & i), Phase, DC Current, and DC Voltage
6. Analyze the resulting data, typically in the form of a Nyquist Plot fitted to an equivalent circuit model





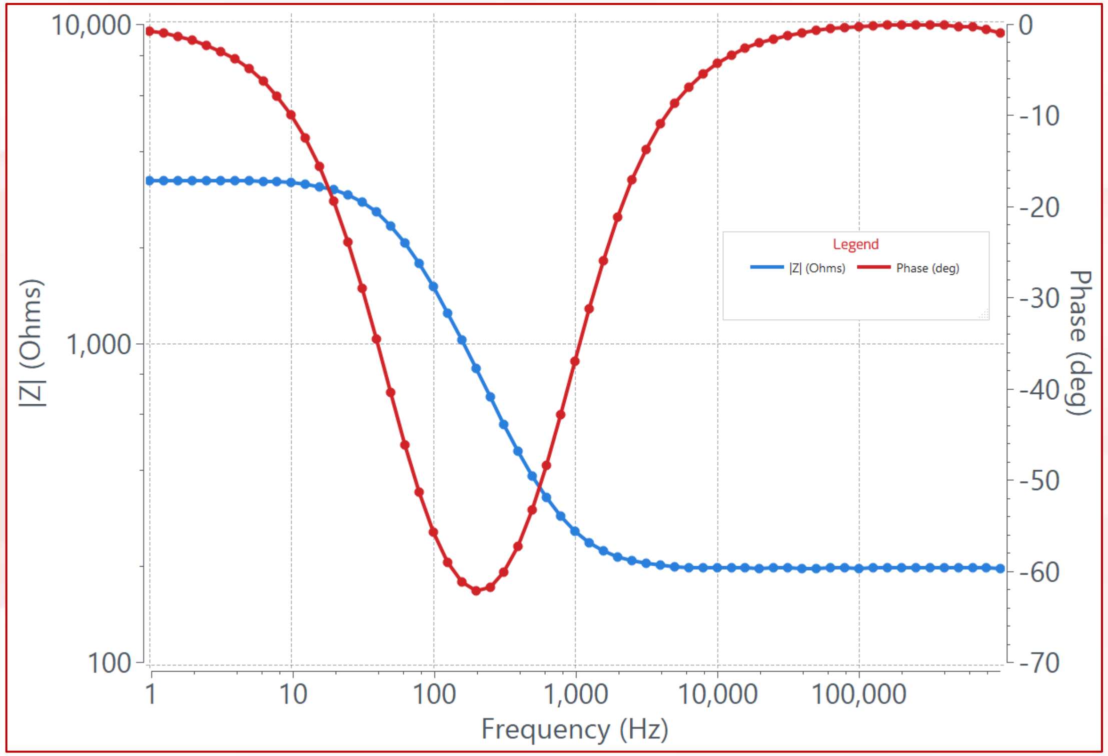
Potentiostatic EIS



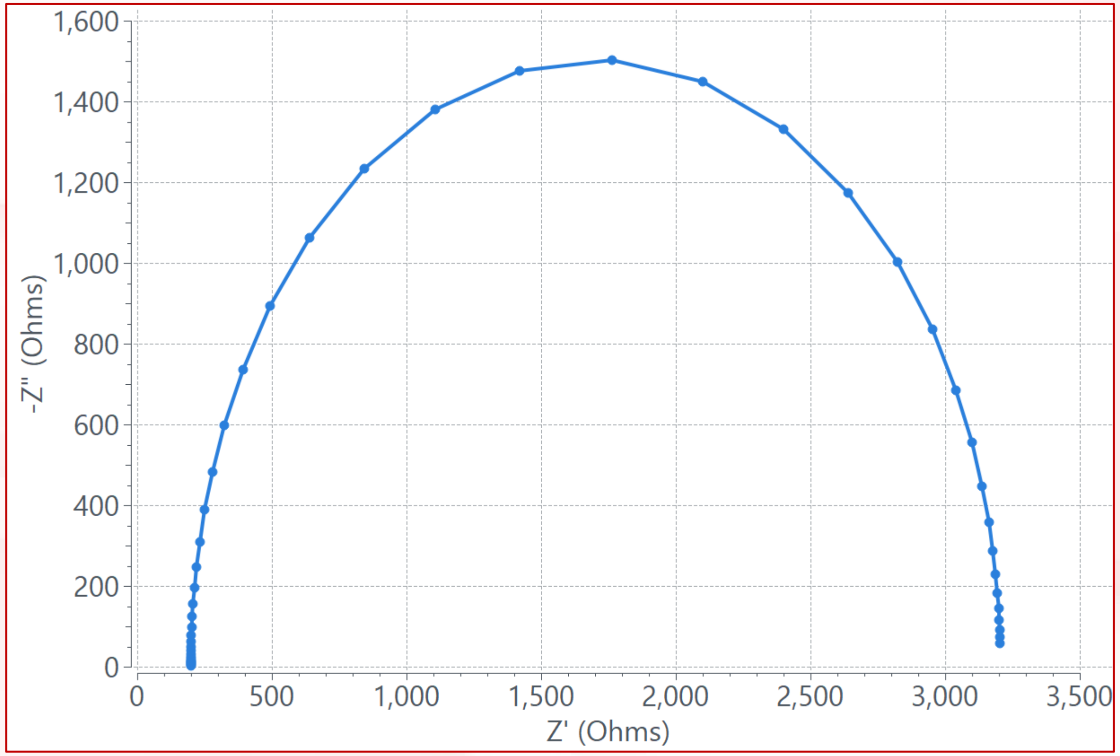
Galvanostatic EIS

EIS Data is Typically Graphed Two Ways

Bode Plot: Abs(Z) and Phase vs. Frequency



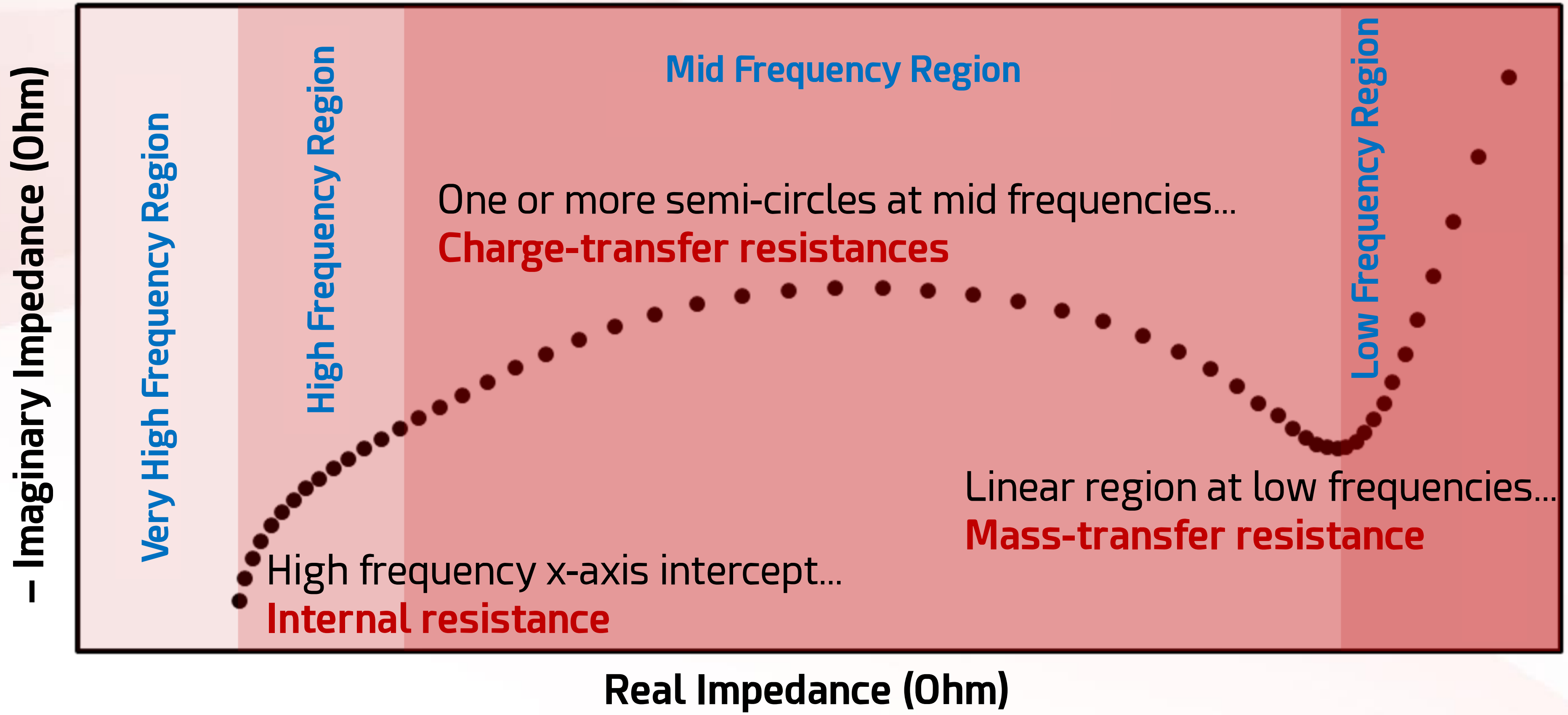
Nyquist Plot: -Imaginary Z vs. Real Z



Nyquist Plots are more often used because several Key Performance Indicators (KPIs) can be quickly derived through quick visual inspection

EIS Profile of a Typical Li-ion Battery

The **Nyquist Plot** of a typical Li-ion battery shows **four** prominent regions



Frequency-dependent regions are correlated to many phenomena inside a battery

Very High Frequency Region
Li-ion conductivity in electrolyte, electronic conductivity

