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Interlaboratory Comparison of Low Impedance for Impedance Spectroscopy

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Abstract – **The paper reports an interlaboratory comparison of low impedance measurements at frequencies relevant for electrochemical impedance spectroscopy (EIS) of commercial lithium-ion cells. The comparisons cover an impedance range from 50 µΩ to 100 mΩ across the full complex plane in a frequency range 0.01 Hz up to 5 kHz. A first comparison covered calibration of low impedance standards by reference digital sampling impedance setups in 4-terminal and 4 terminal-pair connections. A second comparison used commercial 4-terminal EIS meters to measure the low impedance standards characterised in the first comparison.**

I. INTRODUCTION

Electrochemical impedance spectroscopy (EIS) is one of the most common laboratory methods used to investigate internal electrochemical processes of lithium-ion batteries in a non-destructive way. Typical impedances of Li-ion cells may vary from sub-milliohm values for large cells with capacity of tens of ampere-hours up to over 100 mΩ for smaller aged cells. The characteristic features in the frequency spectrum are semicircles in the Nyquist plane, which are associated with processes at the electrode/electrolyte interfaces and lie typically in a frequency range from tens of millihertz up to kilohertz range. The measured impedance has arbitrary phase angle, so a full complex plane measurement capability is needed. Traceability of impedances and frequencies in this range is not well established, even in the primary impedance laboratories of national metrology institutes (NMI) and less so in electrochemistry laboratories. The measurements performed in particular laboratories are often not repeatable or comparable. This situation was identified as a major problem by the consortium of the EMPIR [1] project “LiBforSecUse - Quality assessment of electric vehicle Li-ion batteries for second use applications” [2]. Thus, one of the basic goals of this project was to improve metrology of low impedances down to very low frequencies and values.

The plan of the LiBforSecUse project was to: (i) Develop low-impedance standards; (ii) Develop a reference impedance bridge; (iii) Characterise the impedance standards; (iv) Use the impedance standards for an interlaboratory comparison of EIS meter measurements. On top of the original plan, one more bilateral comparison was conducted between ČMI and RISE to validate the characterisation of standards in step (iii).

II. SELECTION OF IMPEDANCE STANDARDS

Several types of impedance standards were developed within the scope of the LiBforSecUse project. The standards covered a wide range of impedance in the full complex plane, and covered an impedance range from sub-milliohm to over 1 Ω. Apart from the new standards, several commercially available standards were used in the project. The following standards were included in the comparisons:

- **4TP/4T resistors**: Commercial low impedance standards manufactured by Hioki with values 0 - 1 - 3 - 10 - 100 mΩ. The standards are equipped with four BNCs with split-ground topology and banana terminals for a 4-wire measurement with return current loop. Thus, the standards have a minimal difference of impedance between 4TP and 4T measurement (below ±0.5 nH), so they are suitable for both 4TP measurements and 4T measurements using EIS analysers.
- **4TP reactance**: ČMI developed a reactance standard with a controllable DC bias source [3] having four ranges: ±340 nH and ±3.4 µH. The difference between 4TP and 4T measurement is below 1 nH.
- **4T simulators with arbitrary phase angle**: PTB developed two simulators based on the combination of a current shunt and an active modifying circuit producing semicircles in complex impedance space. The simulators provided 13 different simulated impedance values (ranges) covering an impedance range from 0.5 to 10 mΩ.
- **Analogue impedance multiplier**: RISE designed an impedance multiplier simulating a capacitance of 1 F.

III. BILATERAL COMPARISON ČMI - RISE

The first phase of comparisons conducted in the project was a bilateral comparison between ČMI and RISE of low impedance measurements using digital sampling setups.

