Three-Electrode Battery Testing:
A Low-Cost, Easy to Use Commercial Solution

One could reason batteries first became a disruptive technology over 200 years ago. The energy storage capacity, size, cost, and abundance of batteries has changed *dramatically* since then, and there are thousands of organizations and researchers continuing these improvements every day. Batteries have become essential to our modern society and our dependence will only grow as technology spreads and population increases. The demands on battery performance also continue to rise, and technology is often limited by the battery cost, capacity, size, or combinations of all these factors.

All batteries function in the same fundamental way using two electrodes composed of different materials commonly known as the cathode and the anode. Researchers experiment with both various anode and cathode materials to build a better battery. However, it is critical to identify and measure the impact of each material or other change in the battery. The traditional and simplest way to do this is by experimenting with half-cells that only measure the performance of one material at a time and is non-ideal. When testing a full-cell battery with anode and cathode materials, it is essential to be able to determine which electrode is responsible for the performance degradation, i.e. *which side is limiting the battery*.

“Coin” or “button” cells are the most common method for researchers to test battery materials because they are relatively quick, easy, and inexpensive to make in the lab. Most common battery test equipment will charge and discharge a coincell using a basic positive and negative connection (working and counter electrode) that measures current and voltage across the cell.

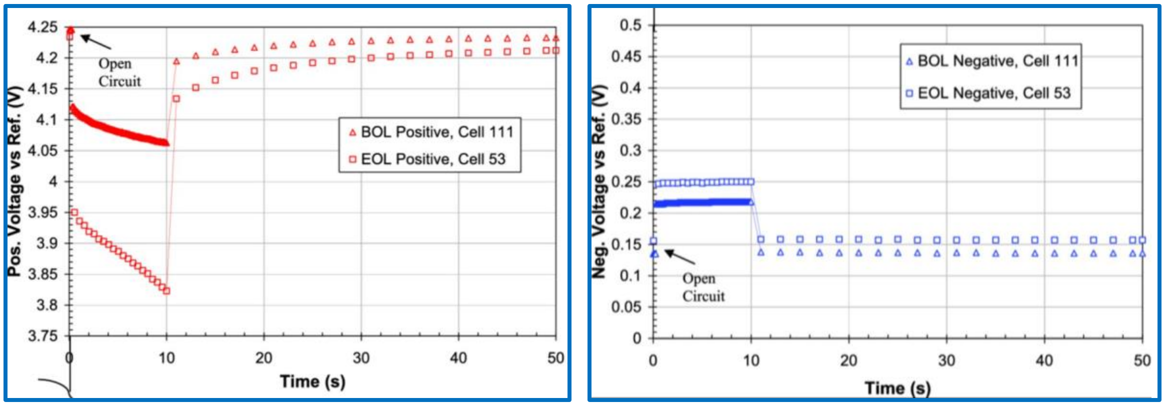
However, there are a few solutions that allow battery test equipment to utilize a third reference electrode to help isolate and analyze the individual contributions of the anode and cathode material in the battery in-situ, thus expediting the overall development process. Historically, these existing three-electrode test cells require unique cell designs that all have significant flaws that limit the use at scale. **Arbin** has licensed a new patented three-electrode “3E” coincell design that was developed by General Motors. This paper will compare both the commercial and common homemade solutions available to perform three-electrode battery testing.

Benefits of Three-Electrode Battery Testing

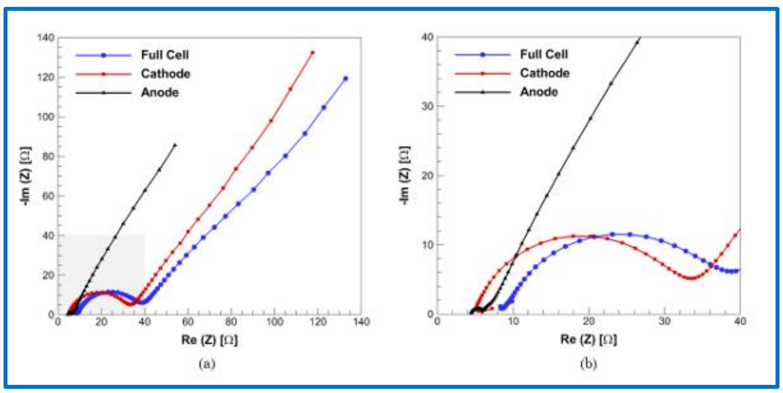
When researching battery materials, the use of a reference electrode (RE) allows researchers to measure and differentiate the contribution of each component of the cell to its overall performance. Three-electrode experiments help identify which electrode (anode or cathode) limits the cell performance during long-term testing. It is important to identify how each electrode is contributing to cell degradation under various test conditions instead of blindly experimenting with one or both.