High Frequency Region
Li-ion transport through solid-electrolyte interphase

Mid Frequency Region
Charge transfer at the electrode-electrolyte interface

Low Frequency Region
Li-ion diffusion in electrode and electrolyte

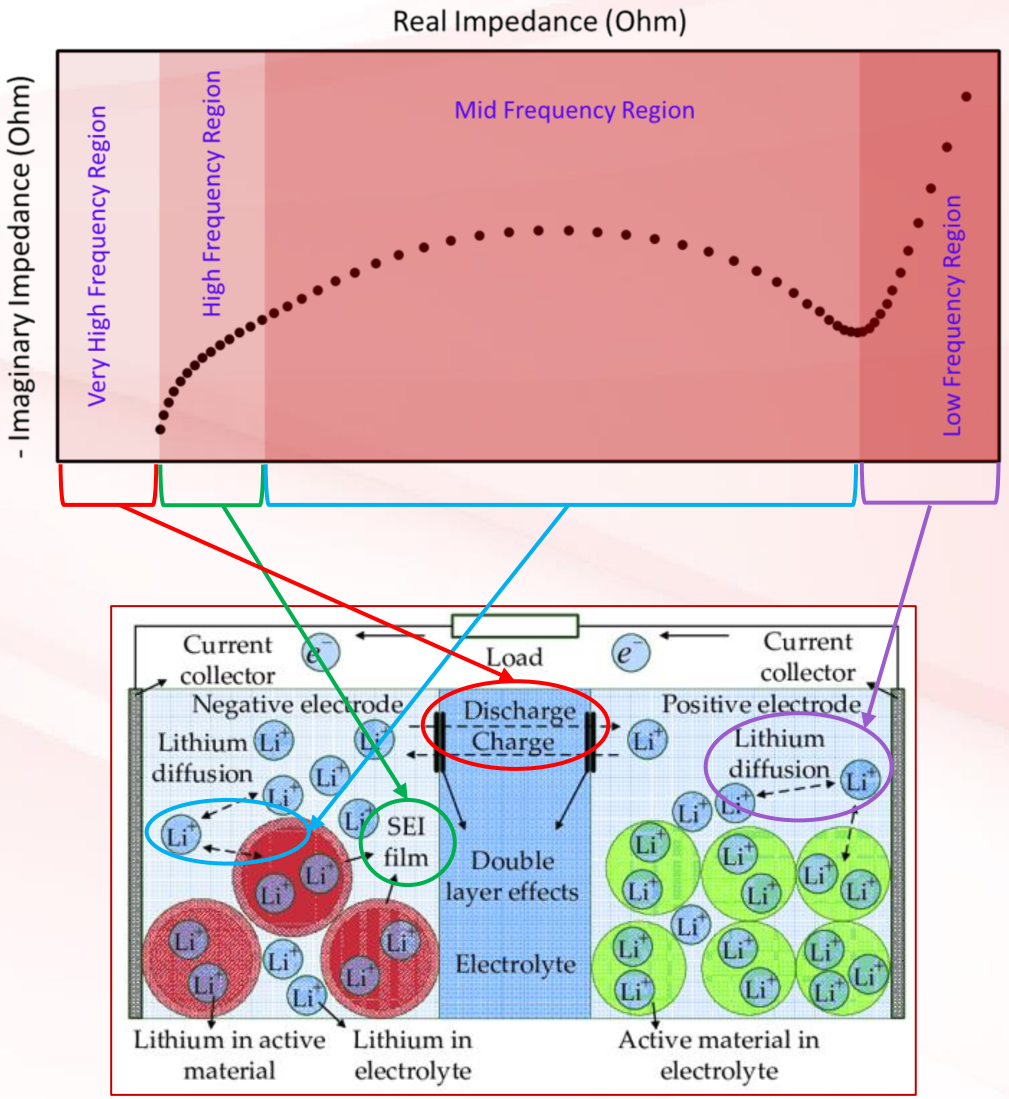
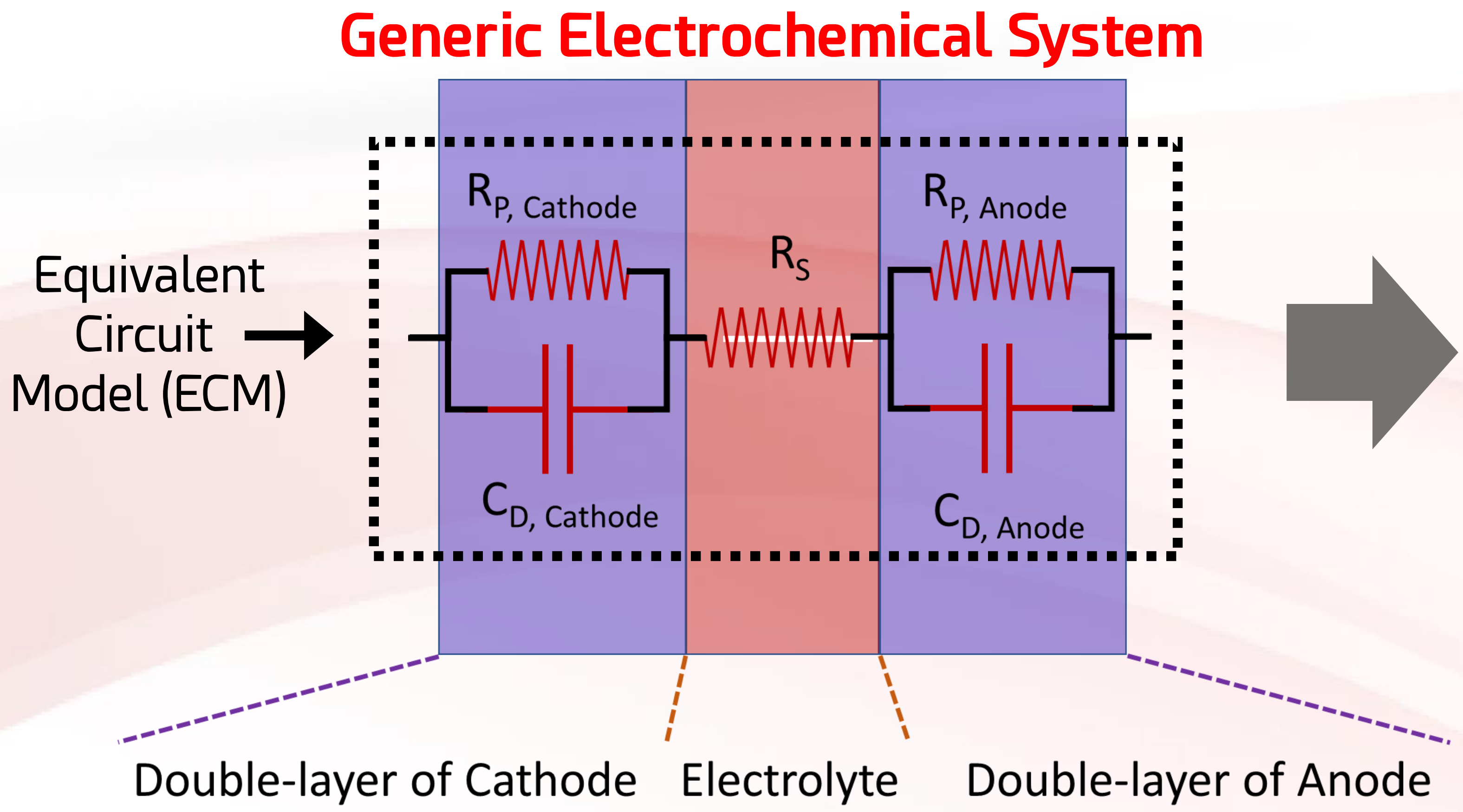
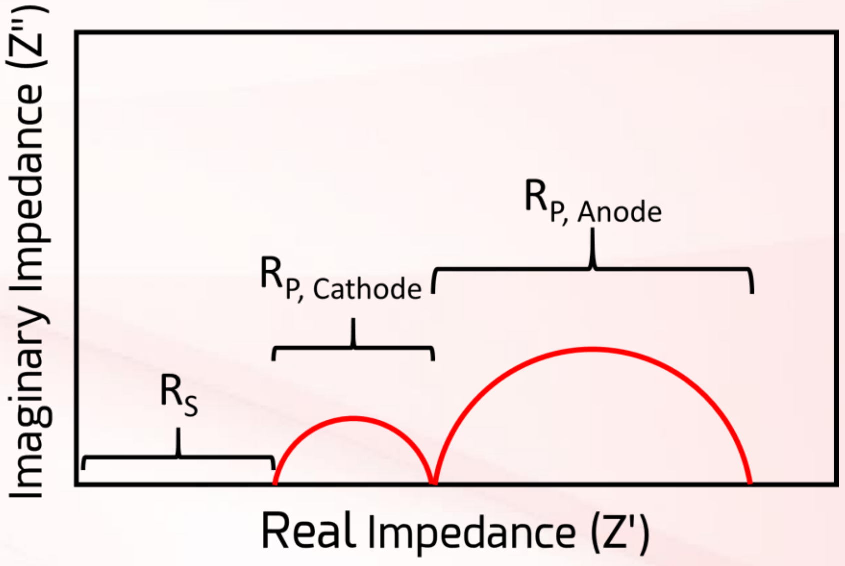