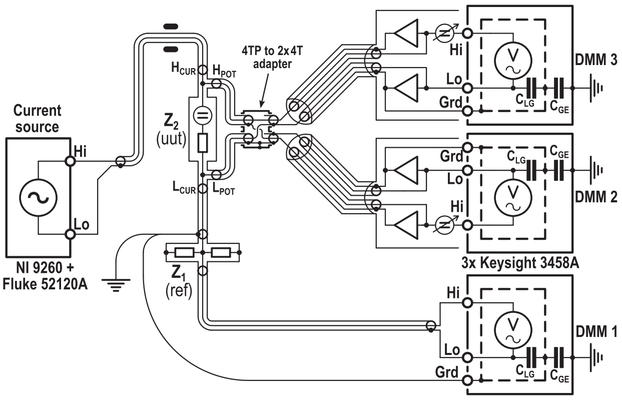

Fig. 1. ČMI digital sampling impedance bridge for mΩ-range EIS measurements.

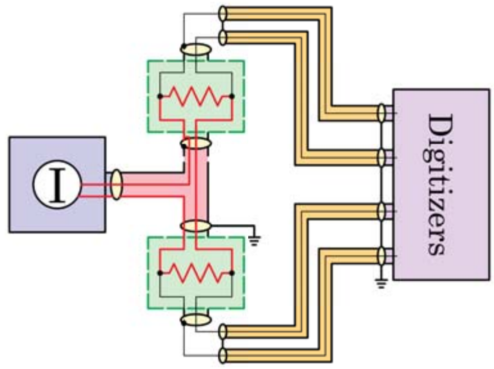

Fig. 2. RISE digital sampling impedance bridge for current shunts calibration.

All measurements were performed without DC bias voltage or current at rms current of 1 A. The frequency range was 10 mHz to 5 kHz with frequency step 1 - 2 - 5.

ČMI used two measurement setups. The first setup was a new impedance bridge setup specialised for EIS based on low the cost digitizer National Instruments NI 9238 with four floating inputs. The setup shown in Fig. 1 was described in detail in [4]. The source of a measurement current was a DDS synthesizer based on the NI 9260 DAC with transconductance amplifier Fluke 52120A to deliver required current. Current output was connected via coaxial cable via measured impedance standard (UUT) and then to the reference coaxial current shunt. The current returns back via the coxial shield of the same cable. This simple arrangement ensured well balanced current in the current cable, so the electromagnetic interference to the potential sensing cables was minimized. Voltage on the reference shunt was digitized in a single ended connection using first digitizer channel DMM 1. The voltage of the UUT was digitized using channel DMM 3 connected between the live potential terminals of UUT. This is sufficient for 4T measurements. For a 4TP measurement, the potential between UUT potential ports shields was digitized by DMM 2 channel of NI 9238. Voltages of both high-side digitizers DMM 2 and DMM 3 were combined to obtain an effective 4TP voltage drop. Connection to the high-side digitizers was via active guarded twin-axial cables to minimize leakage currents. The guarding unit also contained DC bias compensators, but those were not used in this comparison as the measurement was performed without DC bias voltage. Sampling was coherent, so a simple FFT analysis was used to obtain complex voltages which were used for calculation of impedance ratio. This setup covered a measurement range of 0.01 Hz to 5 kHz with expanded uncertainties starting at about 20 μΩ/Ω at low frequencies and up to order of 100 μΩ/Ω at 5 kHz.

The second ČMI setup was a traditional 4TP digital sampling impedance bridge [5] with balancing circuits containing injection transformers. Therefore, its frequency range starts from 20 Hz. Thus, it was used only to validate the measurement using EIS bridge in the higher frequency range from 20 Hz to 5 kHz. The second setup enabled uncertainties below 20 μΩ/Ω across the full frequency range. The reference impedances for both ČMI setups were coaxial current shunts with impedances from 30 to 600 mΩ traceable to calculable resistors. The linearity of both bridge setups was also traceable to the ratio of the calculable resistors.

RISE used a 2 terminal-pair impedance bridge developed for low impedance current shunts [6], [7]. A schematic is shown in Fig. 2. The measured impedances were compared to the impedance of a calibrated wideband coaxial current shunt of 8 mΩ. The normal procedure with this bridge is to reverse the high and low potential of the impedances in order to eliminate loading effects. However, since the impedances were very low, the input impedance of the digitizers and connecting cables had no influence on the results, and the reversing procedure was not needed. The digitizers used were National Instruments NI-PXI 5922 dual channel 24-bit digitizers, and the current source was a Clarke-Hess 8100 transconductance amplifier controlled by an Agilent 33522 waveform generator. The uncertainty was approximately 300 μΩ/Ω for all measurements.