The cases referenced below represent a small handful of examples of how researchers around the world are using three-electrode testing to gain insight into their respective battery experiments and analysis.

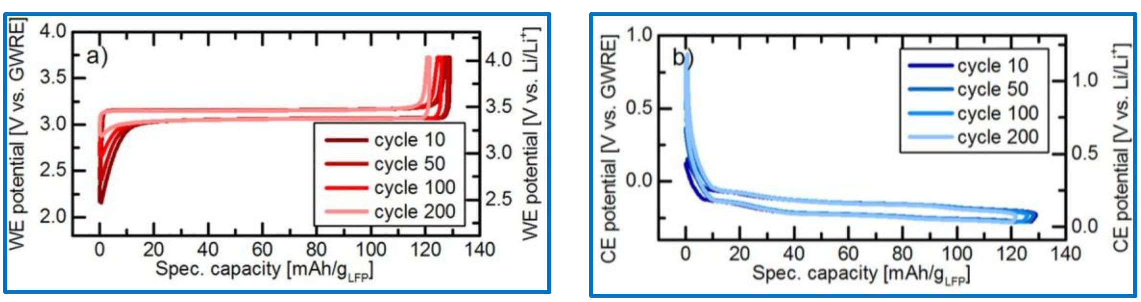
- Belt uses a reference electrode during HPPC test (common for electric vehicle applications) to look at the electrode polarization. [Jeffrey R. Belt et al 2014 J. *Electrochem*. *Soc*. 161 A1116]



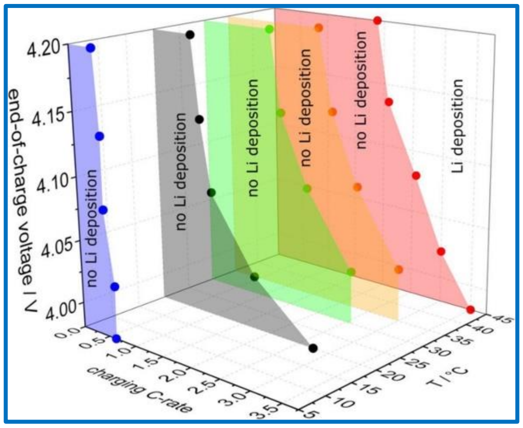
- Using a three-electrode setup for electrochemical impedance Spectroscopy (EIS) shows the decoupled impedance from anode and cathode individually. [Minter RD, Juarez-Robles D, et al 2018 J Vis Exp., (135):57735.]



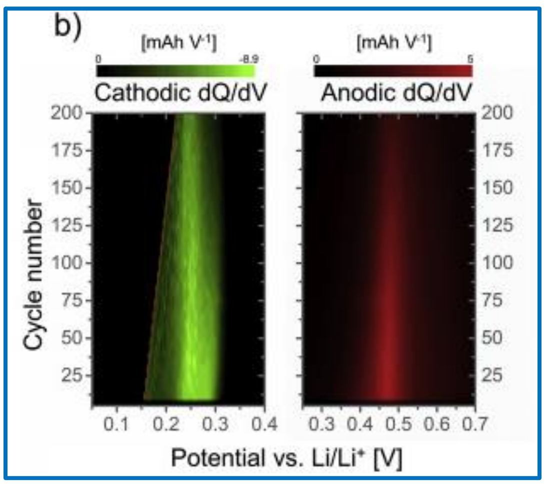
- Solchenbach showed the individual contribution of anode and cathode when demonstrating lithium loss due to SEI growth as a dominate aging mechanism [Sophie Solchenbach et al 2016 J. Electrochem. Soc. 163 A2265]



- Examining charge rate, temperature, and end-of-charge voltage on the anode of a pouch cell allowed Waldmann to gain a deeper understanding of the relationship between these operating conditions. [Thomas Waldmann et al 2016 J. Electrochem. Soc. 163 A1232]