Figure from: Zhou, et al. Energies 9 (3) 123 (2016)

Equivalent Circuit Modeling (ECM) for EIS Data





The behavior of electrochemical systems can be parameterized using the "language" of circuit-like elements (resistors, capacitors, inductors, etc.)

By fitting EIS data to an ECM, the electrochemical phenomena can be ***quantified***

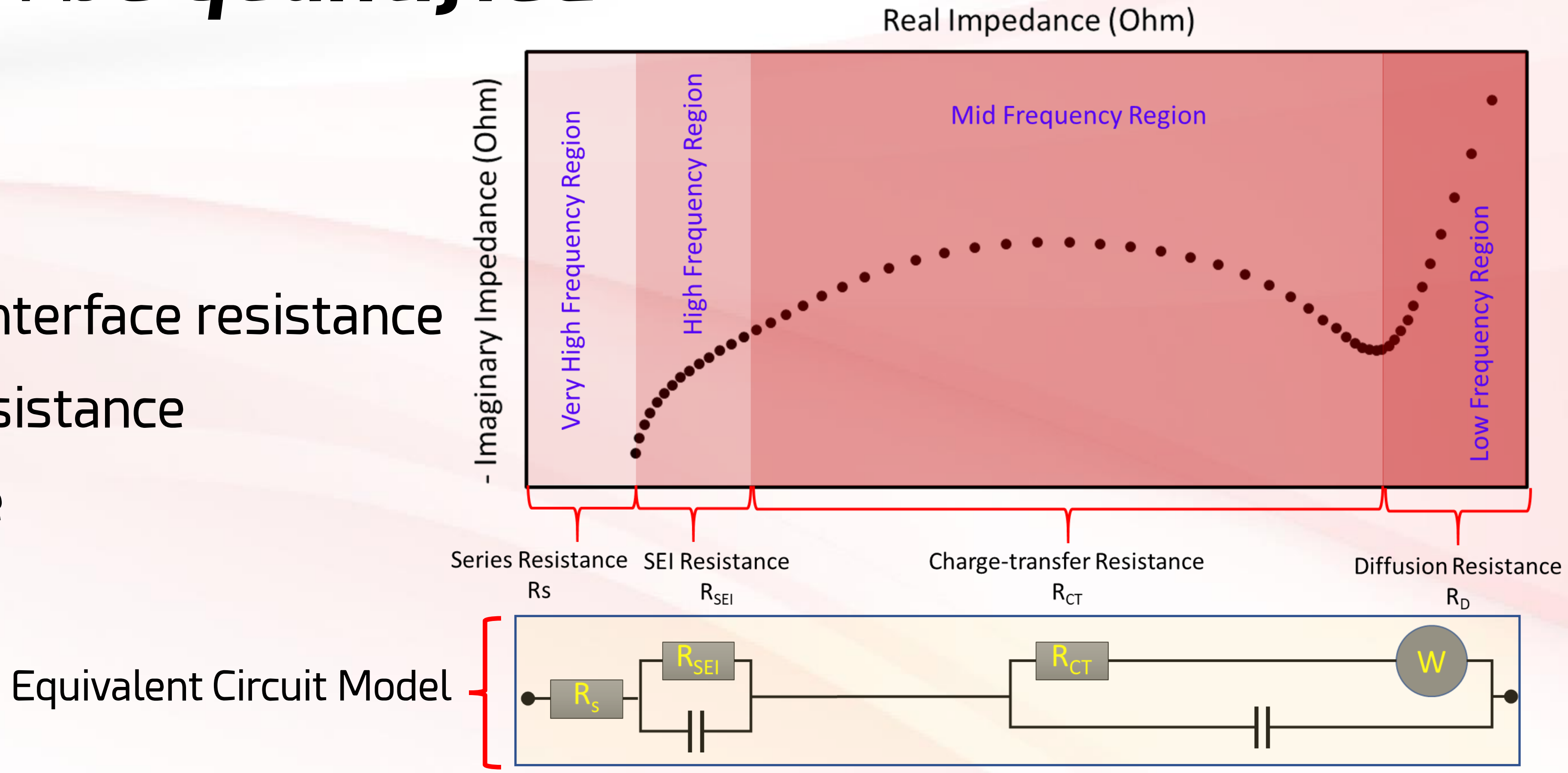
<u>Examples:</u>

R_S : Series resistance

R_{SEI} : Solid-electrolyte interface resistance

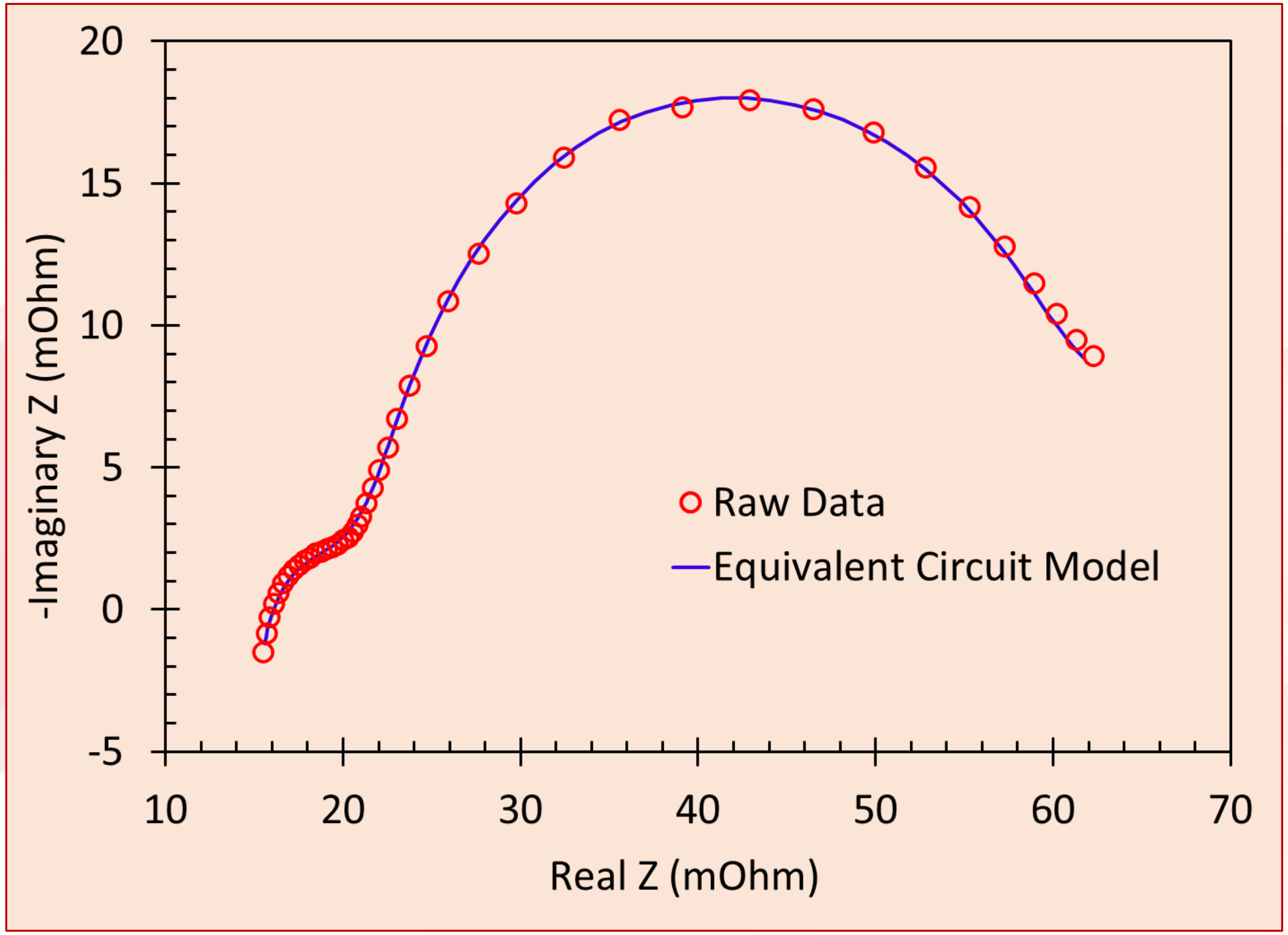
R_{CT} : Charge-transfer resistance

