Technical Note

Electrode Resistance Measurement System RM2610

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***Abstract*—The Electrode Resistance Measurement System RM2610 separately calculates composite layer volume resistivity and interface (contact) resistance between the composite layer and the collector of the electrode sheets in lithium-ion batteries (LiBs). The instrument implements a rational evaluation method for electrode sheets using the technique of inverse problem analysis. This paper provides an overview of the product, describes its functionality and features, and provides an example of measurement using it.**

I. Introduction

In 2019, Akira Yoshino, John B. Goodenough, and M. Stanley Whittingham won the Nobel Prize in Chemistry for their development of lithium-ion batteries. Recognition of LiBs in the market exploded following coverage of the accolade in the news and on information programs. As demand for mobile handsets grew during the IT revolution that began in 1995, LiBs contributed to the worldwide adoption of smartphones and notebook computers due to their performance advantages over other rechargeable batteries. A revolution in environmental and energy technology (ET) followed. Electric vehicles (EVs) and hybrid vehicles (HEVs and PHEVs), which are spearheading that revolution, require medium and large LiBs, and the market has continued to grow.

This market environment places LiB manufacturers under constant pressure to develop more advanced batteries, and personnel involved in R&D focusing on batteries and related materials are working to boost their performance. For their part, workers responsible for managing quality and production processes of mass-produced product are faced with the need to manage processes in a fine-grained manner using theoretically sound indicators and to ship products of more consistent quality. In developing the Electrode Resistance Measurement System RM2610, Hioki focused on positive and negative electrode sheets, key components that are fabricated in the upstream portion of the LiB manufacturing process. This effort yielded a product that can visualize interface resistance, a quantity that could not previously be isolated, using Hioki's measurement and analysis technologies. In addition to interface resistance, this system also isolates the volume resistivity of the electrode sheet's composite layer. Fig. 1 is a photograph of the system. By proposing a new indicator to customers based on a proprietary measurement and analysis system, the RM2610 will contribute to the evolution and quality stability of LiBs.

Fig. 1. External appearance.

II. Overview

Despite the importance of electrode sheet quality in LiBs, no rational evaluation technique has been discovered until now. This state of affairs is due to the lack of a theoretical or methodological basis for electrically evaluating the result of applying a composite material to collector foil (a multilayer structure of two conductors stuck to each other). Consequently, LiB researchers, developers, and manufacturers have tried to electrically evaluate electrode sheets by such techniques as measurement of penetration resistance using weight electrodes (Fig. 2) and the 4-point-probe method (Fig. 3).

While these methods enabled reproducible measurement through setting the fine-grained measurement conditions, it was impossible to verify that the calculated resistance values were correct and aligned with theory since the measurement target was a multilayer structure.

Because it employs numerical analysis using the finite volume method to calculate electrode sheets' composite layer volume resistivity (Ω cm) and the interface (contact) resistance (Ω cm^2) between the composite layer and the collector, the RM2610 meets the needs of many involved in LiB development and production (Fig. 4).

III. Functions and Features

A. System Overview

Fig. 5 provides an overview of the system. The RM2610 includes the following products:

- *Electrode Resistance Meter RM2611:* The RM2611 is a 4-terminal resistance measurement unit with a built-in multiplexer.

- *Resistance Calculation Software RM2612:* The RM2612 controls the system as a whole from a computer and calculates composite layer volume resistivity and interface resistance from resistance values measured at multiple points.
- *Press Unit RM9003:* The RM9003 allows the Test Fixture RM9004 to be precisely raised and lowered by hand.
- *Test Fixture RM9004:* The RM9004 consists of the probes that make contact with the electrode sheet under test.
- *Connection Cable RM9005:* The RM9005 is a multi-core cable that electrically connects the RM2611 to the RM9004.
- *Temperature Sensor Z2001:* The Z2001 is connected to the RM2611 in order to measure the ambient temperature of the electrode sheet.

A detailed explanation of each system component is provided below.

B. Electrode Resistance Meter RM2611

Fig. 6 provides a block diagram of the RM2611.

1) Resistance measurement unit: The resistance measurement unit consists of resistance measurement circuitry that uses the DC 4-terminal method and a multiplexer that switches the connections of the RM9004's probes.

The multiplexer uses semiconductor (MOSFET) relays to deliver high-speed scanning, long service life, and quiet operation.

The resistance measurement unit incorporates an offset voltage correction function to eliminate the effects of thermal electromotive force caused by probe contact and measurement circuitry.

The text fixture connector is connected to the RM9004 via the RM9005.

2) Temperature measurement unit: The included Temperature Sensor Z2001 is connected to the TEMP. SENSOR terminal.

Output from the Z2001 is input to the RM2611's temperature measurement circuit so that the instrument can measure the ambient temperature.

3) Interface: The RM2611's USB terminal is connected to the computer's USB terminal via a USB cable.

Measurement by the RM2611 is controlled by the RM2612 software, which is installed onto a computer.

