



Introduction to Battery Analysis with the BA8100

The BA8100 is designed to test batteries using a complex AC measurement technique known as electrochemical impedance spectroscopy (EIS). Through this technique, the BA8100 derives the internal impedance of a battery across a wide frequency sweep. The acquired data is used to display a graphical representation of electrochemical processes occurring within the battery. The purpose of this paper is to clarify instrument operation and provide a foundation for data interpretation.

Instrument Operation

The BA8100 applies a small amplitude AC signal to the battery under test and compares it to the responding AC voltage signal. The applied AC signal is referred to as the perturbation signal and in the BA8100, this signal is superimposed on a DC signal sourced from the battery. EIS experiments involving both a DC and an AC signal are regarded as dynamic EIS (DEIS). This is in contrast to stationary EIS (SEIS), which is generally just referred to as EIS and does not include the DC aspect. DEIS provides the benefits of capturing transient impedances and reducing the overall test time compared to SEIS.

Before running tests, it is important to define all parameters and consider external conditions. Battery impedance is typically in the low milliohm range, making measurements easily susceptible to electromagnetic interference. Battery temperature and state of charge (SoC) can also affect its impedance. To help you get started, the adjustable parameters of the BA8100 are explained below.

DCI:

The DCI parameter sets the continuous discharge rate that the battery under test will be subjected to. It also sets the DC bias current, which the perturbation current will be superimposed onto. In order to minimize deviation of the battery SoC, it is recommended to set this parameter around 10% of the battery's C-rate (C/10 region) or keep the test short by using frequencies above 10 Hz.

ACI:

The ACI parameter determines the amplitude of the AC perturbation signal applied to the battery. The result of the perturbation signal across the battery is an AC voltage signal that is shifted in phase. Both these signals are measured and the impedance is derived through a ratio between the signals. By default, ACI in the software is set to 10% of the DCI, but it can be increased to improve signal to noise ratio (SNR) or decreased to reduce harmonic distortion.

Frequency:

This parameter sets the frequency of the perturbation signal and in the provided software, settings are available to perform a sweep. The BA8100 can apply signals with frequencies between 50 mHz and 10 kHz. Lower frequencies extend the duration of the test as these signals will have longer periods and multiple samples are measured to improve accuracy.

Note: The recommendations listed above serve as a starting point, but all parameters can be adjusted as needed based on the application. It is important to keep in mind that a well-defined setup is necessary for minimizing variations between measurements.

Data Analysis Tools and Interpretation

The BA8100 records impedance, frequency, phase, voltage, and current measurements into an exportable CSV file. The data can be evaluated using the graphical analysis tools in the provided software or exported for analysis using a 3rd party tool such as MATLAB or NI DIAdem. Before going over the two main plots used in EIS, it is important to establish a minimum level of understanding as to how a battery works.

Battery fundamentals:

In typical circuit schematics, we idealize a battery as a perfect source that supplies infinite current at a constant voltage. However, we know a battery can only supply a finite amount of current and its voltage changes over time when connected to a load. These non-idealities are the effects of a battery's internal impedance. To understand why this intrinsic quality exists and why it changes over time, we must understand the workings of a battery at the molecular level.

Inside a battery, a redox (reduction-oxidation) reaction is physically separated into two half-cell reactions using a porous plate (separator). At each electrode, a reduction or oxidation reaction occurs with the chemical compounds in the electrolyte solvent. Each reaction produces a potential and the maximum potential difference between half-cells is the battery's electromotive force (emf), which we measure as the open circuit voltage (OCV). In secondary batteries, reactions can be reversed by applying a potential greater and in opposite polarity to the battery's emf.

When the two electrodes are connected through an external load, the emf drives the electrons from the anode, through the load, to the cathode. Simultaneously, positively charged ions in the electrolyte will mobilize through the fluid and separator in order to stabilize the charge discrepancy. The rate at which the positively charged ions and electrons flow is the electrical current.

In the ideal scenario, infinite current would mean these charged particles move from electrode to electrode in zero amount of time. However, that can never be the case as it takes time for the reactions to yield the charged particles and for the particles to move through the system. Therefore, there will always exist a minimum impedance relating to the maximum speed at which these processes can occur. Over time, physicochemical changes will occur within the battery, slowing down the underlying mechanisms involved in mass transport and charge transfer kinetics. This will result in an increase of the battery's impedance.

Nyquist Plot:



Figure 1: Nyquist Plot

Nyquist plots are an important tool used in EIS. They display impedance on a coordinate system, with resistance (real) plotted on the x-axis and reactance (imaginary) plotted on the y-axis. The curve generated represents the impedance of the system as a function of frequency. As mentioned, battery impedance is determined by its physicochemical structure, but is also affected by environmental factors such as temperature. Changes in the battery structure or surrounding environment can be observed as changes to the battery's Nyquist plot.