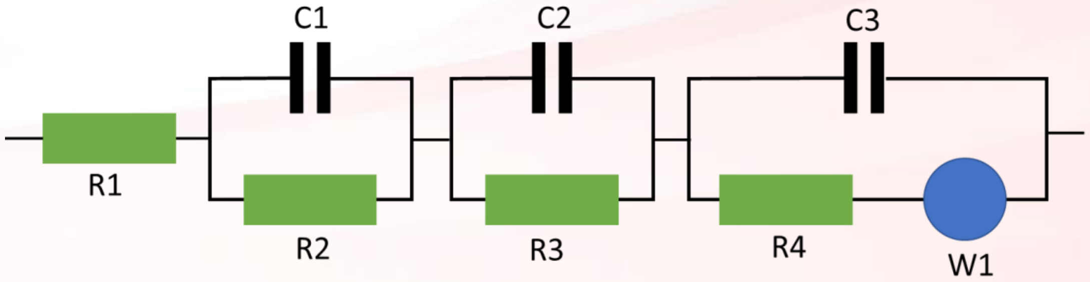
R_D : Diffusion resistance



State-of-Charge (SOC) and State-of-Health (SOH) values can be derived from the constants calculated by the equivalent circuit model

Calculating ECM Constants Needs Special Software





Circuit Elements	Fitted Values
R1	152 mOhm
C1	5.53 F
R2	22.5 mOhm
C2	21.1 F
R3	67.6 mOhm
C3	27.3 F
R4	8.85 mOhm
W1	3.04 mDW

ECM software is available from most potentiostat vendors to perform analysis

Series resistance (R_S) increases with cycle life, as shown by the larger x-axis intercept at higher cycles

