TITLE: Standard operation procedure (SOP) on Electrochemical Impedance Spectroscopy (EIS) for low impedance batteries

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DOCUMENT PURPOSE: This document is intended to provide a generic and instrument-unspecific guideline to help in the process of acquiring reliable and reproducible data with Electrochemical Impedance Spectroscopy (EIS) especially for low impedance batteries. The areas covered are battery under test (BUT) and instrument handling, data storage, and general data analysis. Extensive advice on data analysis is beyond the document's scope.

ABBREVIATIONS / TERMINOLOGY:
EIS – Electrochemical Impedance Spectroscopy
BUT – Battery Under Test
AWG – Arbitrary Waveform Generator
ESD – Electrostatic Discharge
SOC – State of Charge
AC – Alternating Current
EEC – Electrical Equivalent Circuits

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1. Introduction

This document attempts to provide a generic and instrument unspecific guideline for use of Electrochemical Impedance Spectroscopy (EIS) for batteries. The intention is to provide basic information needed to perform reliable, repeatable and safe measurements.

EIS consists of applying an alternating current (AC) signal (galvanostatic mode) or voltage signal (potentiostatic mode) to the battery under test (BUT) and record the system response, which is the voltage drop across the BUT terminals or the resulting current through the BUT, respectively. The frequency of the excitation signal is swept within a defined frequency window. The response of the BUT is a complex function which results in the characteristic amplitude and phase shift of the flowing current with respect to the voltage signal. The frequency dependence of the BUT is used to separate the different electrochemical and physical contributions from the total response, such as electrochemical reactions at the anode and cathode, physical phenomena (e.g. diffusion, electrode kinetics), or the capacitive and inductive properties of the system.

Impedance measurement equipment typically comprises some sort of excitation signal generation like swept sine sources or arbitrary waveform generators (AWG) followed by a power amplifier that provides the desired voltage or current amplitude to stimulate the BUT. The excitation signal is provided by the equipment's "force" terminal while the current is accurately measured. With low impedance batteries, current mode excitation (galvanostatic mode) is preferred while current amplitudes can be in the range of 10mA up to 100A+. The attribute "low impedance" has no sharp definition but 1 Ohm seems to be a practical threshold. The resulting voltage drop at the BUT terminals is sensed by individual contacts in the test fixture (4-wire connection) and connected to the equipment's "sense" terminal. Coaxial wiring for both, force and sense connection, can reduce the susceptibility to cable referred systematic and random errors significantly. Note that the test fixture should be specifically designed for the battery form factor that is measured.

The battery impedance measurements described in the following sections employ the galvanostatic method which is done by feeding a sinusoidal current into the battery terminals while measuring the voltage response across the terminals. The current and voltage signals are digitized and transformed into the frequency domain where the actual impedance $Z(\omega) = V(\omega) / I(\omega)$ is calculated. Frequency sweeping is used to cover the broad spectrum.

The following sections contain advice and procedures to ensure the stable and reliable operation of the EIS to obtain high-quality data.

2. Operator and equipment safety

Performing EIS measurements may expose the operator to the BUT and to the instruments and mechanical fixtures. Necessary precautions should be considered to avoid injury (e.g. from exposure to battery thermal runaway, sharp objects, or exposure to other harmful substances). Additionally, due to typical instrument specifications, in some cases high voltage safety measures ought to be considered.

EIS instruments are sensitive to static electricity, therefore special care should be taken to avoid damage from electrostatic discharge (ESD). Conducting wrist straps are advised to be used to prevent high voltages from accumulating on workers bodies, also anti-static mats or conductive flooring materials are desirable.

3. Setup and calibration

A typical measurement system using EIS method consists of the measurement hardware, the software to control the hardware and to calculate impedance, a fixture to connect the BUT, cables and connectors (see Figure 1).

Initially, proper connection of the cables from the instruments to the fixture is ensured. All connectors should be checked for damages and residues. Ensure the cables are firmly connected and have a stable position, while respecting their specific minimal bending radius. Moving cables can lead to a change in the impedance measured, especially for low impedance values. Furthermore, make sure all cables are specified to work in the current and voltage range used in the experiments.

