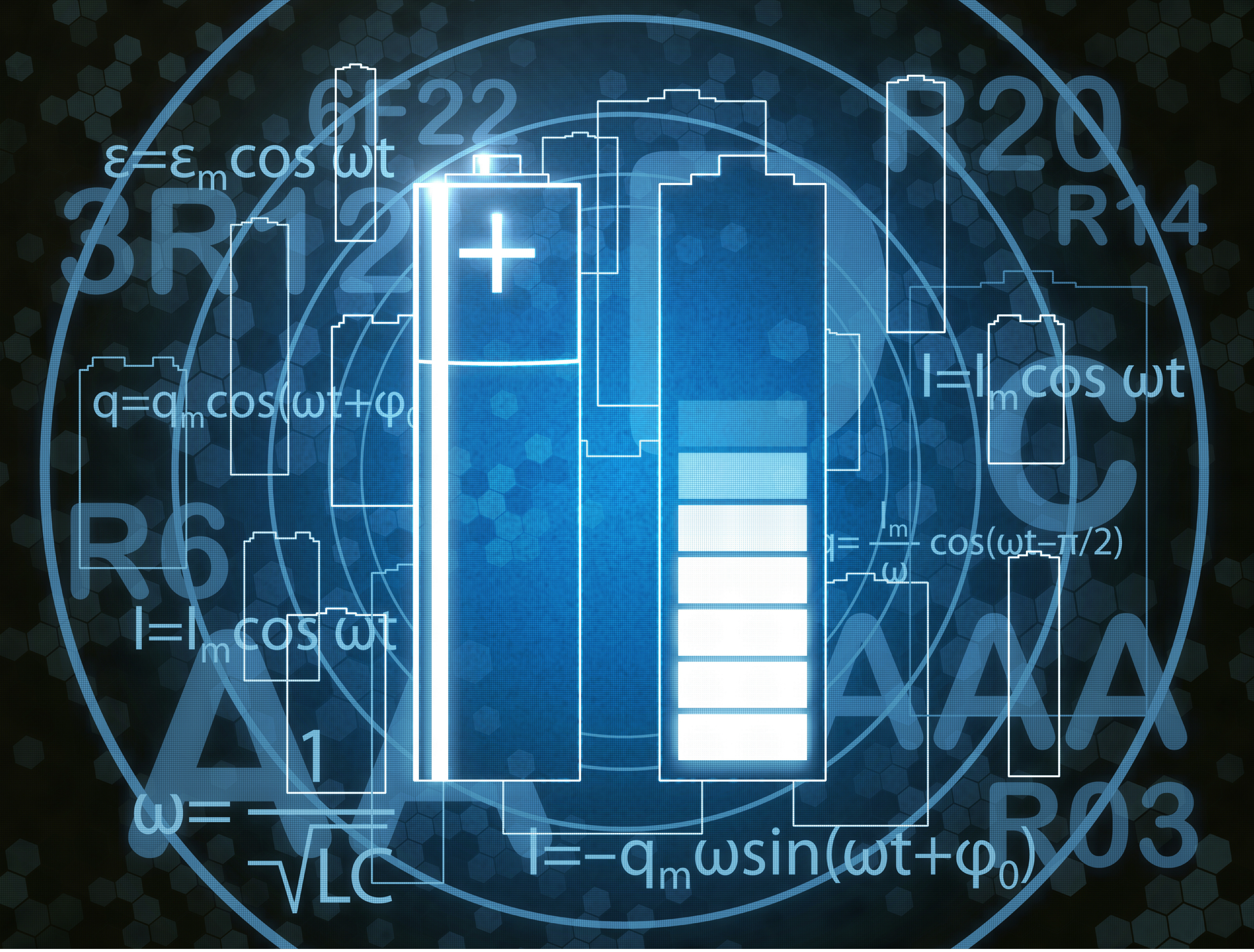

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY: PROVIDING BETTER BATTERY CELL INSIGHT

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Abstract

Observing rapid growth in the energy storage sector, advanced battery diagnostics are becoming more significant. In the problem statement, this white paper acknowledges the existing gap for battery testing methods. Electrochemical Impedance Spectroscopy testing is then identified as a suitable method providing a solution to the matter. An introduction to the experimental method and the basic concept of the method is discussed in the following sections. Lastly, the possible applications and strengths of the method are also outlined.