4) Maintenance unit: The RM2611 provides a dedicated maintenance interface that is used by Hioki for calibration and repair purposes.

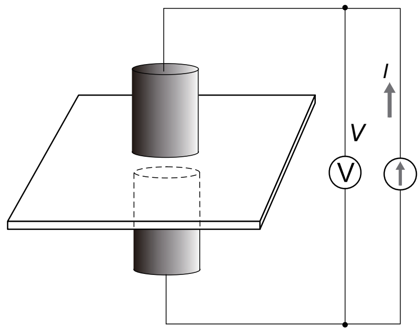

Fig. 2. Conceptual diagram depicting penetration resistance measurement.

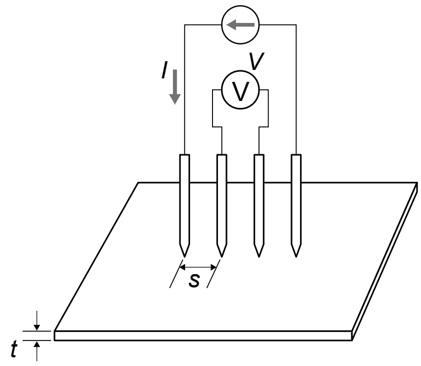

Fig. 3. Conceptual diagram depicting the 4-point probe method.

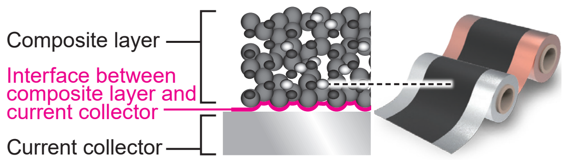

Fig. 4. Cross-sectional view of an electrode sheet.

5) Measurement control: Setting of the measurement range and speed, switching of the multiplexer, and measuring are all carried out in response to commands from the RM2612. (The RM2611 cannot be operated using the keys on its panel.) Measurement sequences consisting of combinations of measurement probes are managed using the RM2612 software.

The RM2612 software multiplies measured resistance values from the RM2611 by current values to convert them to electric potential values.

C. Architecture

1) Test Fixture RM9004: A total of 46 super-fine probes with a diameter of approximately 75 µm extend at an angle from the synthetic resin part on the bottom of the RM9004 (Fig. 7). This design allows the probes to bend with a small amount of force so that the damage to the measurement

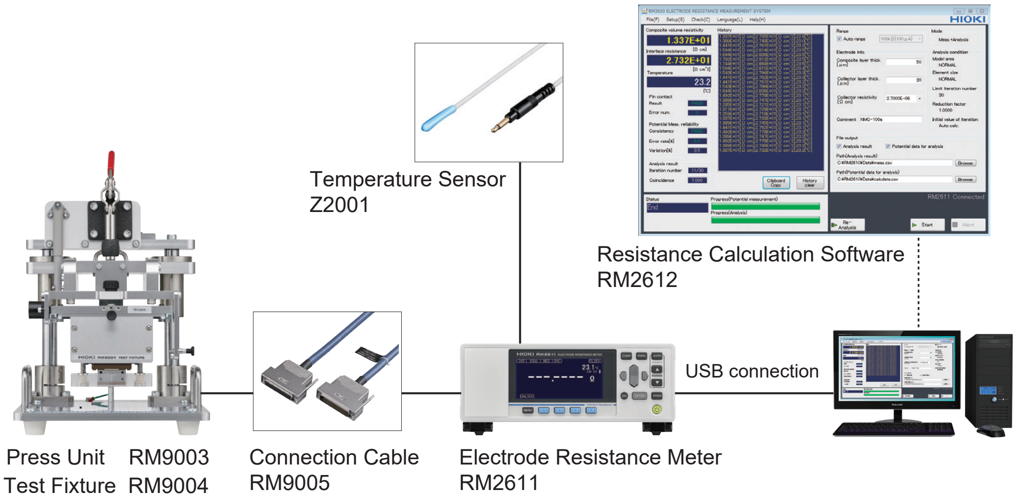

Fig. 5. System overview.