Before the BUT measurement, a calibration process is performed. Several calibration workflows of different complexity and accuracy level are available depending on the equipment. The methods include simple offset subtraction with a short measurement and three-term methods where three well-known standards are used. The calibration process is used to determine the systematic (repeatable) error that is added by the equipment to the measurement result. In a subsequent correction step this information is used to correct actual BUT measurements. It is important to use calibration standards specifically designed for the fixture in use.

To summarize:

1) Ensure all connections of cables are properly assembled, tightened and checked for any damage prior to calibration start
2) Maintain a stable position of all the cables and comply with their specific minimal bending radius. Keep cables as short as possible and make sure the cables used are specified to work in the frequency and power ranges needed.
3) Calibration is used to remove undesirable systematic errors from the experiment by measuring the difference between the predicted and actual values. The three commonly used calibration standards are: short and two resistors of known values (resistance and inductance).
4) The different calibration standards with the corresponding standard definition are applied subsequently and special care is taken to ensure a proper contact and a proper mechanical position of the standards in the test fixture.

4. Measurement

General points to consider:

1) Ensure proper connections from the instruments to the fixtures and BUT, and all relevant devices are switched on. Depending on the instrument a warm-up period of 15 minutes up to 1 hour should be considered before measurements are started. In order to check if any drift has settled repeated measurements can be done each 5 minutes. The warm-up has finished when the differences have become lower than the instrument's noise floor.
2) Make sure the BUT is properly installed in the specific fixture and the cable connectors are firmly attached to the BUT.
3) Maintain a stable environment to assure repeatable measurements, such as stable and known environmental and BUT temperature.

4) Record all measurement metadata, e.g. ambient temperature, BUT specifications, SOC.

Measurement case I: EIS at a constant temperature and constant SOC

1) Choose a suitable frequency range for the experiment (e.g. 10 mHz to 10 kHz)
2) Choose a proper excitation amplitude to ensure linear operation (in galvanostatic mode 1/100C – 1/10C is adequate for many cases).
3) If a temperature chamber is used, set a specific environment temperature and keep the BUT at this temperature long enough in order to adapt and settle to this temperature.
4) Record the SOC and temperature of the BUT.
5) Set the remaining experiment parameter values including number of frequency points, logarithmic or normal frequency sweep, instrument sampling speed. In case of very low frequency measurements it can be beneficial to swap the frequency sweep direction and start from high frequencies first.
6) Start the EIS measurement.

Measurement case II: EIS with varying temperature and SoC

A) SOC for outer loop and temperature for the inner loop:	**B) Temperature for outer loop and SOC for the inner loop:**
• Starting from the desired high SOC level of the BUT, begin the temperature loop (e.g. 50, 35, 25, 5°C) • Maintain enough rest time at each temperature level to assure BUT temperature is stable and no changes in the BUT are occurring (e.g. for batteries charge redistribution or open circuit voltage OCV changes are settled at the new temperature) • At each temperature conduct the EIS measurement and repeat process for all temperatures, while maintaining enough rest time for each new temperature level. • Once EIS is measured for all temperatures proceed to the next SOC level and repeat the process above.	• Starting from the desired starting temperature value of the BUT, start the SOC loop (e.g. from 100% to 0% SOC) • At each desired SOC level conduct the EIS measurement and repeat process for all SOC levels, while maintaining the enough rest time at each new SOC level. • Once EIS is measured for all SOC levels proceed to the next temperature level (e.g. 50, 35, 25, 5 °C) and repeat the process above. • Maintain enough rest time for each temperature level to assure DUT's temperature has adjusted, is stable and no changes in the DUT are occurring (e.g. for batteries charge redistribution or open circuit voltage changes are settled)

After a measurement session is completed it is recommended to measure a known standard with an impedance in the range of the BUT impedance to check if calibration is still valid and if the system parameters have changed.