A few tens of comparison measurements were performed in total. The following paragraphs will cover just a selection of them. The first selected result, a comparison of the PTB cell impedance simulator, is shown in Fig. 4. The object of comparison (UUT) had an equivalent impedance of $\hat{Z} = 1\,\mathrm{m}\Omega + 2\,\mathrm{m}\Omega \parallel 4\,\mathrm{F}$. The PTB standard contains also a 0 Ω-range which was used as a short correction for all measurements. This eliminated most of the mutual couplings between current and potential leads that would otherwise worsen the reactance match by several or-

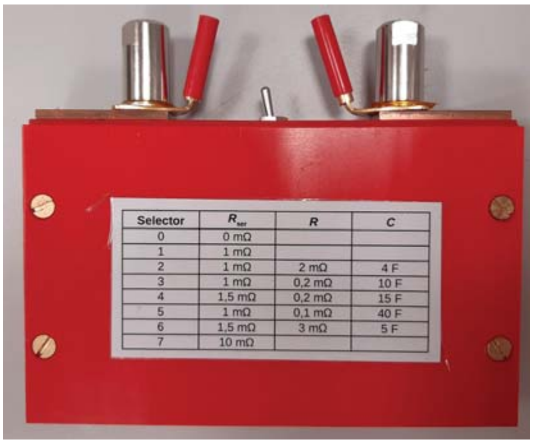

Fig. 3. PTB designed multi range Lithium cell impedance simulator with 4T connection terminals.

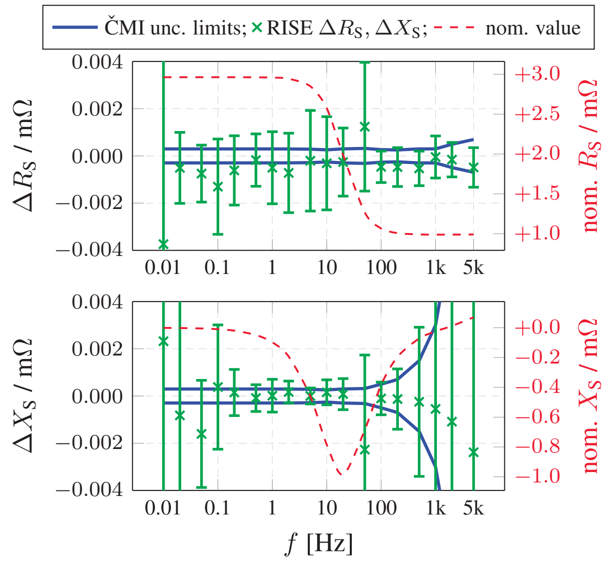

Fig. 4. ČMI - RISE comparison on PTB standard, range no. 2 ($\hat{Z}$ = 1 mΩ + 2 mΩ || 4 F). The blue lines are ČMI expanded uncertainties, the green marks are RISE absolute deviations from ČMI, the green error bars are RISE expanded uncertainties and the red trace is nominal value of R_S and X_S parameter, respectively.

ders of magnitude. Deviations were mostly below ±1 µΩ, with most of the error being standard deviation of the RISE measurements. The increasing uncertainty of reactance at higher frequencies was caused by the mutual couplings between the potential and current leads which was conservatively estimated to ±1 nH. The deviations on about half of the 7 impedance ranges provided by the first PTB standard were of a similar order. The other half showed deviations on a real component up to a few microohms, sometimes even outside assigned uncertainties. The most likely explanation is the limited stability of the active modifying circuit of the standard, which was observed during characterisation at ČMI.

The next comparison was performed with another PTB cell impedance simulator with an impedance of $\hat{Z}$ = 0.5 mΩ + 1 mΩ || 4 F. The results are shown in Fig. 5. In contrast to the previous comparison, the standard contains no 0 Ω-range, so no short correction was performed in this case. This was possible due to good geometrical separation between the current input and potential sensing terminals and thus very little mutual coupling between the potential and current leads. The stability of the standard was also superior to the previous case. The deviations between ČMI and RISE were of the order of ±100 nΩ for both the real and imaginary components. A similar order of errors was obtained on all other ranges of the PTB simulator, covering an impedance range 0.5 to 10 mΩ. These measurements confirm the assumption that the failure to match the real component of the first PTB standard was caused by its instability, as the measured impedances here were of the same order.

