

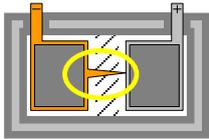
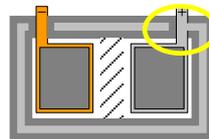
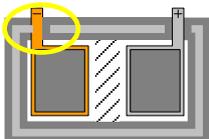
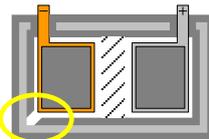
Measurement of the package potential of laminated lithium-ion batteries

This paper addresses measurement of the package potential of laminated lithium-ion batteries (lithium-ion polymer rechargeable batteries), including by describing the causes of package potential and associated measurement precautions.

1. Internal insulation failures in lithium-ion batteries

Internal insulation failures in lithium-ion batteries cause degradation in the characteristics of the battery, and may occasionally lead to a serious accident. These batteries experience a variety of insulation failures, as outlined in Table 1.

Table 1 Internal insulation failures in laminated lithium-ion batteries

| | Location of insulation failure | Cause | Phenomenon |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| (1) | Between the positive electrode and the negative electrode  | Separator penetration due to metallic deposits; presence of metallic particles; misaligned winding, etc. | Increase in self-discharge; abnormal heating |
| (2) | Between the positive electrode and the package aluminum  | Presence of metallic particles; defective seal on aluminum laminate film | No effect on the characteristics of the lithium-ion battery |
| (3) | Between the negative electrode and the package aluminum  | Presence of metallic particles; defective seal on aluminum laminate film | Subsequent occurrence of cracking in the package aluminum's insulating film will cause degradation of lithium-ion battery. |
| (4) | Between the electrolyte and the package aluminum  | Cracking in aluminum laminate film | No effect on the characteristics of the lithium-ion battery |

Insulation failures between the positive electrode and the negative electrode will lead to increased self-discharge and abnormal heating. Generally speaking, batteries are subjected to aging for a certain

amount of time and then sorted based on the magnitude of the post-aging voltage drop (Table 1[1]).

In the event of an insulation failure between the positive electrode, negative electrode, or electrolyte and the package aluminum, no current pathway via the package aluminum forms, so the phenomenon is not immediately problematic (Table 1[2] through [4]).

When lithium-ion batteries are subjected to repeated expansion and contraction due to charging and discharging, the insulating film that coats the surface of the aluminum laminate film becomes prone to cracking. Once cracks form in the insulating film, insulation between the electrolyte and the package aluminum deteriorates. Consequently, when there is an insulation failure between the positive electrode and the package aluminum, or between the negative electrode and the package aluminum, the likelihood increases that a current pathway will form via the package aluminum and the electrolyte, as shown in Fig. 1.

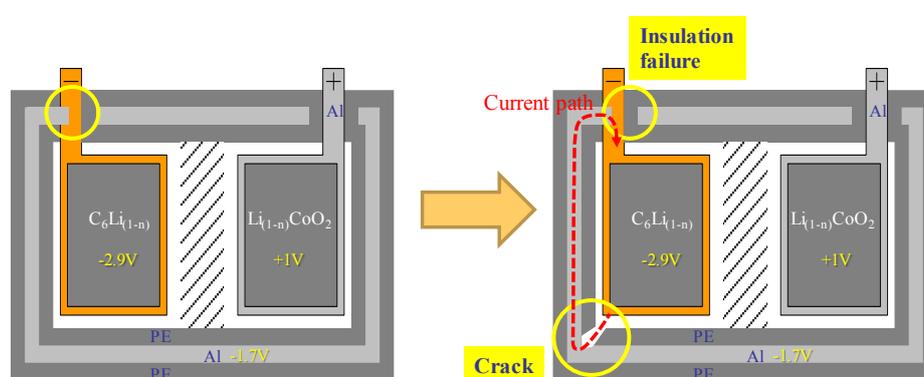


Fig. 1 Cracking in the insulating film

Table 2 lists the standard electrode potentials for the materials that are generally used in lithium-ion batteries.

Because the package aluminum has a high potential relative to the negative electrode, degradation in the insulation between the electrolyte and the package aluminum while there is simultaneously an insulation failure between the negative electrode and the package aluminum will cause the aluminum package to undergo a reduction reaction, producing a Li-Al alloy (Fig. 2). This Li-Al alloy is extremely brittle, allowing pinholes to form in the package aluminum. If moisture gets into the battery through these pinholes, it will react with the electrolyte to produce gas, significantly shortening the life of the lithium-ion battery.