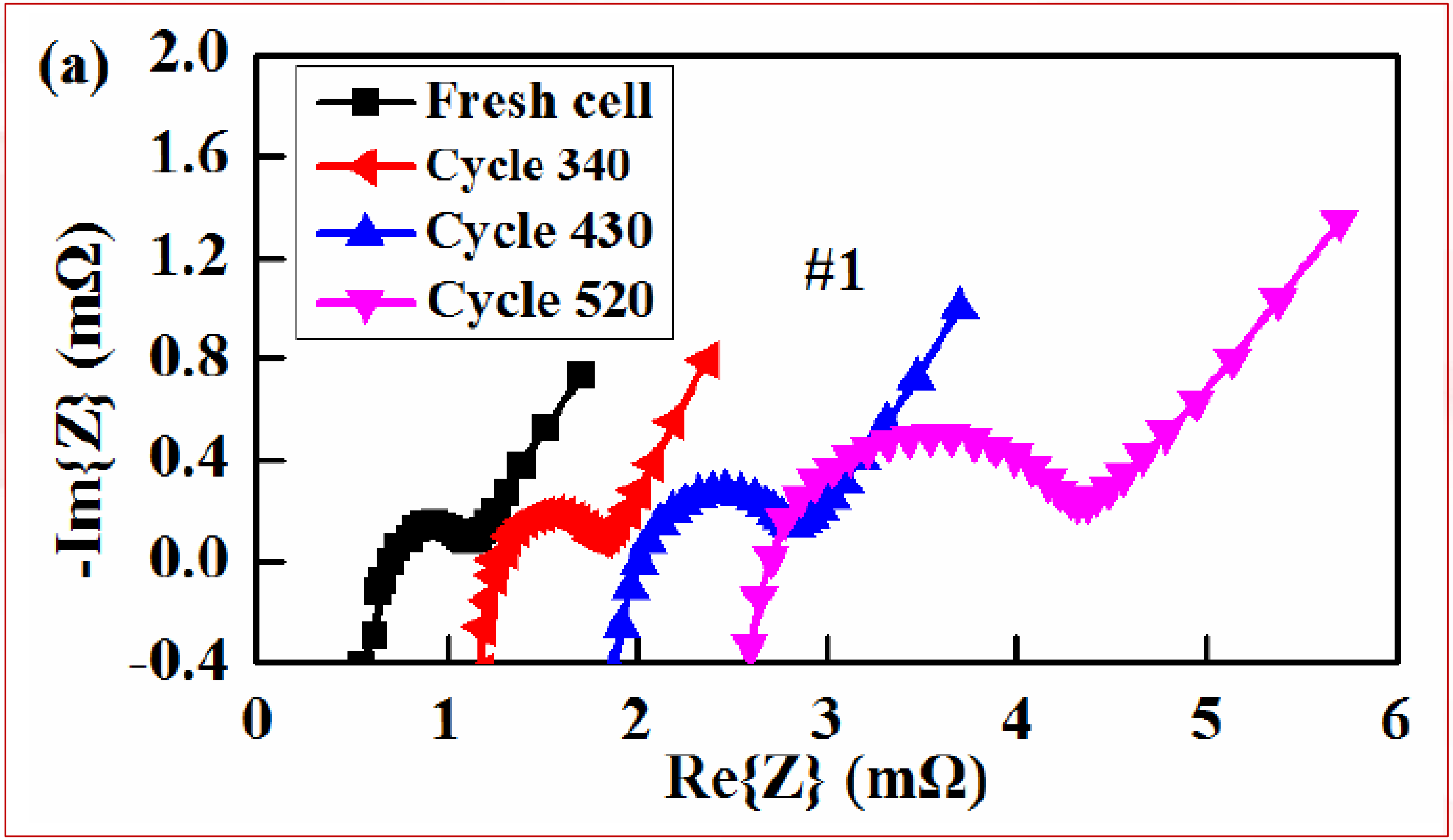


Figure from: Jiang, et al., *Energy Procedia* 105 (**2017**)844-849

Charge-transfer resistance (R_{CT}) increases with SOC, as shown by taller & longer "humps" in the middle