Problem Statement

The global market demand in 2019 for primary and secondary batteries are estimated to rise by 7.8% per year, up to $120 million. The main driver behind this phenomenon is the rapid expansion of electric vehicle (eV) industries in Western Europe and the rise of the renewable energy sector. It is forecasted that in 2025 the processing of modules or cells per annum to be in the order of 10^7.

A growing dependency on batteries requires diagnostics to maintain or predict battery reliability. There were many battery testing methods available, such as voltage reading, Coulomb counting and so on. However, these methods seldom provide full scale accuracy or have long testing periods, becoming a limiting step in battery processing throughput. This created a need for not only accurate but fast testing technologies for energy storage devices with good demonstration of reliability and repeatability.

One of the testing methods that can potentially close the gap for advance battery diagnostics is the Rapid-Test. They commonly utilize a time domain by activating the battery with pulses to observe the ion flow in cells or a frequency domain by scanning a battery with range of frequencies.

Electrochemical Impedance Spectroscopy (EIS), with a typical test time of 15 seconds, generates data plots for analysis after scanning a battery with multiple frequencies. This test provides much greater insight on the battery chemistry, taking Rapid-Test on a higher level of complexity.

Background

Experimental Techniques

Impedance can be measured using an Impedance Analyzer. Alternatively, a combination of electrochemical interface and Frequency Response Analyzer (FRA) can be applied. A DC cell bias current or voltage is first provided using the electrochemical interface, a small AC current from the FRA is then superimposed. The data collected is displayed and analyzed through software on a personal computer. Equivalent circuit modelling is used to investigate the measured data which will be discussed in more detail in the next section.

Electrochemical Impedance

The basis of EIS testing is the concept of electrochemical impedance. Impedance is known as the measure of the ability of a circuit to resist electrical current. Impedance is unlike resistance, which obeys the Ohms law at all current and voltage levels. In real life applications, impedance is favored as most circuits exhibit a much more complicated behavior.

To measure impedance, a small sinusoidal potential of fixed frequency is applied to the cell. The response of the cell is recorded and the impedance is computed. This procedure is then repeated at different frequencies.

The frequencies provided ranges from kiloHertz to milliHertz. The mid-range frequency provides valuable insight to the charge transfer of the system. This domain represents battery kinetics which indicates the state of health (SoH) of a cell. This aspect will be discussed more in the next section. The low-range frequencies provide additional information on the diffusion of battery internals. The impedance at a particular frequency can be calculated using the equation below:

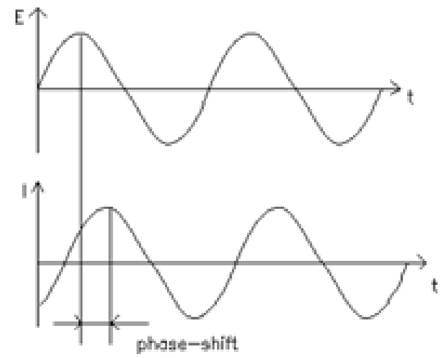

Figure 1: Sinusoidal excitation and response signal in a linear system

$$Impedance = Z_t = \frac{E_t}{I_t} = \frac{E_0 sin\omega t}{I_0\, sin(\omega t + \phi)}$$

Where E_t is the excitation signal, I_t is the response signal, ω is the frequency and ϕ is the phase shift.

Impedance is then represented as a complex number using the Euler relationship:

$$Z(\omega) = Z_0\, exp(j\phi) = Z_0(cos\phi + jsin\phi)$$

These data are then represented as the Nquist plot or Bode plot.

Nquist Plot

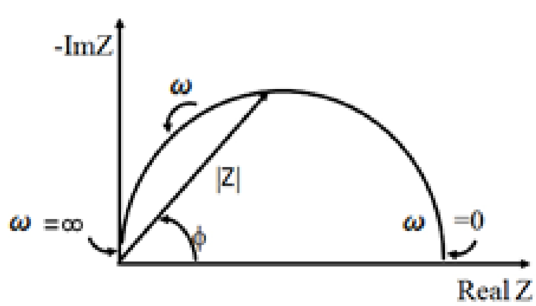

Figure 2: Nquist Plot with Impedance Vector

Bode Plot

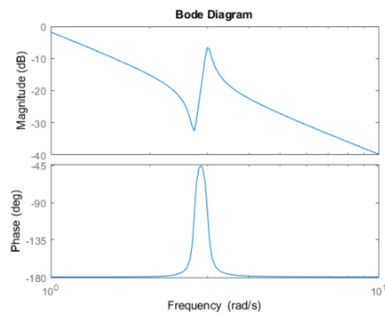

Figure 3: Bode plot

For a Nquist plot, the real component is plotted on the x-axis while the imaginary component on the y-axis. The Bode diagram plots the log frequency on the x-axis and the absolute impedance value and phase shift on the y-axis. The down side of a Nquist plot is the frequency at any point of the graph is not known, unlike the Bode plot where it is shown explicitly.