On the other hand, degradation in the insulation between the electrolyte and the package aluminum when there is simultaneously an insulation failure between the positive electrode and the package aluminum will cause the package aluminum to undergo an oxidation reaction, which will not result in the production of unstable Li-Al (Fig. 3). In short, insulation failures between the positive electrode and the package aluminum do not affect the life of the lithium-ion battery.

Insulation resistance testing or dielectric strength testing provides a means of detecting insulation failures in the materials that make up lithium-ion batteries. However, this testing approach will not

only deem a battery with cracks in its aluminum laminate film but no adverse effect on the battery's characteristics (Table 1[4]) to be defective, but also will risk breaking down the battery's electrolyte.

For the above reasons, the potential difference between the positive electrode and the package aluminum is measured in order to detect insulation failures between the negative electrode and package aluminum of laminated lithium-ion batteries. This paper will use the term "package potential" to refer to that potential difference.

Table 2 Standard electrode potentials for materials used in lithium-ion batteries

| Part | Material | Standard electrode potential |
|--------------------|---------------------------------|------------------------------|
| Positive electrode | $\text{Li}_{(1-n)}\text{CoO}_2$ | +1V |
| Package | Al | -1.7V |
| Negative electrode | $\text{Li}_{(1-n)}\text{C}_6$ | -2.9V |

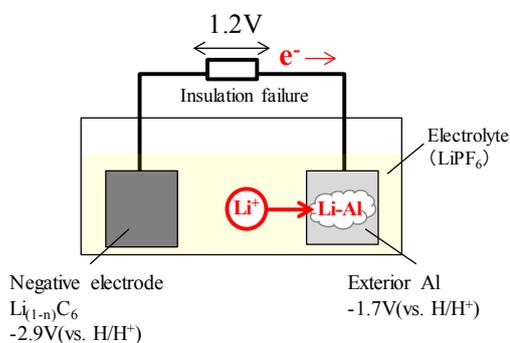


Fig. 2 Negative electrode insulation failure and cracking in package film

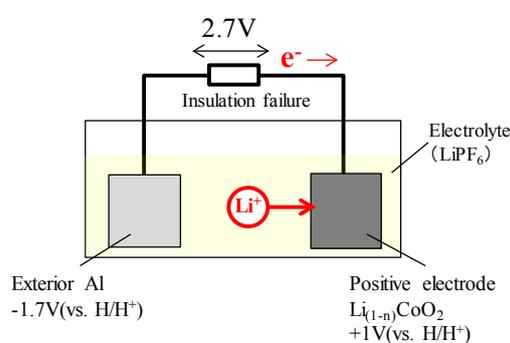
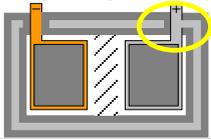
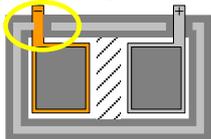
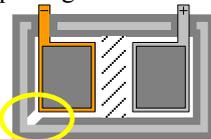
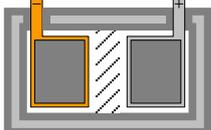


Fig. 3 Positive electrode insulation failure and cracking in package film

2. Measurement of package potential

The potential difference between the positive electrode and the package aluminum varies with the nature of the insulation failure inside the lithium-ion battery (Table 3). Generally speaking, a package potential close to 4 V suggests an insulation failure between the negative electrode and the package aluminum (Table 3[2]). In a battery whose only defect is cracking in the insulation film, the package potential will be 2.7 V or less (Table 3[3]). When a battery with normal internal insulation is measured, the package potential will be indeterminate since the package aluminum is insulated from battery's internal materials (Table 3[4]). Ordinarily, a resistance (RIN) from 10 MΩ to 1 GΩ is connected between the voltmeter's high and low terminals so that the package potential of a battery without any internal insulation failures will be 0 V.

