

# Evaluate Self-Discharge of Lithium-Ion Cells in a Fraction of the Time Traditionally Required

## Overview

Whether you are a lithium-ion cell designer or manufacturer, evaluating cell self-discharge is both a priority and a challenge for you. Cells exhibiting high levels of self-discharge have higher likelihood of failure and must be sorted out and the cause identified. Unfortunately, this has traditionally been a long and tedious process to perform.

What is a cell's self-discharge? Self-discharge of an electrical cell is the loss of charge over time while not connected to any load. Some amount of self-discharge is a normal attribute resulting from chemical reactions taking place within the cell. Compared to other types of rechargeable cell chemistries, lithium-ion cells have rather low self-discharge. On their own they may typically lose about 0.5 to 1% of their charge per month.

Additional self-discharge can result from leakage current paths existing within the cell. Particulate contaminants and dendrite growths produce internal "micro-shorts", creating such leakage current paths. These are not normal attributes and they can lead to catastrophic failure of the cell. Because of this it is a top priority during the design of the cell to eliminate possible causes of high self-discharge. In manufacturing, it's critical to screen out any cells exhibiting abnormally high self-discharge as early as possible in the process.

Traditionally self-discharge is evaluated by measuring the decrease of a cell's open-circuit voltage (OCV) over time. While it is not challenging to measure a cell's OCV, the bigger challenge is that it is very time-consuming. Because lithium-ion cells have very little change in OCV as they discharge, it takes days to weeks to detect a significant loss of a cell's state of charge (SOC), in order to discern a good cell from one having high self-discharge.

An alternate means to determine a cell's self-discharge is to instead measure its self-discharge current. When such a measurement is correctly implemented, cells exhibiting excessively high self-discharge can be identified and isolated in a small fraction of the time required by the traditional OCV approach. This mitigates the associated expenses, complexities and hazards of a large amount of work-in-progress (WIP). Now the challenge you are faced with is having a suitable solution for this task. Equipment possessing required stability and resolution has not previously existed to make it practical.

In this application note, details of these two methods for determining a cell's self-discharge will be examined and compared, along with the approach Keysight has taken to create a solution that greatly reduces measurement time.

## Delta Open-Circuit Voltage (OCV) Method

The delta open-circuit voltage (OCV) method for measuring a cell's self-discharge is depicted in Figure 1. The self-discharge behavior is represented as a resistance,  $R_{SD}$ , whose value is equal to the cell's OCV divided by the self-discharge current  $I_{SD}$ .  $I_{SD}$  is simply the rate of charge loss in coulombs per second. As would be expected,  $I_{SD}$  is very small, typically a few to a few hundred microamperes, depending on cell size. As charge is slowly lost, the cell's voltage very slowly drops. A high accuracy, high resolution voltmeter is required to measure the cell's voltage loss over an extended period.

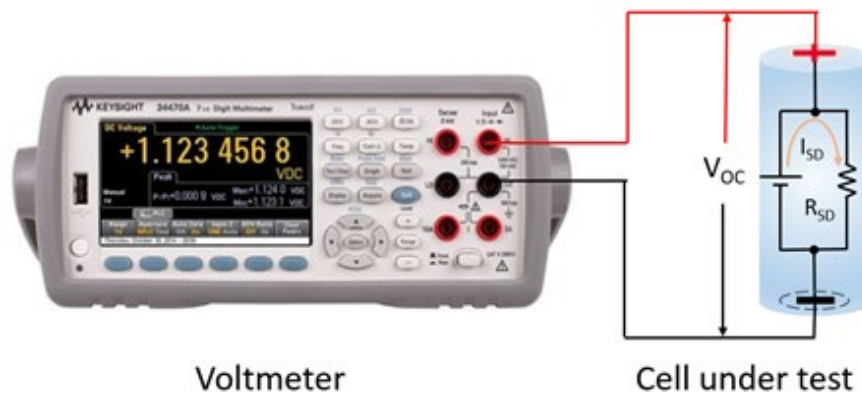


Figure 1. Open-Circuit Voltage (OCV) method for measuring a cell's self-discharge