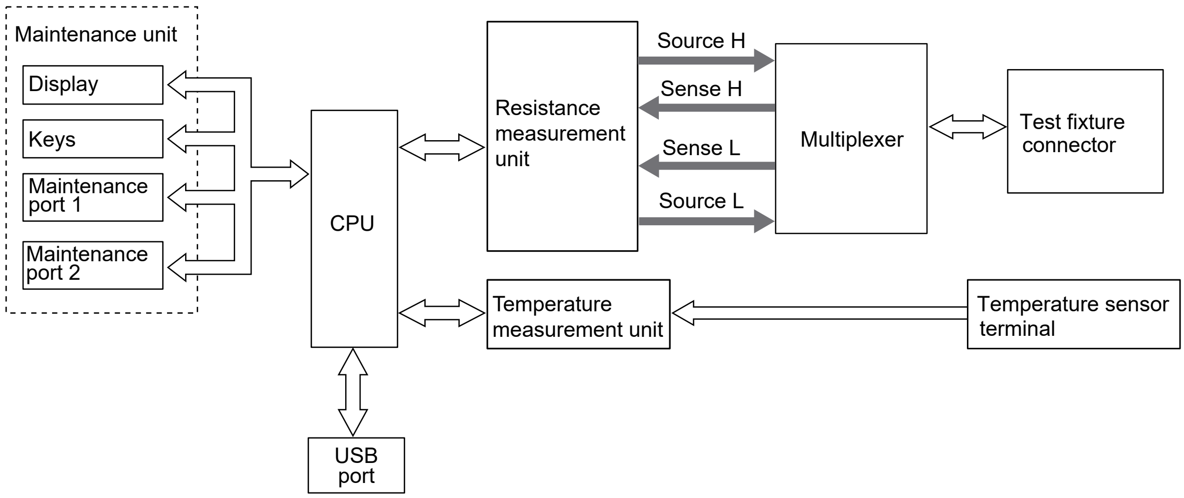

Fig. 6. RM2611 block diagram.

target can be reduced compared to that of a design in which the probes contact the measurement target at a right angle. Fig. 8 shows a probe after making contact. The left picture shows a pin in the moment of making contact. The right picture shows the probe after it has been press further, allowing you to see it bend. There is a certain amount of space (between points A and B) to allow the pin to bend.

Although the probes have sufficient strength in the axial direction, they are susceptible to force in the radial direction. If, during measurement, the electrode sheet being measured moves due to an external force, the probes will be subjected to a radial force, causing them to break. To protect the probes, the sheet holder shown in Fig. 9 keeps the sheet from moving. The measurement process is kept efficient since a single operation clamps the sheet in place and contacts the probe onto the sheet.

2) Press Unit RM9003: The RM9003 has three lock states that can be set to match how the operator is using it. In the fully locked state, the press unit is prevented from moving, and this state is used when transporting or storing the RM9003. The semi-locked state (triggered by simultaneously pulling the two levers which causes the RM9004 to move down) can be used to prevent the RM9004 from being lowered unintentionally. The unlocked state (in which pulling one lever causes the RM9004 to move down) is well suited to continuous testing.

During measurement, it is not possible to check the measurement locations since the points at which the probes will make contact cannot be observed. Hioki addressed this issue by adding a graduated plate that provides a rough guide for use when placing electrode sheets into the device so that the sheets can be positioned properly (Fig. 10). The plate is attached to the metal base (measurement stage) at one location and pressed against the plate by screws at three other locations so that it won't float free of the plate. The purpose of this design is to prevent flexing of the resin plate due to thermal expansion and contraction when clamping it to the metal base.

D. Resistance Calculation Software RM2612

The RM2612 application software, which runs on a Windows® computer, calculates composite layer volume resistivity and interface resistance based on potential data. The computer is connected to the RM2611 via a USB cable.

The RM2612 software provides contact check functionality to detect contact between the probes and the electrode sheet. Measurement starts automatically once the probes have made contact with the electrode sheet.

The software provides functionality for entering the information needed for measurement and improving operator convenience, and it also indicates whether potential measurement and its associated analysis have been performed properly.

- *Entry of information about electrode sheets:* The operator enters the following information, which is necessary in order for the RM2612 software to perform its analysis: the thickness of the electrode sheet's composite layer (µm) and the thickness (µm) and volume resistivity (Ω cm) of its collector.
- *Selection of the operating mode:* Three operating modes are available to facilitate efficient calculation of resistance values: "potential measurement and analysis", "potential measurement", and "analysis".
- *Display of potential measurement reliability:* The RM2612 software displays the following three indicators so that the operator can judge whether potential measurement was performed properly: consistency, error rate, and coefficient of variability.

E. Principal Functionality

1) Auto-range function: The RM2610 selects the optimal range for the measurement point based on the highest resistance among multiple measurement points. In this way, the man-hours that would otherwise be required in order to select a range manually can be saved. Probes with contact errors are excluded from the automatic selection process of the measurement range.

2) Test fixture tilt mechanism: The RM9003 incorporates a tilt mechanism to simplify the cleaning of the RM9004 (Fig. 10). When the point at which the RM9004 is mounted is rotated in the direction shown by the arrow in the figure, the RM9004's side with the probes faces forward. This feature boosts work efficiency by making it possible to clean the RM9004 with air without first removing it.

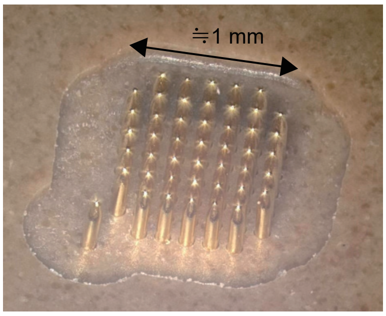

Fig. 7. Probe pins.