- Wagner used differential capacity analysis to reveal changes in the voltage profile of anode and cathode and how they individually contribute to the cell degradation. [N.P. Wagner, et al 2019 J. Power Sources, 437, p. 226884]



Most *all* electrochemical experiments and battery tests provide greater understanding of the cell when the anode and cathode results can be decoupled through use of a reference electrode. This extends to what are traditionally considered "industrial" applications as well. The dynamic charge-discharge profiles and fast charge simulations associated with commercial devices and electric vehicles can draw unique performance from a battery compared to low-rate constant current cycling. Belt from Ford Motor Company describes some of these results in his work [Jeffrey R. Belt et al 2014 J. *Electrochem*. *Soc*. 161 A1116]. While industrial/commercial organizations are less likely to publish results compared to academic and government laboratories, utilizing three-electrode battery testing is a staple to reduce the development time in bringing a new battery material to market.

Arbin licensed the new patented 3E coincell kits for commercialization that were originally developed and used by General Motors in-house. Batteries are one of the biggest differentiating factors between electric vehicle companies. It is no surprise that innovations in testing methodology and tools happen in such a competitive environment. Bringing a new battery technology to market faster than a competitor that is proven as safe and reliable through extensive testing can yield great rewards.

Three-electrode testing is also beneficial for evaluating battery safety. Minter and Juarez-Robles highlight how fast-charging, which is a highly sought characteristic for electric vehicles, creates a great need to detect and monitor lithium plating occurring on a cell anode. [Minter RD, Juarez-Robles D, et al 2018 J Vis Exp., (135):57735.] This can best be achieved using a three-electrode cell during testing.

One fundamental goal of battery research is to develop cells that are long-lasting. This is especially important for electric vehicle and grid storage applications where the commercial cells and battery packs must last thousands of cycles and up to 10 years. Three-electrode testing allows researchers to identify the limiting factor in their cell to focus attention where improvement is needed most. The work by Belt [Jeffrey R. Belt et al 2014 J. *Electrochem*. *Soc*. 161 A1116] shows how three-electrode testing can be used to expand previous research and shed new light on which electrode of a commercial EV battery is contributing more to its degradation. The knowledge gained from this testing can be *most* impactful when it starts at the lab-scale (coincells) before entering commercial production. **Therefore, making three-electrode battery testing more common in lab-scale applications is critical to accelerate the development process of new battery materials and innovations.**

Comparison of 3-Electrode Battery Solutions

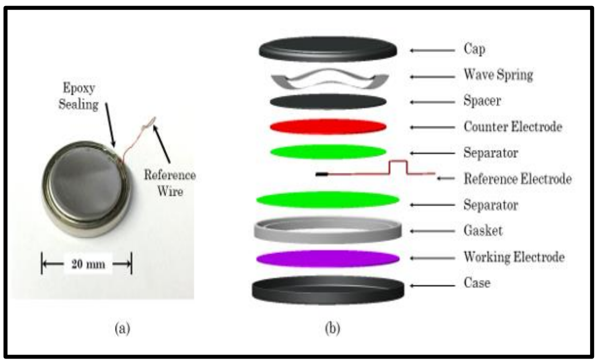
	Arbin 3E Coincell	El-Cell	Swagelok & Split Cells	Other Homemade Cells
Cost	$	$$$$$$	$$$$$$	$
Ease of Use (generate consistent results)	★★★★★	★★★★	★★★	★
Comparability to Published Data without Normalization	★★★★★	★★★	★★★	★★★★
Reusable After Cleaning	No	Yes, but contains consumables	Yes, but contains consumables	No
Suitable for Mass-Scale Testing	Yes	No	No	No
Robustness (ability to avoid damage or disruption to cell)	★★★★★	★★★★★	★★★	★