Looking at a representative example of a lithium-ion cell's discharge characteristics in Figure 2 it can be seen there is very little change of voltage over most of the range of the cell's state of charge (SOC). It can also be seen that the voltage change varies considerably depending on the exact % SOC. For this cell by itself without any load, assuming a self-discharge of 1% per month equates to a voltage loss of about 3 to 12 mV per month, depending on its % SOC. The decrease of a cell's OCV over time is an indirect and imprecise indicator of what the cell's self-discharge rate is.

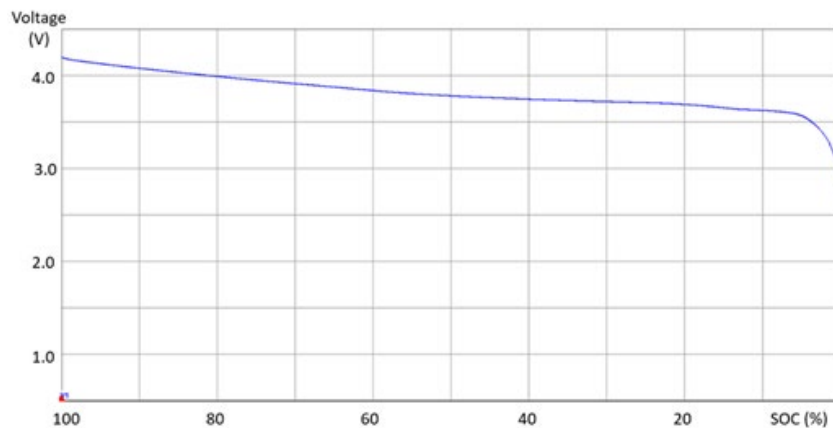


Figure 2. Example of a lithium-ion cell discharge characteristics

In addition to the variance of a cell's voltage loss with % SOC, other factors affect a cell's voltage, such as temperature drift. Because of these factors the test challenge is days to weeks of monitoring the voltage is typically required to detect meaningful changes in a cell's % SOC and discern good cells from ones having unacceptably high self-discharge.

The challenge of evaluating a cell's self-discharge by using the delta OCV method can be found:

- **In development as** it adds a lot of time to the schedule, with resultant loss of opportunity (e.g. time-to-market).
- **In manufacturing** as it adds considerable work-in-progress (WIP), with complexities and hazards of storing large quantities of cells for extended periods of time.

## Potentiostatic Method

The potentiostatic method for measuring a cell's self-discharge measures the cell's self-discharge current. This is a direct measurement of the self-discharge rate, as current is coulombs per seconds, which is charge loss over time. The potentiostatic method is illustrated in Figure 3.