Table 3 Insulation failure locations and observed potentials

| | Location of insulation failure | Package potential |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| (1) | Between the positive electrode and the package aluminum  | 0 V |
| (2) | Between the negative electrode and the package aluminum  | Max. 4 V {+1 - {-2.9}} |
| (3) | Between the electrolyte and the package aluminum  | Max. 2.7 V {+1 - (-1.7)} |
| (4) | No insulation failure  | Indeterminate |

The authors measured the package potential of two lithium-ion batteries using the measurement circuit shown in Fig. 4. They used a voltmeter with an input resistance of 10 GΩ or greater and made measurements while reducing RIN from 10 GΩ to 1 MΩ to investigate the effect of the package potential's load resistance. Fig. 5 illustrates the measurement results. Although RIN values of 100 MΩ and greater yielded a package potential of about 2 V, RIN values of 10 MΩ and 1 MΩ caused the package potential to decrease to 1 V and 0.5 V, respectively. Based on the observed voltages, it can be inferred that the measured lithium-ion batteries suffered from low insulation between the electrolyte and package aluminum due to a factor such as cracking in the aluminum laminate film.

Fig. 6 illustrates the change in package potential over time. The voltage quickly fell when the input resistance was varied from 10 GΩ to 100 MΩ (or 10 MΩ). When the input resistance was subsequently reverted to 10 GΩ, the voltage had only recovered to 87% of its previous value after 60 minutes.

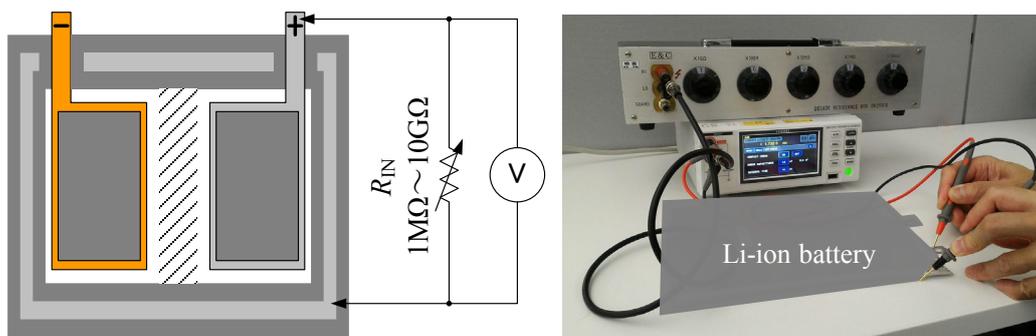


Fig. 4 Method for measuring package potential

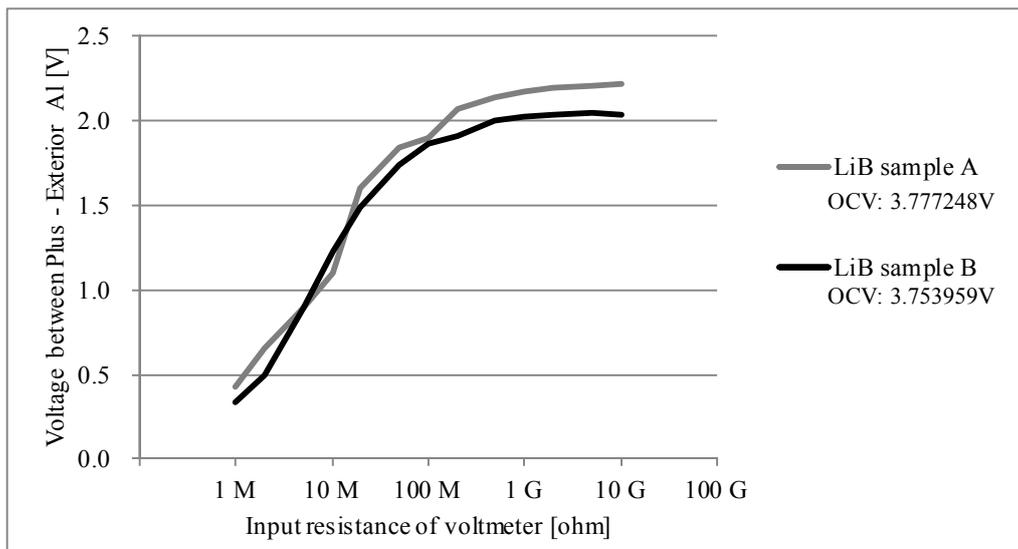


Fig. 5 Effect of package potential load resistance (voltmeter input resistance)