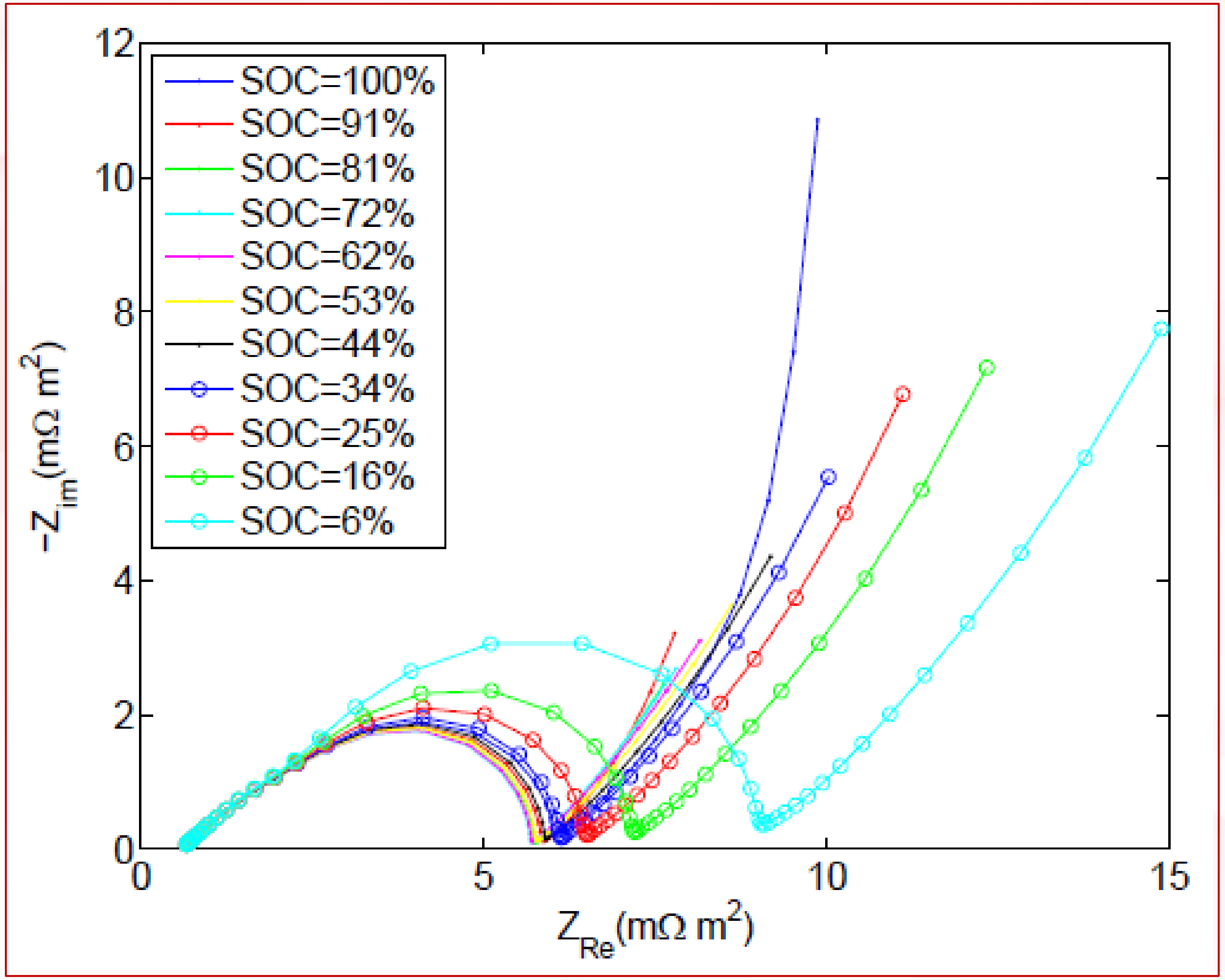


Figure from: M. Li, Renewable Energy 100 (2017) 44-52

Pros & Cons of EIS Versus Traditional DC Techniques

Pros

- EIS is a non-invasive method (won't prematurely age cells, unlike some DC methods)
- EIS generates results in **seconds** or **minutes**, versus hours or days for charge-discharge tests
- EIS does not require as high-power of test instruments compared to DC-IR tests
- ECM reference data can be a "one-stop-shop" for KPIs like SOH, SOC, rather than running separate DC tests to obtain one KPI at a time

Cons

- EIS data analysis is generally more complicated than interpreting DC data
- ECMs can be inaccurate if reference data is not collected or analyzed properly
- Must carefully review EIS equipment specs to ensure they are compatible with your battery characteristics
- EIS is more sensitive to external sources of measurement noise

The ultimate solution is to have equipment capable of running both EIS and DC techniques. Most potentiostats (and some battery cyclers) can.

How To Incorporate EIS Into Your Testing Protocols

Identify the Key Performance Indicators (KPIs) that you want to measure (SOH, SOC, etc.)

❯

Run EIS on reference batteries operating with known KPIs in well-controlled conditions

❯

Develop Equivalent Circuit Models (ECMs) using EIS data from reference batteries

❯

Measure KPIs of unknown batteries by running EIS on them & mapping data to ECMs

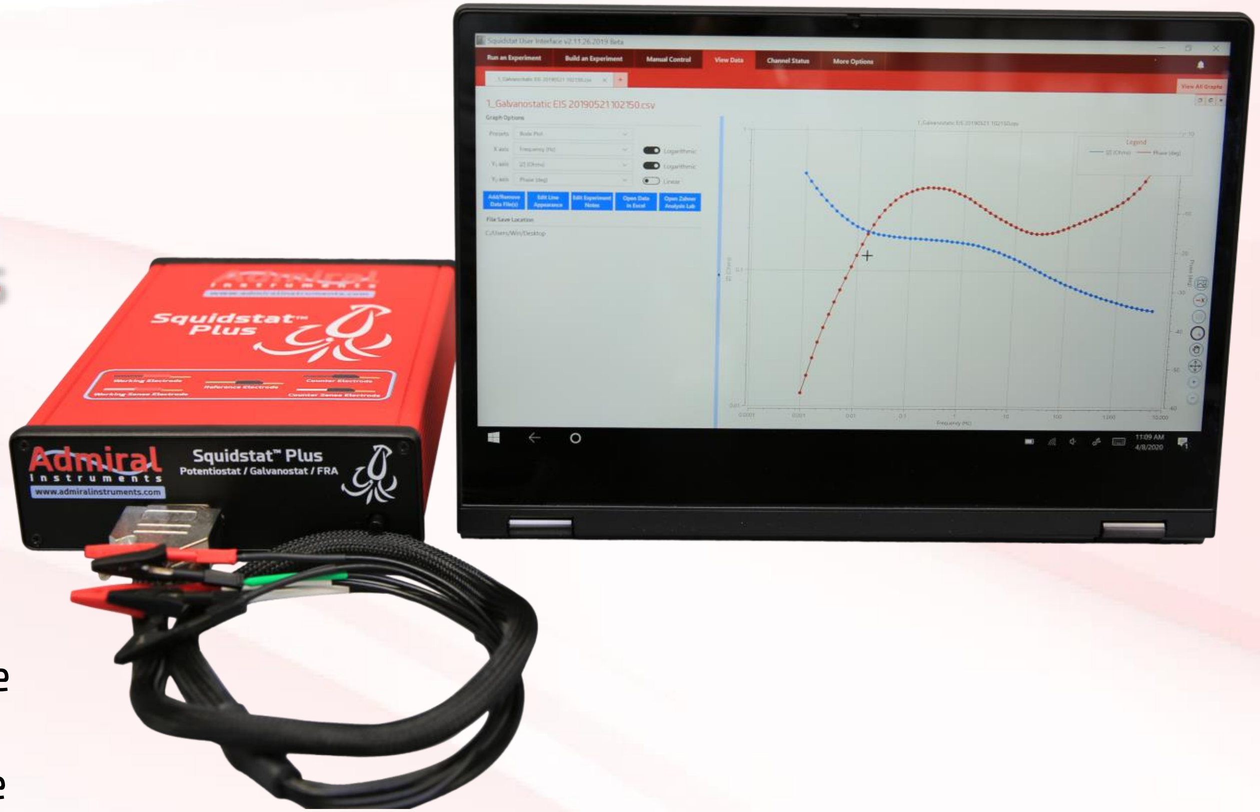
The accuracy and sensitivity of these KPI measurements depends upon the quantity and quality of reference data used to make the ECMs!

Ready to run EIS on your batteries but don't have the right tools?

Squidstat™

NEXT GENERATION

Electrochemical Testing Tools



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