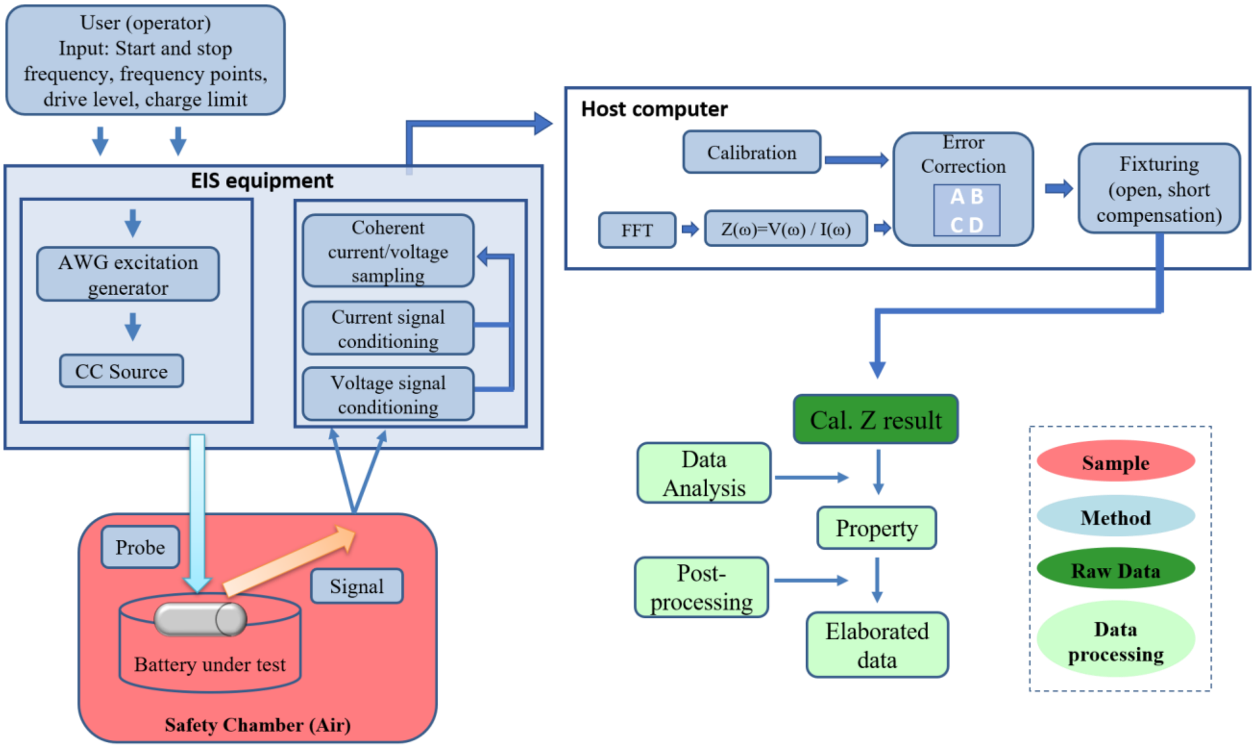

Figure 1: Flow chart for battery EIS. The sketch is based on the EIS CHADA template (characterization data templated developed by EMCC, European Materials Characterization Council)

5. Data acquisition, fixtures, and error sources

Data processing through calibrations: the systematic error correction is processed by defining an appropriate error model and measuring certain calibration standards in order to solve and obtain the error coefficients, which is done by the computer software.

The raw impedance as a function of frequency is measured, containing information on the amplitude and phase, as well as the inductance, capacitance, and resistance information of the BUT. The SOC is computed and the temperature is measured. The values are derived from digitizing the current and voltage data across the battery terminals and transforming them into the frequency domain where the actual impedance is computed.