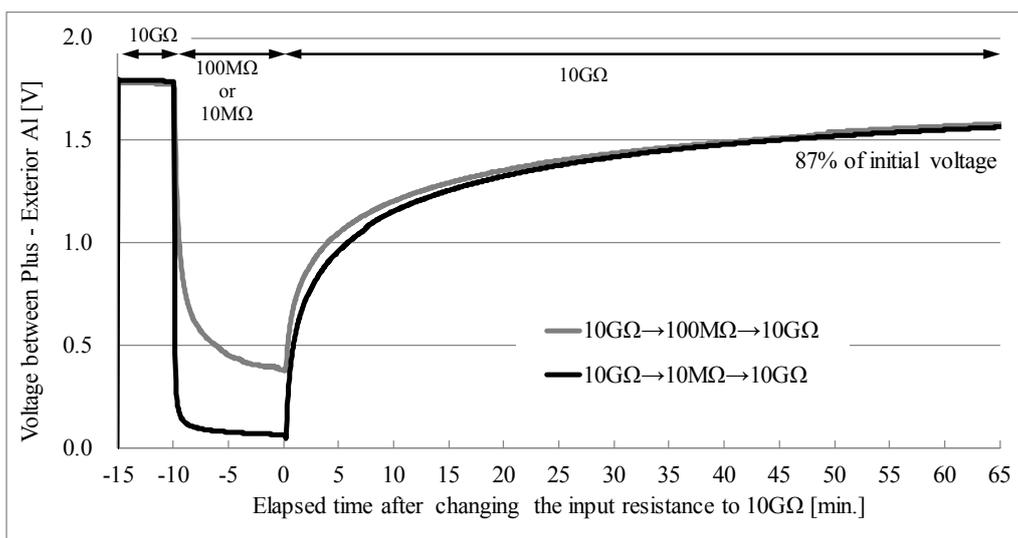


Fig. 6 Variation in package potential over time

Next, the authors simulated an insulation failure by connecting a high resistance (R_{IR}) between the negative electrode and package aluminum in the measurement circuit shown in Fig. 7. They then measured the package potential using a voltmeter with an input resistance of $10\text{ G}\Omega$ or greater with the resistance between the high and low terminals (R_{IN}) set to $100\text{ M}\Omega$ or $10\text{ M}\Omega$. Fig. 8 illustrates the measurement results. The measured package potential value increases as the insulation between the negative electrode and package aluminum (R_{IR}) decreases. As an example, an insulation failure of approximately $30\text{ M}\Omega$ or less can be detected with an upper limit of 2 V for the package potential and an R_{IN} value of $100\text{ M}\Omega$.

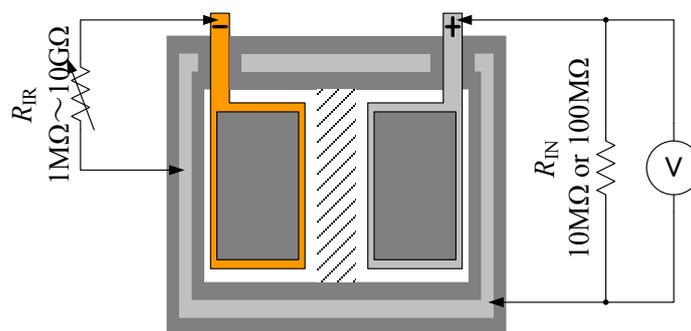


Fig. 7 Method for measuring package potential while simulating a negative electrode insulation failure