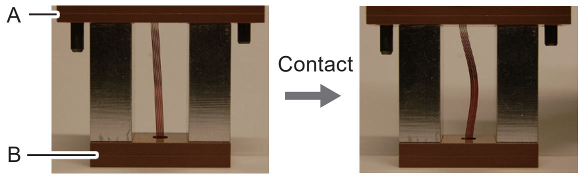

Fig. 8. Probes designed to reduce damage to DUT.

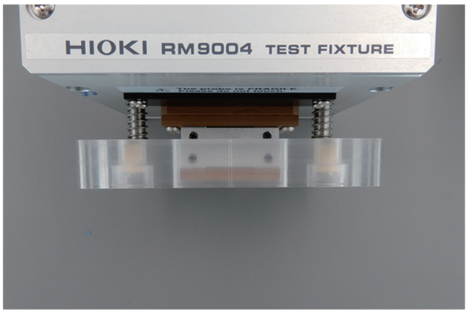

Fig. 9. Sheet holder.

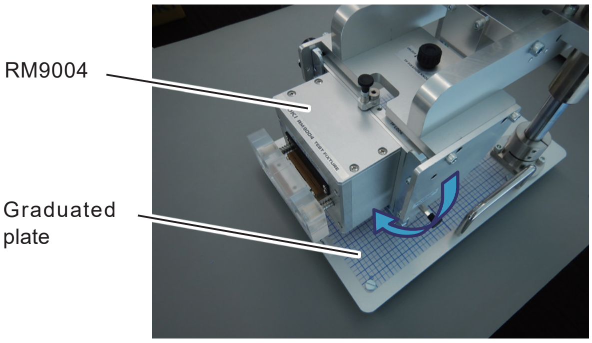

Fig. 10. Tilt mechanism and graduated plate.

3) Contact check function: The electrical contact of the RM9004 probes is detected one probe at a time using the multiplexer. First, probes adjacent to the probe that is sensing are shorted together. Then the resistance between the shorted probes and the probe being tested is measured using the 2-terminal method. This resistance value includes the probes' contact resistance. The software determines whether the value is less than or equal to a preset threshold value. Each probe is tested in this manner to verify proper electrical contact.

4) Inspection function: This function is used to carry out an electrical inspection of the RM9004. A probe check board, illustrated in Fig. 11, is provided for this purpose.

- *Short inspection:* This inspection checks each probe's continuity resistance value, which includes its contact resistance. It is accomplished by placing the RM9004's probes in contact with the conductive gold-plated surface on the probe check board.

  As with the contact check function, 2-terminal measurement is used. All probes are inspected.

  The threshold is 100 Ω, and an error results if it is exceeded.

- *Open inspection:* This inspection diagnoses the insulation resistance between each probe and all the probes surrounding it. It is accomplished by placing the RM9004's probes in contact with the non-conductive surface on the probe check board.

  As with the contact check function, 2-terminal measurement is used. All probes are inspected.

  The threshold is 100 Ω, and an error results if the measurement falls below it.

F. Calculating Interface Resistance

Generally speaking, a method known as "inverse problem analysis" or "fitting" is used by the RM2610 to calculate interface resistance. Fig. 12 illustrates the process in question.

1) Potential distribution measurement: The 46 probes are placed in contact with the surface of the electrode sheet, and current is applied between two probes. The applied current spreads out three-dimensionally throughout the electrode sheet, creating a potential distribution on the surface of the sheet. This potential distribution is measured using the voltage measurement probes. Hioki refers to potential values obtained in this manner as the "measured potential." Current is applied in a variety of directions, and the resulting potential distributions are averaged in order to boost the reproducibility of potential measurement (Fig. 13).

2) Modeling: A model of the electrode sheet consisting of a composite layer, collector, and the interface resistance between them is created. The volume resistivity of the composite layer and collector layer, and their interface resistance, are assumed to be uniform. The composite layer's volume resistivity (composite resistance) and the interface resistance are unknown, while the composite layer thickness, collector thickness, and collector volume resistivity (collector resistance) are known (since they are operator-entered values) (Fig. 14).

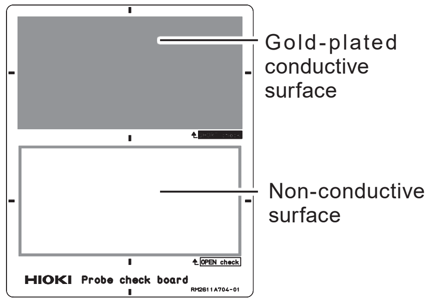

Fig. 11. Probe check board.

3) Potential distribution calculation: The potential corresponding to the measured potential is calculated for the modeled electrode sheet by solving an equation in which the potential is represented by an unknown function using the finite volume method. Hioki refers to potential values obtained in this manner as the "calculated potential." Appropriate initial values are entered for the composite layer volume resistivity and the interface resistance, which are being treated as variables, and the potential is calculated (Fig. 15).

4) Comparison with potential distribution and update: The measured potential and calculated potential are compared to assess how closely they match. In the absence of a match, processing steps (a) and (b) below are repeated, in that order.

(a) The model's composite layer volume resistivity and interface resistance value are updated as appropriate, and the potential distribution is calculated.