For visualizing the EIS data, typical plots are used such as:

- Bode plot: a magnitude plot, expressing the magnitude (usually decibels) of the frequency response, and a phase plot, expressing the phase shift versus frequency.
- Nyquist plot: representing the negative of the imaginary versus the real parts of the complex impedance of a BUT, by convention this is plotted with equal y and x axis scales.
- Resistance/inductance plot: illustrating the resistance versus frequency and an inductance versus frequency, where typically the frequency on the x-axis is in the logarithmic scale

The EIS data and related complex plots are often interpreted using electrical equivalent circuits (EECs). An appropriate EEC model can be developed to describe the electrochemical reaction that takes place at the electrode/electrolyte interfaces, both on anode and cathode. Several EEC models are available in literature [4].

The accuracy of an EIS measurement is limited by systematic and random (stochastic) errors. Systematic errors can be corrected to a certain degree by calibration and correction methods while random errors like system noise and fixture repeatability are not corrected. The correction capabilities of calibration methods are, however, limited by the accuracy of the used calibration standards. An overview on random errors for EIS is given in below table.

error source	physical process	relative importance [4]	frequency behavior	IQ behavior	typical range [5]	max range [6]
fixture DUT position accuracy	DUT current path changes with position: inductance changes, eddy currents in conductive structures changes	* * * * *	linear with frequency	Re and Im ΔIm > ΔRe	ΔRe < 100μΩ ΔIm < 500μΩ	ΔRe < 1mΩ ΔIm < 5mΩ
calibration standard definition accuracy [1]	error propagation through correction process	* * * * *	equal for all frequencies	Re and Im		
cable movement	changed mutual coupling between sense and force	* * * * (single wires) * (coax)	linear with frequency	Re and Im ΔIm > ΔRe	ΔRe < 5μΩ ΔIm < 5μΩ ΔRe < 100μΩ ΔIm < 500μΩ	ΔRe < 5μΩ ΔIm < 5μΩ ΔRe < 1mΩ ΔIm < 5mΩ
fixture contact repeatability	variying contact resistance (pressure, oxide layers): error terms in cobination with instr. terminal impedance, current distribution in DUT contact (pad)	* *	typically constant	typically Re	10μΩ	100μΩ
instrument noise [2]	random noise	* *	typically constant above 1 ... 10 Hz	typically equal for Re and Im	1μΩ ... 10μΩ	
instrument drift [3]	low frequency noise, typically not gaußian	* *	increasing with lower freq.	to be studied	1μΩ ... 10μΩ	
instrument nonlinearity	signal level dependent response error	*	typically constant	typically equal for Re and Im	< 1μΩ	10μΩ [7]
contact thermal voltages	thermoelectric DC offset due to temp. gradients	*	DC	DC resistance	< 1μΩ	

[1] definition error propagates thorough calibration and correction to the calibrated result – an individual sensitivity analysis needs to be done for each calibration method
[2] narrowband swept sinewave measurement, state of the art electronics, $|Z_{DUT}| = 1m\Omega$, $I_{force} = 1A$
[3] 1mHz – 1Hz, 1 period of test signal is analyzed, state of the art electronics, $|Z_{DUT}| = 1m\Omega$, $I_{force} = 1A$
[4] five stars is most important, one star is least important
[5] state of the art electronics, optimized fixture design, trained operator – values are given for 10 kHz
[6] state of the art electronics, no optimized fixture design, no trained operator – values are given for 10 kHz
[7] estimation based on typical gain structure and typical ADC specification (e.g. 18 bit +/- 2LSB INL)

As shown in the table, in low impedance battery EIS the measured value depends strongly on the spatial position of the BUT in relation to the test fixture. Figure 2a shows how different BUT positions with respect to the measurement plane lead to different current paths. The measurement plane is defined by the “short” calibration standard. The different BUT positions lead to different current paths and thus, they lead to changes in mutual magnetic coupling and lossy eddy currents in conductive structures. The latter two effects have a strong influence on the impedance at higher frequencies. The empirical formula

$$\overrightarrow{|\Delta Z|} = \frac{1e5 * |\Delta Z_{max}(f_{max})|}{f_{max}}$$