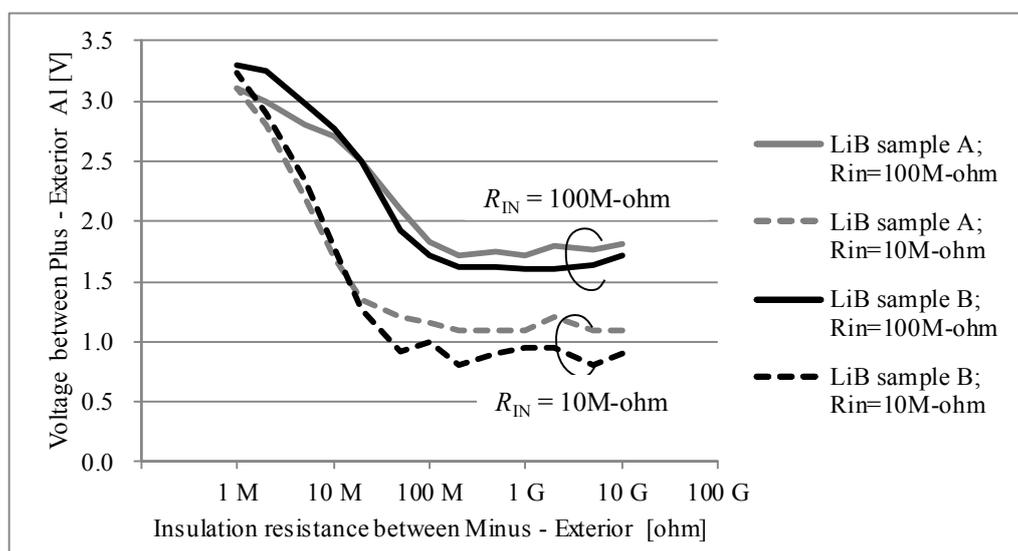


Fig. 8 Negative electrode insulation failures (simulated resistance) and package potentials

3. Precautions when measuring package potential

The following precautions should be observed when measuring package potential:

-1. Input resistance

As described above, the measured voltage will be indeterminate when measuring a non-defective lithium-ion battery (a battery without insulation failures). Consequently, it is necessary to fix a potential by connecting a high resistance (RIN) between the high and low terminals. If an RIN value of 10 MΩ is sufficient, a voltmeter with an input resistance of 10 MΩ, for example a digital multimeter, can be used as-is. If an RIN value of 10 MΩ is too low, use a voltmeter with a high input resistance and connect RIN externally.

-2. Response time

If the resistance between the high and low terminals (the voltmeter's input resistance) is given by RIN and the capacitance between the lithium-ion battery's electrodes and its package aluminum by CP, the time constant (63% response time) can be calculated as follows:

$$\text{Time constant} = C_P R_{IN}$$

As an example, a CP value of 10 nF and an RIN value of 10 MΩ result in a time constant of 0.1 s. When measuring voltage, allow a stabilization time of 3 to 5 times the time constant after placing the probes in contact with the measurement target.

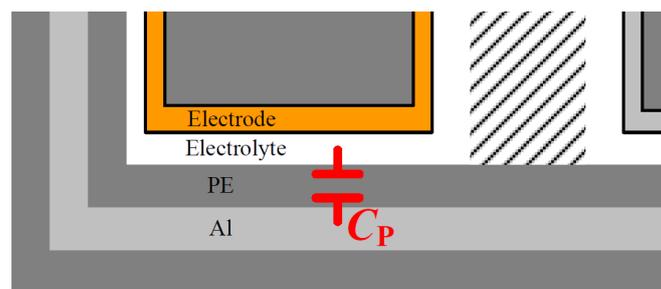


Fig. 9 Capacitance C_P between the package aluminum and electrodes

-3. Contact check

When measuring package potential, a voltage of 0 V is generally interpreted as indicating a non-defective battery. By contrast, a voltage reading close to 0 V will be observed even if the probes are not connected to the measurement target, as shown in Fig. 10, due to the resistance RIN connected between the high and low terminals. The package aluminum is particularly prone to connection issues because it is coated with an insulating film. In addition, caution is also warranted when the top of the aluminum laminate film and the bottom of the aluminum laminate film are insulated, as shown in Fig. 11. If contact is only made with one surface of the aluminum laminate film when there is a defect on the other side, the defect may be overlooked.

A DC voltmeter with a contact check function, for example the DM7275, provides an effective way to avoid judging measured values when there is a connection issue. Fig. 12 depicts the DM7275's contact check function setup screen. This function measures the capacitance between the high and low terminals and determines that good contact has been established if the capacitance exceeds a preset value (Fig. 12.a). If the test probes are only in contact with one side

of the aluminum laminate film, the capacitance will be halved, allowing detection of a contact error (Fig. 12.b).