(b) The corresponding measured potential and calculated potential are compared.

Once the measured potential and calculated potential match, the repeated calculations end, and the composite layer volume resistivity and interface resistance values to which the model that generated the match was set are output (Fig. 16).

G. Effect of Potential Measurement Uncertainty on Analysis Values

Since no standard exists for interface resistance, it is necessary to verify the uncertainty that characterizes the measurement system being proposed by Hioki. Hypothesizing that the two factors described below account for the principal effects on analysis values, Hioki estimated their respective effects on analysis values under certain conditions using simulations. This process allowed the company to calculate the measurement system's uncertainty under specific conditions relative to the proprietary indicator of interface resistance.

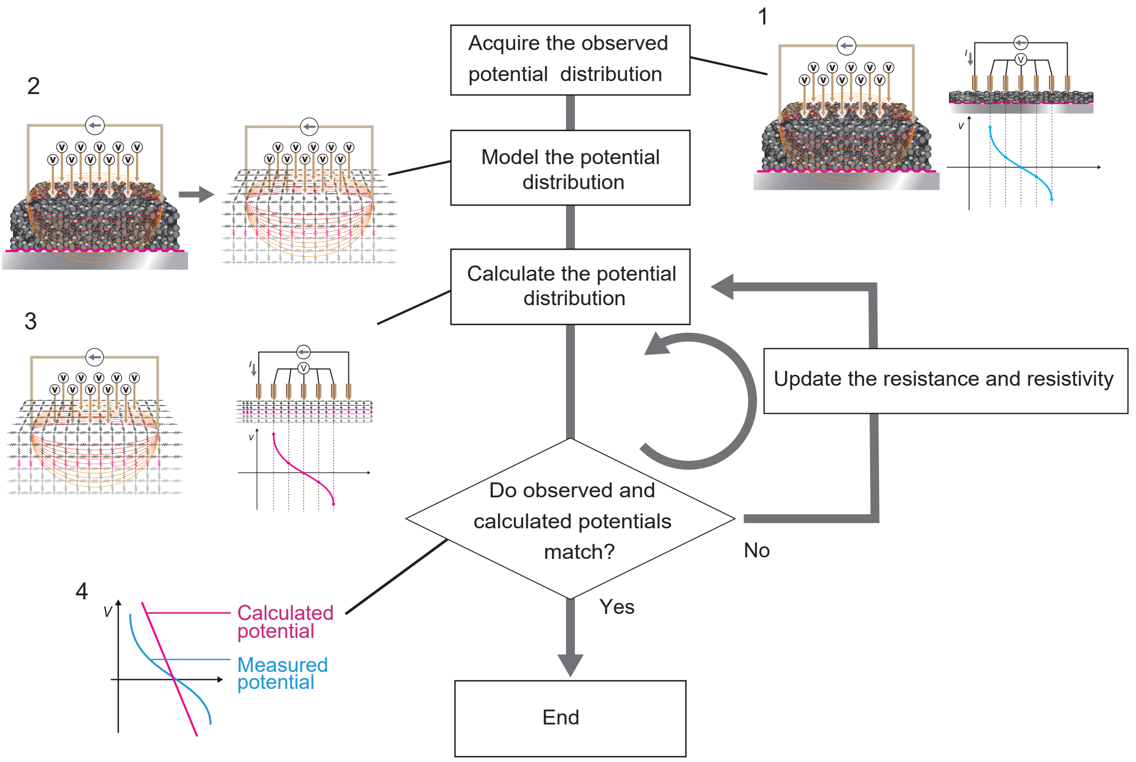

Fig. 12. Procedure for calculating interface resistance.

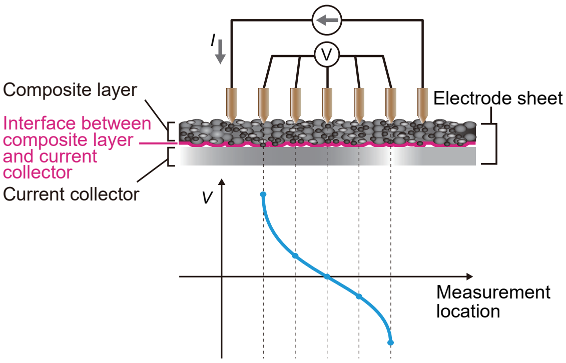

Fig. 13. Potential distribution measurement.

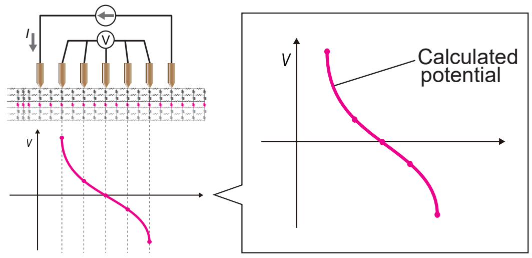

Fig. 15. Potential distribution calculation.