with the maximum frequency f_{max} (Hz) and the maximal acceptable absolute impedance change $|\Delta Z_{max}(f_{max})|$ (Ohms) provides a practical estimation of the required position accuracy. The absolute spatial error $|\overrightarrow{\Delta Z}|$ is given in millimeters and describes the acceptable variation of the BUT in relation to the calibration plane. For instance, an absolute repeatability error lower than 100 µΩ at 10 kHz requires typically a position accuracy of better than 1 mm in all three dimensions. A measurement is given in Figure 2b where the differences in the imaginary part of the impedance are shown for a 1 mΩ verification standard that has been misaligned by 0.5 mm, 1 mm, and 2 mm, in z-direction, respectively. The misalignment increases the non-coaxial area and therefore the inductance, see Figure 3.

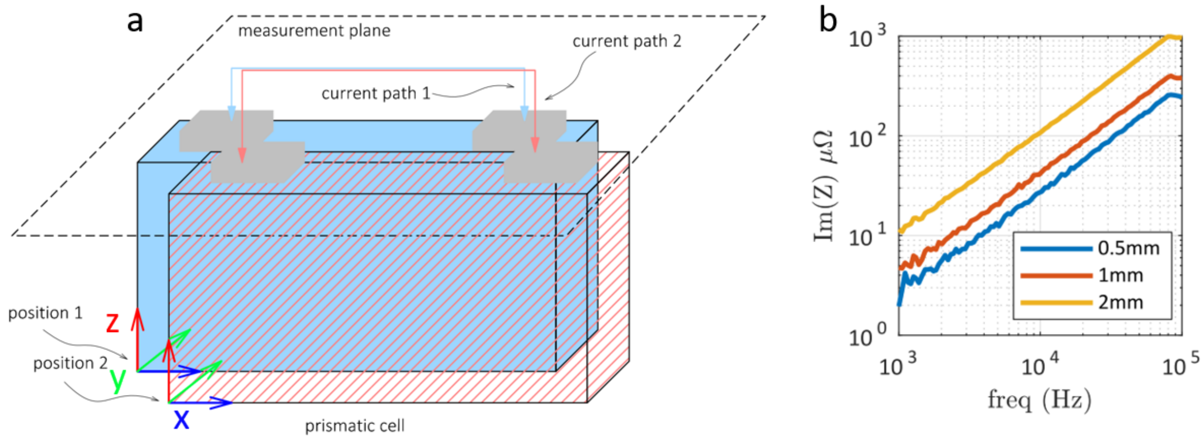

Figure 2: (a) Relative position of the BUT with respect to the measurement plane. (b) Measured example of a 1 mΩ verification standard shows the effect of misalignment in z-direction.

Random errors can be minimized if the following points are considered adequately (see also Figure 3):

- The test fixture should be mechanically rigid and stable, and a position guide should accurately define the position of the BUT as well as the position of the calibration standards in all three dimensions.
- The calibration standards should be of low drift and fit mechanically to the test fixture and resemble the BUT from a current path perspective.
- The standard's definition should be as accurate as possible and most preferable the definition should be traceable to an accredited calibration laboratory.
- Special care should be taken on the wiring between the instrument and the test fixture. If possible, coaxial wiring as shown in Figure 3 is highly preferred since it is much less susceptible to cable movement induced errors. Single wire cabling should be kept as stable as possible after calibration.
- The contacts that interface the test fixture and the BUT need to be kept clean and for increased repeatability a defined contact pressure should be ensured. For example, spring loaded contacts can be used or screw terminals can be tightened up to a defined torque.

- The instrument's noise and drift need to be taken into account. Random thermal noise typically occurs at frequency above 1-10 Hz and can be cured by narrowband measurements and averaging at the cost of longer measurement times. Instrument drift is especially relevant for very low frequency measurements (e.g. 1 mHz).
- Instrument nonlinearity could introduce response errors depending on the measured impedance level. However, depending on the instrument this effect needs to be individually characterized but typically instrument nonlinearity is not a major error source.
- A settled constant ambient temperature and a suitable warm up period are recommended. Thermal contact voltages can introduce a constant offset voltage but this does not effect the EIS results since the measurements are done at AC signals. Only at very low frequencies errors could arise if the equipment temperature changes during one measurement cycle.