EIS Modelling

EIS data are usually analyzed by comparing it to an equivalent circuit. A network of passive electrical circuit elements is used to model an electrochemical cell; therefore, a more complex system would require a more complex circuit. Each element in the circuit needs to reflect the physical electrochemistry of the cell system. The common circuit components used are the resistor, inductor and the capacitor. Other modelling elements include the Warburg impedance, representing mass transfer resistance and the Constant Phase Element, usually to represent imperfect capacitors. The best practice is to model the cell system with the simplest circuit available.

EIS measures several factors that contribute significantly to the impedance of a cell such as the electrolyte resistance. Since uniform current distribution in a definite electrolyte area is rare, manual calculations to solution resistance using the solution conductivity are not accurate. EIS results are able to provide accurate values on this parameter.

When an electrode is immersed in an electrolyte, an electric double layer will be formed from the ions adsorbed on the electrode. This insulating layer causes the electrode-electrolyte interface to behave like a capacitor, which will be reflected in the EIS data.

The process to transfer the electrons from a solid state (electrode) to the liquid phase (electrolyte) is associated with a certain resistance known as the charge transfer resistance, which can be determined through the EIS data analysis.

Applications and Strengths

EIS is a reliable testing method to measure critical battery parameters. One of the most important is estimating the SoH of a battery. Most digital and analog monitoring methods failed to predict the battery end of life effectively as the voltage and internal resistance do not correlate with capacitance. EIS testing overcomes this issue by delivering information on the capacitance behavior of the system. Specific algorithms were developed for different types of cells with varying cell chemistry. With the increasing number of eVs, a minimum SoH of 80% is now required to meet minimum safety standards during vehicle inspection. A battery with of SoH between 70-80% will be used for 2nd life applications, whereas those beyond 70% will be recycled to reclaim valuable components. The rapid testing and non-invasive nature of EIS is suitable for eVs battery grading initiatives.

EIS testing also provides accurate diagnostics for state of charge (SoC), which is important to allow users to predict battery usage at a certain discharge rate. Unlike the common practice of Coulomb Counting, EIS retains its accuracy as the battery ages. The SoC is first measured using the open circuit voltage or under a real load. The full frequency response of the battery is then auto fitted with EIS from an equivalent circuit model, enabling the charge transfer resistance and solid electrolyte interface impedance to be determined. By comparing to a look up table, the SoC of a particular cell can be acquired.

The growth of fast charging batteries increases research on low impedance cells. Typically, Shunt technology is used to study these cells. However, the accuracy of this method changes significantly as a function of temperature. EIS testing overcomes this issue by maintaining the circuit temperature from 1Amp up to 300Amp current, providing a full scale accuracy towards the research in this field.

For applications that utilize modular cell system, particularly in eVs, EIS testing is useful for troubleshooting purposes. Oftentimes, battery faults are overlooked in voltage monitoring. A battery that is approaching end of life might still have the same open cell voltage as a new battery. Since EIS uses a broadband frequency, a false positive can be avoided as an overview of the electrochemical properties of the cell is provided. For example, a faulty cell in the pack can be easily detected if a higher impedance value is returned in the results. The cell limiting the system can then be removed and replaced.

EIS is also used as a basis for algorithm development to determine the relationship between SoC, SoH and cell temperature. With knowledge of two, it will be possible to determine the third parameter. This research is important for material research for advanced batteries and also eVs and automation industry to prevent cell thermal runaway.

Conclusion

EIS testing is becoming increasingly significant not only for battery grading and characterization in industries but also a useful tool for battery research. EIS contributes valuable insight for detailed modelling of battery systems in the form of a complex equivalent circuit, allowing the usage of electrochemical and physical variables. This non-invasive and fast testing technique is effective in reflecting the true state of a cell system, allowing data collection for high-voltage charge management, thermal management, performance monitoring, performance forecasting and operation strategy and so on.

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