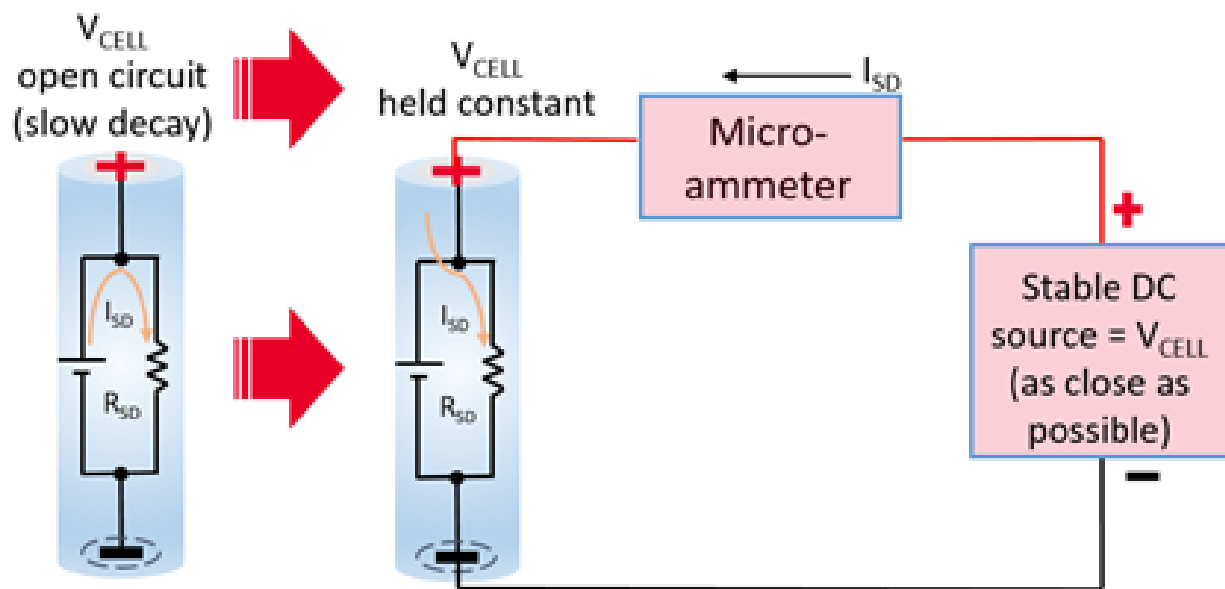


Figure 3. Potentiostatic method for measuring a cell's self-discharge

When the cell is open-circuited, the self-discharge current  $I_{SD}$  internally drains charge from the cell, causing its OCV and SOC to slowly decrease. With the potentiostatic method, a low noise, very stable DC source is set to match the cell's OCV. The DC source is then connected to the cell through a micro-ammeter to measure the current flowing between the DC source and cell. Now when the cell continues to self-discharge, the DC source takes over, furnishing sufficient current to maintain the cell at a constant voltage and SOC. When the DC source comes to equilibrium with the cell, the self-discharge current  $I_{SD}$  transitions from being sourced internally to being totally furnished externally from the DC source.  $I_{SD}$  can then be directly measured using the micro-ammeter.

Advantages of this measurement method include:

- Test time is a few hours or less to determine the self-discharge current. Cells having unacceptably high self-discharge can be discerned from good cells in even less time, typically well under an hour.
- The result,  $I_{SD}$ , is a direct measurement of the rate of the cell's self-discharge.

The real impact of the advantage of the potentiostatic method is:

- In development, greatly reduced schedules to more quickly capitalize on opportunities.
- In production, greatly reduced WIP, simplifying storage logistics and associated hazards.

## Addressing the Challenges of the Potentiostatic Method

When using the potentiostatic method the main challenge becomes how closely you can match the cell's OCV with the DC voltage source and then maintain a high level of voltage stability for the duration of the test. Close initial matching is critical as a mismatch must change the charge on the cell to get back to equilibrium, adding considerably more time to the process. A high level of stability must be maintained to settle at a final level as opposed to drifting up and down over time. Ideally the level of stability needs to be on the order of microvolts. Existing commercially available DC voltage sources do not possess the accuracy, resolution, and stability to closely match a cell's OCV and then maintain that voltage for the duration of the test.

Achieving microvolt-level stability on a few to several volts, typical of most cells, requires single parts-per-million (ppm) level resolution and stability. To address this challenge, the Keysight BT2152B Self-Discharge Analyzer incorporates specialized design features to provide this level of performance. The BT2152B is depicted in Figure 4.