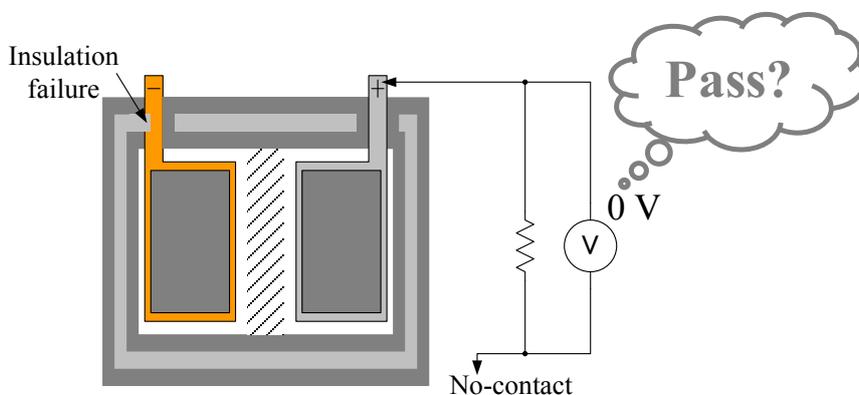


Fig. 10 Indication of 0 V due to a connection issue

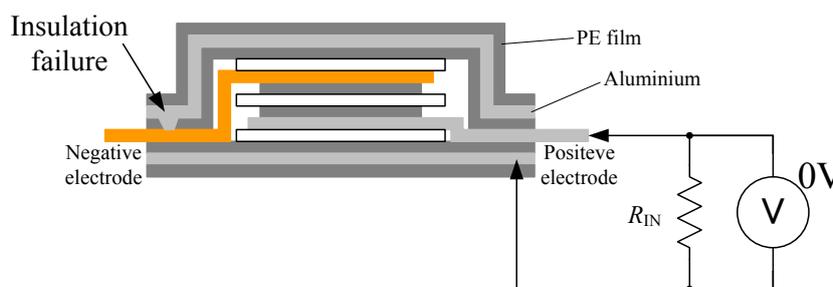
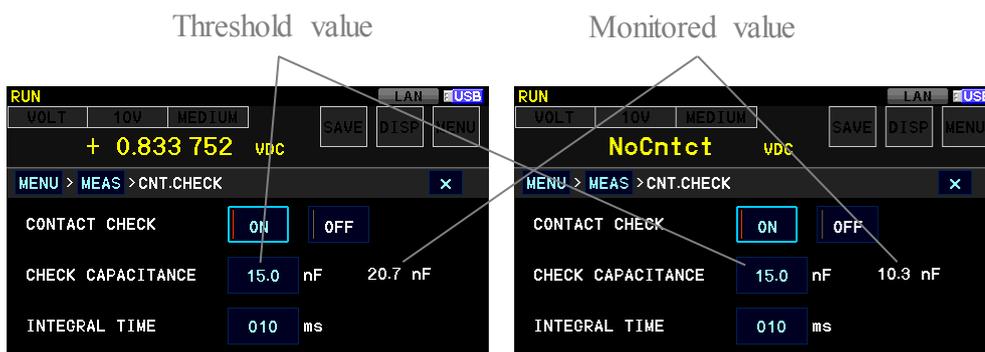


Fig. 11 Contact with a defect-free surface



(a) Good contact (b) Contact error

Fig. 12 Contact check screen

-4. Charge state

The package potential depends on the battery's charge state. To increase measurement reproducibility, keep the charge state as consistent as possible.

-5. Noise countermeasures

It is necessary to implement adequate noise countermeasures since the output resistance for the package potential is extremely high.

(1) Use shielded measurement cables and connect the shielding to the voltmeter's low-impedance terminal (generally the low terminal). Choose shielded cables that use either teflon or polyethylene as the insulator between the shielding and the internal conductor. Shielded cables that use polyvinyl chloride as the insulator have low insulation resistance and will result in measurement error.

(2) Shield the measurement target with a metal plate and connect the shielding to the voltmeter's low-impedance terminal.

(3) Synchronize the voltage measurement integration time to the power supply period (50 Hz: $n \times 20$ ms; 60 Hz: $n \times 16.7$ ms).

(4) Always ground the measuring instrument.

4. Summary

-1. When there is an insulation failure between the negative electrode and the package aluminum of a laminated lithium-ion battery, the package aluminum will degrade with use, shortening the life of the battery.

-2. When there is an insulation failure between the negative electrode and the package aluminum, the package potential (the voltage between the positive electrode and the package aluminum) will approach 4 V.

-3. Caution is warranted concerning the following three points when measuring package potential:

(1) Connect a suitable resistance R_{IN} between the voltmeter's high and low terminals.

(2) Measure the voltage after a suitable response time (several times the product of CP and R_{IN}) has elapsed.

(3) Always perform a contact check.