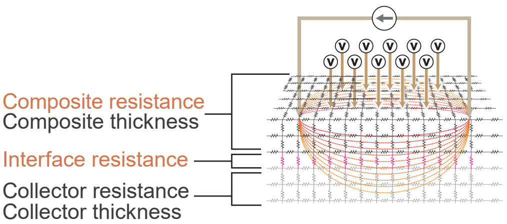

Fig. 14. Modeling.

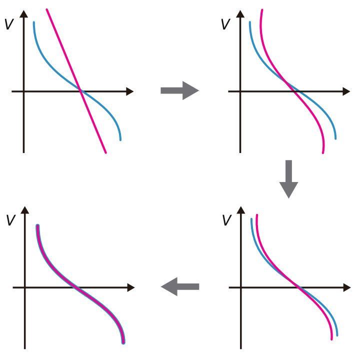

Fig. 16. Comparison and updating of potential distribution.

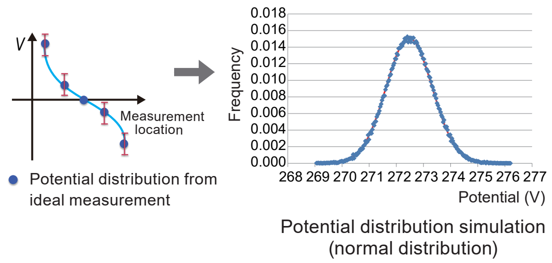

Fig. 17. Simulation of potential measurement uncertainty.

1) Uncertainty of potential measurement by the RM2611: The uncertainty of potential measurement by the RM2611 is reflected in the composite layer volume resistivity and interface resistance analysis values. Its effects were estimated using a Monte Carlo simulation, the results of which support the following assumptions:

- Uncertainty is normally distributed.
- The measurement unit's accuracy can be defined as a standard deviation of 3σ.

The simulation used representative positive electrode parameters and envisioned an applied current of 1000 mA. As a result, the effect of uncertainty in resistance measurement using the RM2611 is on the order of several percent (Fig. 17 and TABLEs I, II, and III).

2) Uncertainly in the geometrical position of the RM9004 probes: The RM9004's probes are arrayed at a narrow interval of approximately 120 μm. Error in the positions at which holes have been drilled in the plate that holds the probes in place causes the probes to diverge from their theoretically accurate positions. The effects of this uncertainty were estimated using a Monte Carlo simulation, the results of which support the following assumptions:

- Uncertainty is normally distributed.
- The standard deviation σ characterizing the error in the X and Y directions using the theoretically accurate locations as the reference is 5 μm.

As a result, the effect of misalignment in the RM9004's geometrical position on resistance values was found to be on the order of several percent (Fig. 18 and TABLEs IV, V, and VI).

H. Confirmation of the Convergence in the Finite Volume Method

The system provides three surface areas for its electrode finite volume model (Normal, Medium, and Wide). In Medium mode, the analysis is performed using a model area that is approximately 2.5 times that of Normal mode, while in Wide mode, the analysis is performed using a model area that is approximately 4 times that of Normal mode. Although measurement more closely approaches the actual physical phenomena in question as the model area increases (becomes larger), larger area translates into

TABLE I. Simulation Conditions

Number of attempts	50 000
Composite layer volume resistivity without variability	4.937 Ω cm
Interface resistance without variability	1.390 Ω cm²

TABLE II. Simulation Results (composite layer volume resistivity)

Average	4.937 Ω cm
Standard deviation	0.017 Ω cm
Standard deviation / average	0.34%

TABLE III. Simulation Results (interface resistance)

Average	1.390 Ω cm²
Standard deviation	0.015 Ω cm²
Standard deviation / average	1.1%

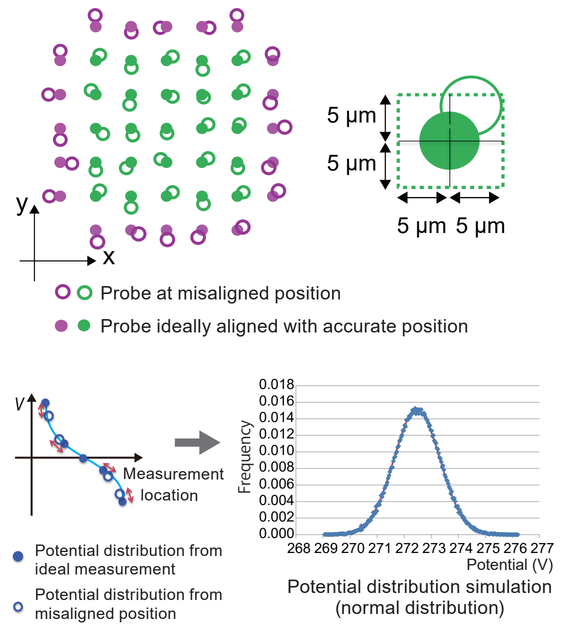

Fig. 18. Simulation of uncertainty in probe location.