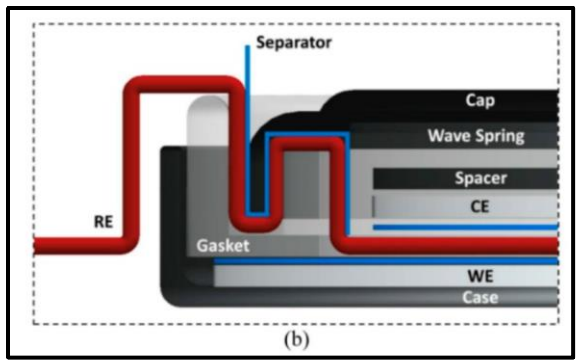
There are various commercial and homemade cell designs available for utilizing a reference electrode during battery testing. All cell architectures: cylindrical, pouch, and coin can be modified to incorporate an internal reference electrode. The chart above provides a brief comparison as to the advantages and disadvantages of the four most common solutions available. The "other homemade" cell category applies to any manual modification of a traditional cell. Examples cited by Raccichini [Raccichini 2019 Batteries 5, 12] show how cylindrical cells, pouch cells, and coincells can all have a reference electrode inserted. There are both commercial and homemade solutions for Swagelok and split-style cells utilizing a reference electrode, and El-Cell represents a premium commercial split-cell.

Comparing results from a new three-electrode experiment to other published results needs to keep as many variables consistent as possible, such as electrode size, material amount, cell uniformity, etc., or else attempt to normalize results. This is a principal reason why traditional cell types are modified to incorporate a reference electrode as "homemade" cell, so results are easier to compare with minimal normalization. Researchers wish to demonstrate and compare their results to existing two-electrode data of the same cell type (cylindrical, pouch, coin). However, since most battery material work is conducted using coincells, this is the natural choice for three-electrode experiments to compare the new results with the vast amount of tradition two-electrode data in publication. The new experimental data will decouple the anode and cathode and provide new insights.

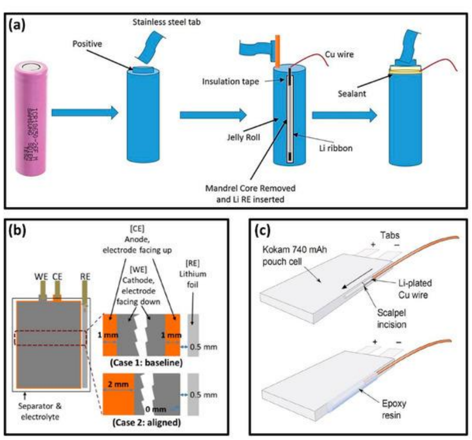
Poor Consistency, Limited Cycle Life, and Limited Scale Testing

Coincells are the preferred test cell format for battery materials development due to the relatively low cost and abundance of supplies, and the relative ease of cell creation and testing. What coincells have traditionally lacked is the ability to decouple results from the anode and cathode when testing a full cell. However, this limitation has not stopped battery materials scientists from adapting the coincell design with a reference electrode. Two examples are shown below where a small wire has been coiled and placed inside a cell assembly to act as a reference electrode.





LEFT: Homemade three-electrode coincell by Minter and Juarez-Robles. [Minter RD, Juarez-Robles D, et al 2018 J Vis Exp., (135):57735.]
RIGHT: Coin Cell with reference electrode for three-electrode experiments [Raccichini 2019 Batteries 5, 12]



Examples shown by Raccichini with other cell designs modified to use a reference electrode. [Raccichini 2019 Batteries 5, 12]

Other cell formats including cylindrical cells and pouch cells have also been adapted by scientists to insert a thin wire as reference electrode. Raccichini referenced a few examples of both cylindrical and pouch cells with reference electrode inserted in his review of this topic. [Raccichini 2019 Batteries 5, 12] These formats are desired since they are more common in commercial battery applications. Modifying the existing cell design for detailed study of cell degradation mechanisms on the anode and cathode can reveal key information in a failure analysis.

All these homemade solutions to perform three-electrode experiments on a battery suffer from similar limitations. The creation/modification of such "homemade" cells can lack consistency in results data, may be prone to leakage, which limits the long-term cyclability, and are not practical for large-scale testing due to the time and labor involved. Variation in the placement and position of the reference electrode produces inconsistency of test results. The reference electrode inserted can also be delicate and easy to damage or be disrupted during a long-term test.

The material used for a homemade reference electrode is also limited by the size of these wire inserted into the cell, often lithium metal. Thus, restricting which cell chemistries can be used in experimentation.