A further comparison was performed with the ČMI reactance simulator. The exemplar results shown in Fig. 6 are for the low, positive range, i.e. roughly +340 nH with negligible series resistance. Deviations were up to few microohms on both real and imaginary axes, except at high frequencies. The deviations were most likely caused by different terminal configurations. ČMI measured in 4TP, whereas RISE measured in 4T with the return current via a shorted L_{CUR} BNC port of UUT. The characterisation performed within the scope of [3] showed that there is a reactance difference of roughly 1 nH, and of a few microohms in the real component, between 4TP and 4T connection, so small deviations were expected. Similar results were obtained in the other three ranges of the ČMI reactance standard.

Several comparison measurements between RISE and ČMI failed completely. Some failed due to limited stability of the travel standard (the RISE capacitance multiplier) and some failed due to incompatible wiring. One example for all is attempt to compare the Hioki resistance standards. In theory, it should have been the easiest measurement of all. However, yet unidentified mistake in the wiring caused a massive deviation of the measured reactance roughly equal to 26 nH for all measured values, which is almost 1 mΩ at 5 kHz. That is already comparable to reactance of larger li-ion cells. Most likely explanation of this fail is effect of unwanted mutual coupling due to different wiring among the participants.

IV. COMPARISON OF EIS MEASUREMENTS

A second phase of comparisons focused on calibration and use of commercial EIS meters. The procedure for the comparison was following: (i) Use calibrated refer-

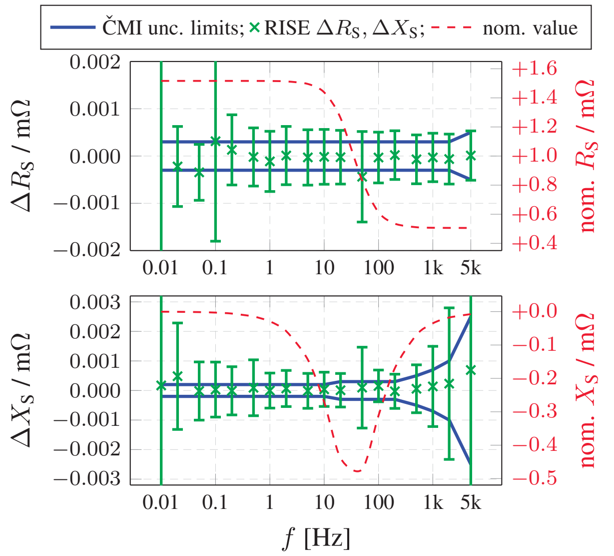

Fig. 5. ČMI - RISE comparison on PTB standard, range no. 1 ($\hat{Z}$ = 0.5 mΩ + 1 mΩ || 4 F). See Fig. 4 caption for details.

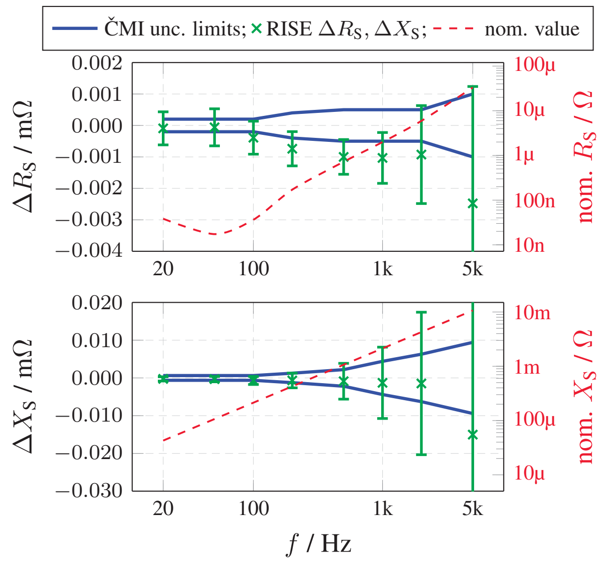

Fig. 6. ČMI - RISE comparison on ČMI reactance standard, at positive reactance range of approx. 340 nH. See Fig. 4 caption for details.

ence impedance standards to calibrate the EIS meter; (ii) Use the EIS meter to measure another impedance standard characterised by reference laboratory ČMI; (iii) Compare to the ČMI reference measurement of the standards.