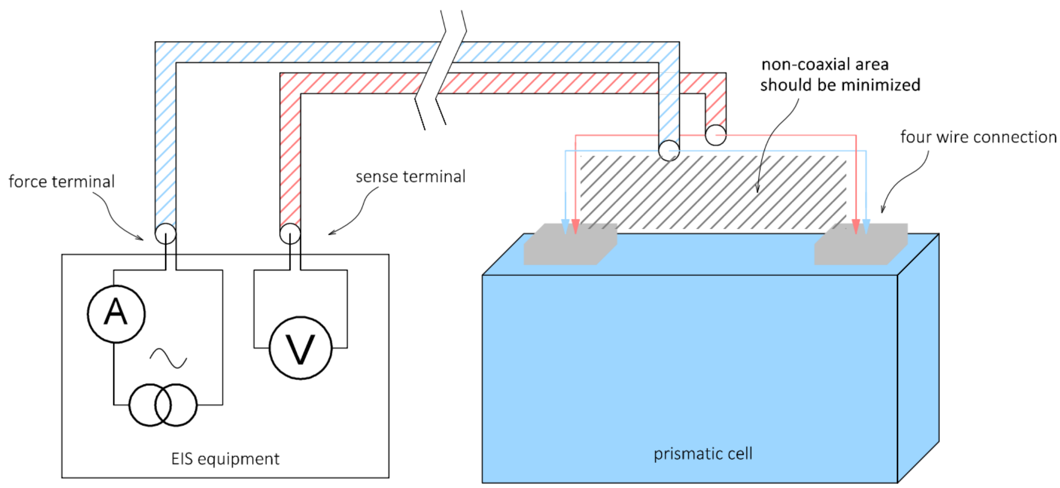

Figure 3: Coaxial wiring diagram including force and sense terminals, as well as four-wire connection

6. Uncertainty and meta-data

In order to allow for comparable and traceable measurements it is recommended to not only store basic experimental data (frequencies, calibrated complex Z(ω)) but also metadata that contains at least the following information:

- basic metadata: date and time, manufacturer and type of instrument, ambient temperature, BUT temperature, connection type (fixture type or no fixture)
- detailed measurement setting (galvanostatic or potentiostatic mode, excitation amplitude, averaging-, windowing-, and smoothing settings)
- type of calibration (name of procedure, name of used standards, position of calibration plane); options for specific applications can be considered (e.g. prismatic cells, cylindrical cells, pouch cells)

Moreover, depending on the requirements, the accuracy of the measurement can be specified in an extended experimental data part that describes:

- the uncertainty of the result for each frequency point
- or the full covariance matrix of the result for all frequency points
- or the same as above but with additional information on the time dependence (e.g. the influence of aging)

7. Feedback from collaborators

The described low impedance EIS workflow including a three-term calibration approach has been evaluated together with industrial partners (two OEMs, originally equipment manufacturer) for prismatic Li-Ion cell measurements in a frequency range from milli-Hertz to 30 kHz. The impedance level was in the range from several 100 micro-Ohms at low frequencies up to few milli-Ohms at high frequencies. The results showed a repeatability error within few micro-Ohms at low frequencies and not more than 100 micro-Ohms at 10 kHz corresponding to an inductance of 1.6 nH. The measurements were done in a kind-of round-robin setting, including Keysight and the two OEMs. The first report of the results comparing the three different measurement programs is currently established (July 2020), and a technical paper will be done.

The SOP drafts were discussed with Metas (Bern, Switzerland) in May 2020 and in June 2020, and a guidance was provided by Metas to Keysight for the SOP structure and content. Part of this work was done in the frame of the ongoing European Commission project NanoBat.

8. References

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