High Cost, Limited Scale Testing, Difficult to Compare with Published Data

The most widely used commercial three-electrode test solutions are the Swagelok-style or split-cell style that are assembled by hand. The practice of using Swagelok-style and split cells fixtures is relatively common because they were one of the only commercially available solutions for a long time. However, labs have been unable to implement large-scale testing with Swagelok cells due to their cost, and the difficulty in using the holder assembly. The consistency of results can be a challenge for researchers comparing cell composition and design, and users often report test disruption or material leakage that limit the use for long-term cycling. Since other cell formats are easier to build, most labs report a decline in the use of their split-style cells and revert to tradition two-electrode formats.

Split cell design from MTI Corp.

Split cell design from El-Cell.

The challenges presented from Swagelok and other split-style cells led to the introduction of El-Cell's three electrode holder. This product provides users with high quality long-term cyclability data and high consistency of results, however the practicality to implement this solution on a large scale is extremely cost prohibitive and does not allow users to run parallel testing on a large scale without a high up-front investment.

All types of Swagelok and split-style cell commercial solutions also make it difficult to truly compare results to much of the existing published data due to the unique surface area of these cells. Coincells and real-world commercial cell formats (cylindrical, pouch, prismatic, etc.) each have a different electrode surface area from the split-cell assembly designs. Different surface area of the electrodes will produce variation in results that can make it more difficult to compare between test results with normalization. Normalizing data still does not address cell uniformity that can also play a role in conclusions drawn from results.

Due to the challenges presented by both commercial and homemade three-electrode battery test solutions, General Motors developed a cost effective three-electrode design that can be implemented on a large-scale and provide quality long-term data with consistent results. The novel "3E" coincell has the same surface area as a traditional CR2032 coincell and makes it ideal for comparing results across all published coincell data.

Arbin's Three Electrode Solution

The alternative solutions for decoupling test results between anode and cathode described above exist because this data has the ability to expedite battery research and development and bring new battery chemistries to market faster.

Arbin's latest generation of LBT and MSTAT high-precision battery test equipment has attracted attention from both academic and industry researchers due to its ability to also expedite the battery development process. 24-bit resolution, extreme precision, and state-of-the-art thermal management that are standard with Arbin produce more detailed and consistent results than other battery testers. This has led multiple industry partners to team up with Arbin on collaborative projects including ARPA-E grants. General Motors has permitted Arbin to license and commercialize a new three-electrode cell design that can further enhance and accelerate their battery testing program.

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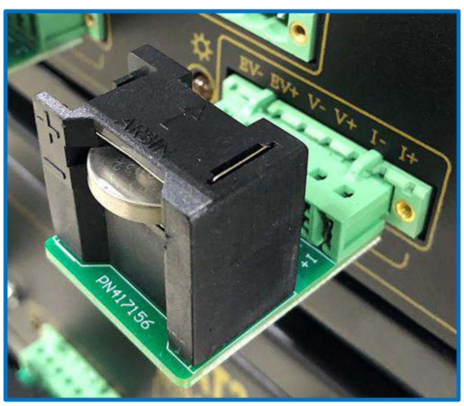
The goals were clear: researchers need a three-electrode cell that is affordable, produces consistent results even during long-term tests, and can be easily used in mass-scale. Since coin cells are already the most used format in the industry, it was the best starting point to modify the existing design to incorporate a reference electrode. The cost of the coin cell assembly equipment and materials provides a low barrier to entry, and most laboratories already have the equipment available. Based on GM's patented design, Arbin moved forward to license and commercialize an easy to access reference electrode in to the standard 2032 coin cell format.



The novel **3E Cell** design provides users with the ability to rapidly prototype new materials by performing large-scale three electrode testing. Traditional methods have proven too expensive and provided inconsistent results. **Arbin's new 3E Coin Cell provides users with an affordable, easy to use three-electrode cell holder that allows for long-term cycling, and provides consistent results between samples.** The low unit cost, disposable design, and easy-to-build coin cell structure allows users to quickly build a large number of cells for materials research testing. The 3E Coin Cell interfaces with Arbin's 3E Coin Cell Holder, and connects directly with our MSTAT product series.