There were three participants apart from ČMI: The National Physical Laboratory (NPL, Teddington, UK), Physikalisch-Technische Bundesanstalt (PTB, Germany) and Institute for Applied Materials - Electrochemical Technologies, Karlsruhe Institute of Technology (KIT, Karlsruhe, Germany). The comparisons were performed using EIS meters from three different manufacturers: Biologic VMP3 with VM3B-10 10 A booster (used by NPL), Zahner Zenium (used by KIT) and Gamry Ref 3000 (used by PTB).

The calibration and measurement procedure of the EIS meter was as follows:

- **Short correction**: Connect the test leads to a short arrangement, twisting current and potential leads separately to minimise mutual coupling between the pairs. Measure the residual "short" impedance $\hat{Z}_S$ for each frequency. Subtract measured short impedance $\hat{Z}_S$ from all subsequent measurements.
- **Range error calibration**: Measure the error of the EIS meter using two impedance standards with known values, one having impedance below and one above the value of the UUT (Unit Under Test) to be measured. Calculate complex correction factors for the EIS errors for each frequency.
- **Error correction**: Use the correction factors to correct all subsequent measurements (so called load correction).

The first step had to be performed manually in postprocessing of the measured data as most of the EIS meters studied do not implement short correction. Problems arose from the load correction attempt. The last two steps in the procedure work well for traditional RLC meters such as Keysight E4980A; the method is able to reduce the error of the RLC meter, especially in phase angle, by orders of magnitude. However, for EIS meters, two major problems were identified. First, the EIS meters mostly do not have a manual range lock function. Thus, when the error evaluation is performed e.g. with resistor of 10 mΩ and the UUT has impedance of e.g. 6 mΩ, there is no guarantee that EIS meter is using the same internal range. It may switch some internal amplifier gain or reference impedance and thus its error may differ. Therefore, trying to apply such corrections may actually increase the error. The second identified problem was that the EIS meters exhibit considerable noise (standard deviation of measurements), which mostly exceeded observed EIS meter errors. Therefore, to make the corrections work, it would be necessary to use extensive averaging; this would not be practical for actual lithium-ion cell measurements, nor even possible due to changes in cell state between discrete measurements. Despite these obvious challenges to the correction method, it was decided to perform the comparison with all three steps of calibration procedure.

The objects of the comparison were a "pure" resistance of 3 mΩ (Hioki resistor) and the PTB cell simulator at two different ranges. Calibration impedances were chosen to be "pure" resistances of 1 and 10 mΩ (Hioki resistors). The short correction for Hioki resistors was made using