Figure 4. Keysight BT2152B Self-discharge analyzer

Specialized features of the BT2152B include:

- The voltage for potentiostatic method measurement is quickly matched to within +/- 5  $\mu\text{V}$  of the cell's OCV before being applied. This minimizes introducing any new charge or discharge changes, thus limiting measurement settling time to a minimum.
- The voltage applied to the cell is extremely stable (+/- 10  $\mu\text{V}$  peak) to minimize on-going current noise on the self-discharge current measurement.
- The BT2152B accurately measures low-level self-discharge currents to +/- (0.3% of reading + 0.25  $\mu\text{A}$ ).
- Incorporates a measurement port for a thermistor to accurately measure the cell's temperature over time.
- Programmable series-resistance setting provides a means of optimizing measurement settling time and measurement sensitivity to external influences, like temperature changes during the measurement period.
- Built-in logging continuously records cell voltage, current, and temperature, independent of any external controller after being initiated.
- Often applications require testing many cells at one time. A primary example is screening suspect cells for unacceptably high self-discharge as part of a manufacturing process. The BT2152B can measure self-discharge current on up to 32 cells at the same time, greatly boosting test throughput and provide a high level of cost-effectiveness.
- The BT2155A Self-Discharge Analysis Software available for the BT2152B provides a quick and easy way make and analyze self-discharge measurements on cells. This greatly simplifies evaluation as well as being indispensable as an R&D tool. See more details in the following section "Self-Discharge Current Measurements with the BT2155A Software".

These specialized features of the BT2152B, along with the BT2155A software, make for a complete solution for quickly measuring, evaluating, and analyzing self-discharge of lithium-ion cells.

The BT2152B is optimized from an equipment standpoint, to measure self-discharge on cells in a minimum amount of time. Correspondingly, it is important that the cells are in a stable, well rested state, to measure their self-discharge current in minimum time. Many factors influence a cell's voltage, which in turn affects its self-discharge current measurement. For more details on this, refer to the sidebar "Cell Considerations for Self-Discharge Current Measurement"

## Cell Considerations for Self-Discharge Current Measurement

The potentiostatic method for self-discharge current measurement requires a very stable voltage source for supplying the very small self-discharge current to the Li-ion cell that is subsequently measured. It is also important that the cell is in a well-rested and stable state to obtain valid results. Major things to consider include:

### **Charge redistribution and equilibrium:**

During charging or discharging, a charge gradient is created while charge diffuses more deeply into or makes its way back out of the cell's structure. Given enough rest time after charging or discharging, the charge will reach equilibrium. The charge will then be uniformly distributed throughout the cell's structure.

This typically may take up to a week to achieve. When measuring the cell's self-discharge current with the potentiostatic method, if the cell is not fully rested, additional current is initially sourced into or drawn from the cell, exponentially decaying until charge equilibrium is reached. After that point the only current being sourced into the cell will then be just the self-discharge current.

### **Cell temperature coefficient of voltage (TCV):**

The voltage of a Li-ion cell exhibits temperature dependency. This can easily be many 10's of microvolts per degree C. Fluctuations in the temperature give a corresponding fluctuation in the cell's voltage. This will in turn cause fluctuations in the self-discharge current being measured. It is important to take appropriate steps to minimize temperature fluctuations of the cell during testing.

### **Thermo-electric effects:**

It is common for cell's terminals to be made of nickel or other metal that gives rise to a thermally-induced voltage when an electrical connection is made with a dissimilar metal. This can be 10's of microvolts per degree C. Opposing connections created by connecting to both the cell's terminals cause the thermally-induced voltage to be cancelled out, providing both terminals are at the same temperature. However, differences in temperature between the two terminals will produce a net voltage.

Any fluctuations in the temperature difference between the two terminals will in turn cause fluctuations in the self-discharge current being measured. It is important to take steps to minimize fluctuations of the temperature difference between the cell's terminals during testing.

### **Cell state of charge (SOC)**

The self-discharge of a Li-ion cell decreases considerably when the cell is at a low SOC and thus becomes more difficult to measure. Also, the cell's TCV is generally increases for a low SOC. It is useful to have the cell at reasonably high SOC when measuring its self-discharge.

Following these best practices greatly improves accuracy of test results and allows for faster measurement settling time.

## Self-Discharge Current Measurements with the BT2155A Software

The BT2155A Self Discharge Analysis Software enables one quickly and easily make and analyze self-discharge current measurements on up to 32 lithium-ion cells. An example of a self-discharge current measurement using the BT2155A is shown in Figure 5.