TABLE IV. Simulation Conditions

Number of attempts	10 000
Composite layer volume resistivity without misalignment	8.879 Ω cm
Interface resistance without misalignment	1.208 Ω cm²

TABLE V. Simulation Results (composite layer volume resistivity)

Average	8.888 Ω cm
Standard deviation	0.24 Ω cm
Standard deviation / average	2.65%

TABLE VI. Simulation Results (interface resistance)

Average	1.208 Ω cm²
Standard deviation	0.031 Ω cm²
Standard deviation / average	2.53%

longer analysis times. The system also provides three model element sizes (Normal, Fine, and Super fine) in its finite volume method. In Fine mode, the analysis is performed using elements that are approximately one-fourth the size of those used in Normal mode, while in Super fine mode, the analysis is performed using model elements that are approximately one-ninth the size of those used in Normal mode. Although measurement more closely approaches the physical phenomena in question as the element size decreases (becomes smaller), smaller element sizes translate into longer analysis times. Hioki examined how calculated potential values vary with model area and element size. Fig. 19 illustrates how model area affects potential difference, while Fig. 20 illustrates how element size affects potential difference. In both cases, results were estimated based on simulations that anticipated a negative electrode sheet, and potential was calculated at points lying 120 µm away from the current applying probe.

Results indicated that values converge on a given potential as the model area increases, and as element size decreases. Consequently, it can be inferred that larger model areas and smaller element sizes result in more accurate calculated values. However, attempting to calculate accurate resistance values increases analysis time.

IV. Example Measurements

The following provides three sets of results obtained by measuring actual electrode sheets using the procedure proposed by Hioki.

A. Resistance Measurement of Commercially Available Electrode Sheets

The resistance of commercially available electrode sheets (positive and negative) was measured. TABLE VII summarizes the conditions of measurement. Six points, labeled (A) through (F), were measured (Fig. 21).

Variability on each sheet from (A) through (F) was calculated as the result of dividing standard deviation by the average, and the differences in resistance values on the positive and negative electrode sheets were determined to be significant (TABLEs VIII and IX).

Additionally, the results indicate that the negative electrode had lower interface resistance and composite layer volume resistivity than the positive electrode.

B. Relationship between Conductive Additive and Resistance

Fig. 22 illustrates how composite layer volume resistivity and interface resistance change in response to variations in the amount of conductive additive. The values on the vertical axis are expressed as ratios, where a value of 1 indicates the composite layer volume resistivity and interface resistance with a conductive additive amount of 3%.

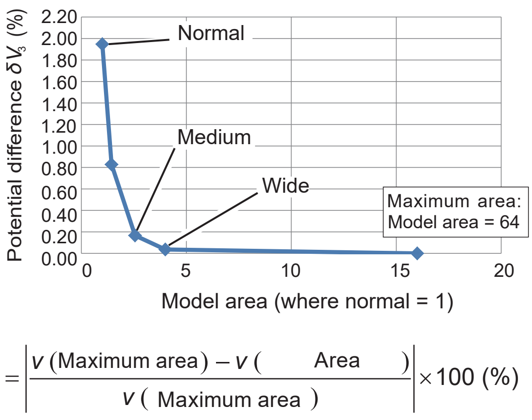

Fig. 19. Differential in model area and potential.

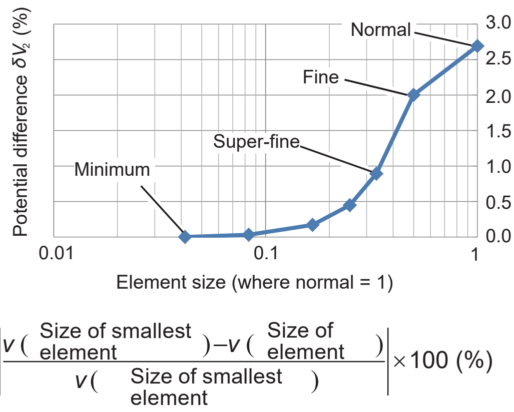

Fig. 20. Differential in element size and potential.

TABLE VII. Conditions of Measurement

Specimen: Positive electrode	
Type	Positive electrode (lithium cobalt oxide)
Substrate	Aluminum foil (15 µm) Volume resistivity: 2.7E-06 Ω cm
Active material	$LiCoO_2$
Prescribed quantity	110.2 g/m^2
Total thickness	92.1 µm
Density	2.95 g/cm^3

Specimen: Negative electrode	
Type	Negative electrode (graphite)
Substrate	Copper foil (10 µm) Volume resistivity: 1.7E-06 Ω cm
Active material	Graphite
Prescribed quantity	50.8 g/m^2
Total thickness	45.6 µm
Density	1.43 g/cm^3

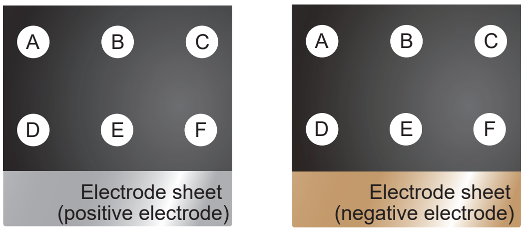

Fig. 21. Measured points.