The Nyquist plot can be broken down into sections, each related to particle movement involved in different processes of the electrochemical reaction. As the signal's frequency is swept, its time interval will gradually decrease until the particles no longer have enough time to move. The impedances stemming from slower processes such as migration and diffusion will no longer have enough time to occur. For this reason, the high impedance points on the right side of the graph are captured at lower frequencies, while low impedance points on the left side are captured at higher frequencies.

There is no limit to the number of sections the Nyquist plot can be broken into, as long as they are justified through theory and experimentation. Equivalent circuit modeling (ECM) is the method of creating an electrical circuit that models the behavior of the overall electrochemical reaction based on its individual processes. Without deep knowledge of the subject, it is very difficult to confidently create an equivalent model. However, there are still key impedance characteristics we can identify from a Nyquist plot using the Randles cell model as an example.

Bode Plot:



Figure 2: Impedance magnitude and phase Bode plots

In contrast to a Nyquist plot, a Bode plot displays the impedance magnitude and phase with respect to frequency. The frequency is plotted on a logarithmic scale, while the magnitude and phase are plotted on a linear scale. This graph is useful for identifying the type of circuit behavior the battery is experiencing at any particular frequency. The values may indicate mixed behaviors or non-idealities in the battery.

Randles Cell:



Figure 3: Randles cell circuit model

The Randles cell is a basic circuit model used to explain the kinetic and diffusion processes occurring at the interface between electrode and electrolyte. It is comprised of a resistor in series with another resistor parallel to a capacitor as shown in Figure 3. The resistor labeled, R_s, is determined by movement of ionic compounds in the electrolyte. The resistor labeled R_{cT} refers to the charge transfer resistance, which stems from the transfer of electrons during the redox reaction. The parallel capacitor labeled, C_{DL}, relates to the double layer phenomena that occurs at the surface of the electrode when exposed to the electrolyte. Lastly, the "W" is the Warburg constant phase element, which was created to describe the diffusion of chemical species.



Figure 4: Nyquist plot of a Randles cell

The Nyquist plot of the Randles cell circuit would have a similar shape to the illustration in Figure 4. Here we can see where each element is derived from. R_s , is the pure resistive value where the zero crossing occurs. This location can shift with changes in temperature or battery age. The parallel RC circuit $(R_{cr} | C_{DL})$ is derived from the semicircle shape, where R_{cr} is the diameter across the x-axis and is affected by battery SoC. The Warburg component (W) is a constant phase element that produces the linear portion extending upwards at a 45° phase angle. The sum of R_s and R_{CT} is associated with the effective series resistance (ESR) of the battery.

It is possible to see more than one semicircle, since additional chemical reactions can occur in the battery. A common example of this is seen in lithium batteries. Apart from the redox reaction, another chemical reaction occurs involving the lithium ions, electrolyte, and the anode. During charging, the lithium ions migrate through the electrolyte to the anode where they will be intercalated. However, some percentage of the ions and electrolyte mix with the anode to form the solid electrolyte interface (SEI). Table 1 summarizes the kinetic and charge transfer mechanisms involved in a battery's electrochemical reaction.

Description	Variable	Characteristics
Electrolytic Resistance	R₅	 Corresponds to the resistance of the electrolyte Changes will shift the zero crossing on a Nyquist plot Affected by electrode geometry and temperature Increases as the battery ages Dominant when the frequency is >1 kHz
Charge Transfer Resistance	R _{cr}	 Resistance occurs from transferring electrons from one atom to another of a different phase Affected by temperature and SoC of the battery Changes will increase the Dominant between 1 Hz to 1 kHz frequency range
Double Layer Capacitance	С	 Occurs between the electrode and the electrolyte Composed of two parallel layers of opposite charges encompassing the electrode Dominant between 1 Hz to 1 kHz frequency range
Solid Electrolyte Interface (Lithium-Ion Battery)	SEI	 Thin layer formation occurs on the surface of the anode Result of lithium ions, electrolyte solvent, and anode material reacting together As the layer grows over time, the SEI semicircle will increase both in reactance and resistance Dominant between 1 Hz to 1 kHz
Warburg (Diffusion) Resistance	w	 Represents a resistance to mass transfer Typically exhibits a 45° phase shift Dominant when the frequency is <1 Hz

Table 1: Mixed kinetic and charge transfer properties

Summary:

The BA8100 uses EIS (Electrochemical Impedance Spectroscopy), a swept frequency technique for evaluating the internal electrochemical and electrical properties of a battery under test. EIS is a method used to characterize the impedance of a system by stimulating it with a small amplitude AC signal. The graphs generated through EIS can be used to observe changes in a battery or compare impedance behavior between batteries. Additionally, the measurements acquired allow users to create an objective and subjective metric for determining a battery's end of life for a given application.