The BT2155A is an interactive graphical interface that allows the user to quickly and easily set up the BT2152B and then log the cell's self-discharge current, voltage, and temperature over time. In this example the BT2155A is displaying a self-discharge current measurement on one of sixteen 18650 cylindrical 2.4 Ah lithium-ion cells.

The self-discharge current leveling off indicates the cell has reach equilibrium with the external voltage source. At that point the external voltage source is furnishing all the self-discharge current. In this example the current levelled off at 7  $\mu\text{A}$  after 2 hours. This is typical self-discharge for a good cell of this capacity rating.

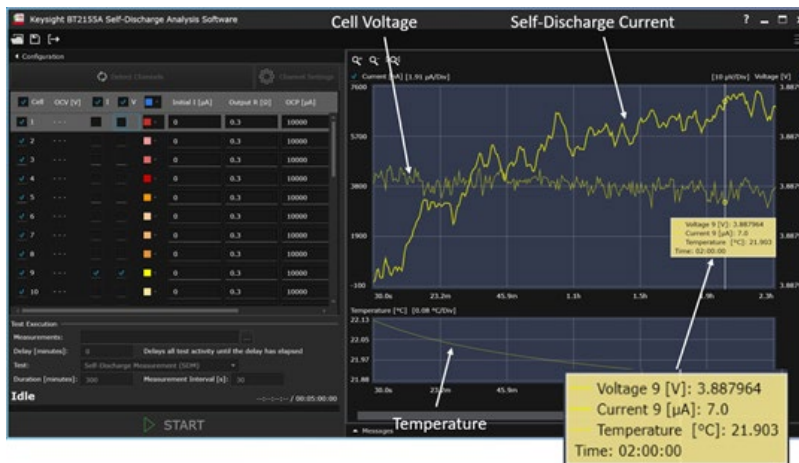


Figure 5. BT2155A displaying a self-discharge current measurement

Separating cells exhibiting high levels of self-discharge current from good cells typically takes much less than it takes to level off at the final self-discharge current values. Figure 6 displays self-discharge currents on all sixteen 18650 cylindrical 2.4 Ah lithium-ion cells previously tested. Three cells exhibited excessive self-discharge compared to the main population, which was readily observable within minutes.



Figure 6. Discerning good from high self-discharge cells

## Summary

It is important that the self-discharge of Lithium-ion cells is tested. High levels of self-discharge are indicative of latent failures. These cells must be identified and separated from good cells to prevent potentially catastrophic failures, and the underlying cause in either the cell's design or manufacturing process be identified and corrected.

Traditionally self-discharge is evaluated by measuring the decrease in a cell's open-circuit voltage (OCV) over time. While it is not challenging to measure a cell's OCV, the challenge is that it is very time-consuming. Because lithium-ion cells have very little change in OCV as they discharge, it takes days to weeks to detect a significant loss of a cell's % state of charge (SOC) and discern good cells from those having high self-discharge.

Alternatively, a cell's self-discharge current can instead be directly measured to determine its self-discharge. Correctly implemented, a cell's self-discharge can be measured in a small fraction of the time required by the traditional delta OCV method, mitigating the associated expenses, complexities and hazards of large amount of work-in-progress (WIP).

The challenge now becomes having the test equipment possessing the necessary stability and resolution required to measure a cell's self-discharge current. Until now, such test equipment has not existed. To address this, Keysight has created the BT2152B Self-Discharge Analyzer, providing 32 measurement channels having microvolt-level stability and resolution. The BT2152B incorporates several other specialized features, making it specifically tailored for quickly and accurately measuring the self-discharge current of cells.

Learn more at: [www.keysight.com](http://www.keysight.com)

For more information on Keysight Technologies' products, applications or services, please contact your local Keysight office. The complete list is available at: [www.keysight.com/find/contactus](http://www.keysight.com/find/contactus)