The results indicate a trend toward lower composite layer volume resistivity and interface resistance as the amount of conductive additive increases. This trend agrees with the well-known fact that conductive additive functions to lower the activity of composite materials' electronic resistivity.

Hioki also examined how use of carbon-coated foil affected interface resistance at 5% conducting additive content. The interface resistance of electrodes with a carbon-coated foil current collector decreased to about 1/10. By contrast, composite layer volume resistivity was unchanged regardless of whether carbon-coated foil was used. These facts demonstrate that composite layer volume resistivity and interface resistance are being calculated separately.

C. Relationship between Electrode Density and Resistance

Fig. 23 illustrates how composite layer volume resistivity and interface resistance change in response to variations in electrode density. The values on the vertical axis are expressed as ratios, where a value of 1 indicates the composite layer volume resistivity and interface resistance associated with an electrode density of 1.5 g/cc.

The results indicate a trend toward lower composite layer volume resistivity and interface resistance as electrode density increases. This trend can be inferred to occur because the increase in electrode density causes particles of the conducting additive to be spaced more closely together inside the composite material, increasing electron conductance.

Furthermore, the results indicate that interface resistance decreases abruptly once electrode density reaches 1.8 g/cc and then stabilizes at a roughly uniform lower value. Since electrode density and ion conductance exist in a trade-off relationship, interface resistance can be inferred to function as one criterion for determining the optimal electrode density.

TABLE VIII. Resistance Measurement Results for a Commercially Available Positive Electrode Sheet

Measurement location	*Composite layer volume resistivity (Ω cm)*	*Interface resistance (Ω cm²)*
A	4.926	1.583
B	4.894	1.824
C	5.182	1.647
D	4.938	1.390
E	4.750	1.433
F	5.312	1.147

	Composite layer volume resistivity	*Interface resistance*
Average of A through F	5.000 Ω cm	1.504 Ω cm²
Standard deviation / average for A through F	4.2%	16%

TABLE IX. Resistance Measurement Results for a Commercially Available Negative Electrode Sheet

Measurement location	*Composite layer volume resistivity × 10^{-1} (Ω cm)*	*Interface resistance × 10^{-2} (Ω cm²)*
A	1.871	2.114
B	2.033	1.839
C	1.774	1.900
D	1.336	2.643
E	1.715	1.828
F	1.827	1.763

	Composite layer volume resistivity	*Interface resistance*
Average of A through F	1.759 × 10^{-1} Ω cm	2.015 × 10^{-2} Ω cm²
Standard deviation / average for A through F	13%	16%

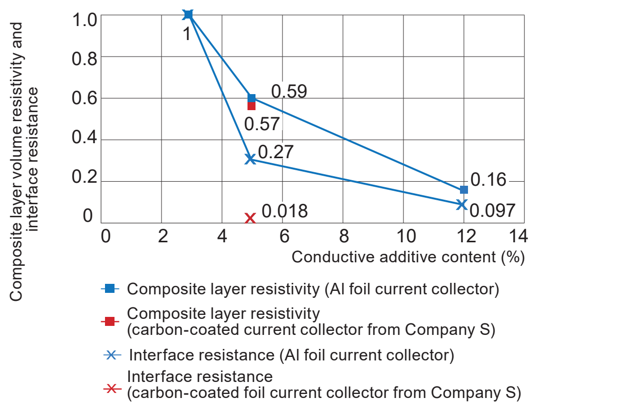

Fig. 22. Relationship between conductive additive content and resistance.

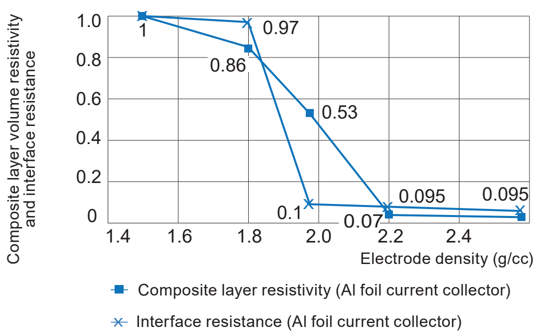

Fig. 23. Relationship between electrode density and resistance.

V. Conclusion

Hioki has proposed composite layer volume resistivity and interface resistance calculated using the inverse problem analysis technique as a reasonable metric for assessing electrode sheets. Assessing these values, which were difficult to measure in the past, makes it possible to move testing further upstream in LiB research and manufacturing. Hioki expects this approach to help increase yields and boost productivity, for example in the screening and evaluation steps of R&D and production processes.

Rechargeable batteries will play an essential role as rising environmental awareness drives the electrification of automobiles and the efficient use of renewable energy. Manufacturers of LiBs in particular will be called upon to deliver additional performance improvements and cost reductions as EVs, IT, and the IoT are widely adopted. Hioki is confident that the RM2610 will open up a new route by which it can contribute to R&D and cost saving iun the LiB industry.

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