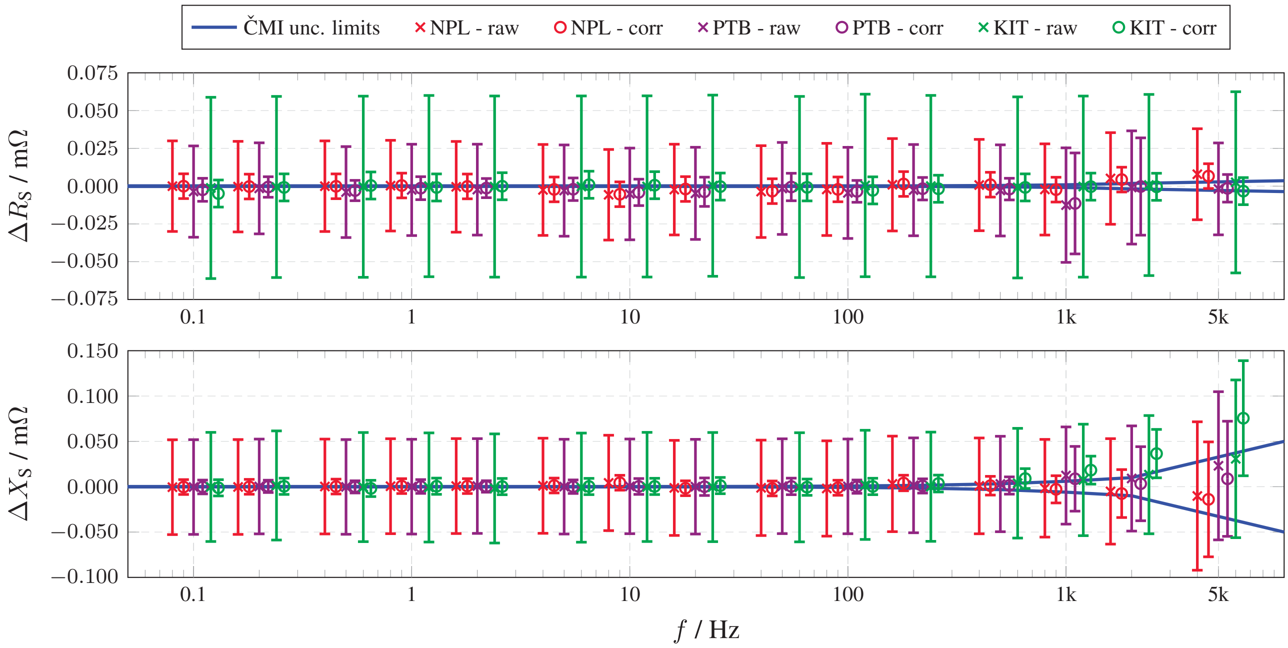

Fig. 7. Comparison of EIS meter measurement of 4-wire resistor 3 mΩ. Blue lines are ČMI reference expanded uncertainties, colored measurements with error bars are participants' absolute deviations from ČMI measurement with expanded uncertainties. "raw" are measurements with just short correction, "corr" are measurement after short and LOAD corrections.

the Hioki 0 Ω resistor and using PTB simulator's internal 0 Ω range for the PTB simulator measurements. This minimised the effect of variable mutual couplings of the test leads.

An exemplar result from the UUT Hioki 3 Ω comparison is shown in Fig. 7. Each participating institution provided two results to the graph. The result marked "raw" is measurement with just a short correction, whereas the result marked "corr" is with the load correction applied. The expanded uncertainty bars for the "raw" measurement are given directly by the specification of the EIS meter expanded in reactance by a mutual coupling uncertainty of ±2 nH. This is a conservative estimate that should cover variations in the mutual couplings when short is performed correctly. The uncertainty bars for the "corr" measurement are an estimated expecting EIS meter range linearity of 0.05 % and are also expanded by mutual coupling uncertainty. As expected, the difference between the results with and without correction is negligible for all of the participants. On the other hand, it must be mentioned that the short correction reduced errors by more than 10 times for both real and imaginary components. The spread of reactances without short correction was up to ±400 µΩ, which would correspond to no match above 1 kHz.

V. CONCLUSION

Two interlaboratory comparisons of impedance in the milliohm range in a full complex plane were conducted. The first comparison was undertaken between ČMI and RISE. It mostly showed agreement in the range from a few microohms down to the order of 100 nΩ, when the compared impedance standards were sufficiently stable. However, in some cases high deviation on reactance were observed, most likely due to different wiring among the participants. These failed results showed utmost importance of clearly defining wiring arrangement as even small differences may lead to the large offsets especially on reactance.

The second comparison was focused on measurements using commercial EIS meters calibrated by reference impedances. The comparison showed good match between the participants on various impedances from 1.5 to 4.5 mΩ across the full complex plane. Short correction was identified as a critical procedure for the reduction of measurement errors at frequencies above 1 kHz despite EIS meters control SW usually implements no such feature internally, thus it had to be performed in postprocessing. Further results will be presented at the conference.

VI. ACKNOWLEDGMENT

The National Physical Laboratory (NPL, Teddington, UK) and Institute for Applied Materials - Electrochemical Technologies, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany contributed to experiments reported in EIS meters comparison in section iv.

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