Customizable Electrode Size

Arbin's 3E cells and holders provide superior contact and convenient electrical connection for the main current and voltage connections (working, counter and reference electrodes). This adds ease of use and proven confidence in a solid connection between all parts of the test set up. The design can still be placed in typical 2-pin spring loaded traditional holders if desired, but Arbin's accompanying 3E cell holder allows independent measurement of each side of the battery (anode-cathode).

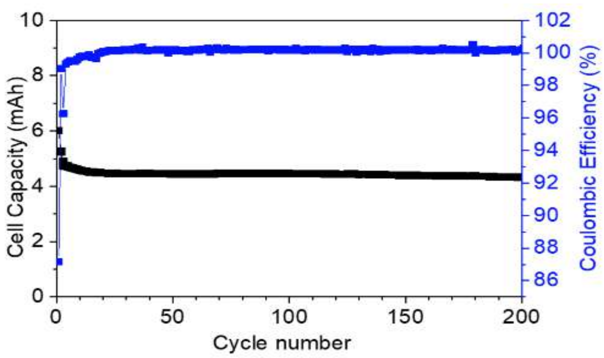
Coincell Format is Easy to Use

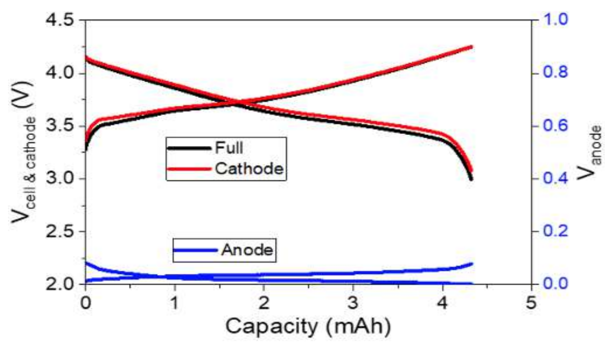
Swagelok cells and other homemade three-electrode cell designs can be complicated to use. They require extreme care by the researcher with little room for error in assembly. Arbin's 3E coincell solution requires little set up and is user friendly. This not only helps researchers do their work more effectively, but greatly speeds up the process and allows mass-scale testing to be conducted. The general 3E coincell assembly parts and process is similar to traditional coincells and does not require a new learning curve.

Low Unit Cost

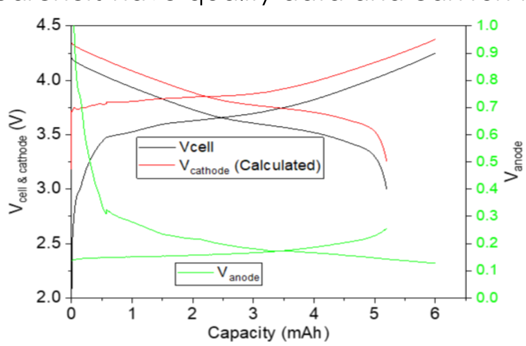
Alternative three-electrode test methods are not cost effective for a large-scale testing lab and Arbin's solution is designed to overcome this issue. Arbin's solution enables more cells to be assembled in one batch as the cost driven limitation has been significantly reduced. The test scope can be increased, and the results are more reliable as the design has eliminated the chance for leakage, opening the possibility for longer cycling.

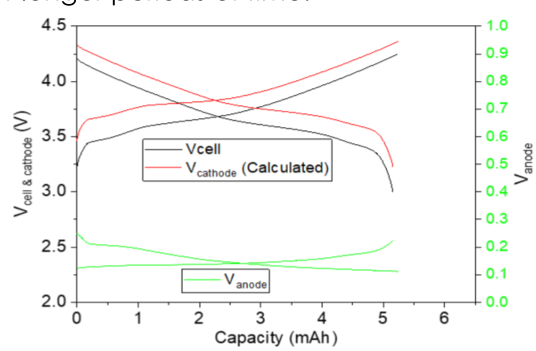
Results





Data gathered by GM show repeatable long-term cyclability, with consistent results across multiple samples. The cell tested in the graph above was subjected to over 200 cycles, and the data reflects a stable housing with no inconsistent results or loss in stability. GM and Arbin have proven this new design has good long cycling stability without leakage. This is important so researchers have quality data and can run tests for longer periods of time.





Along with the novel "3E" three-electrode coin cell holder, researchers can utilize Arbin's MSTAT for testing, MZTC Multi-Chamber for temperature control, and interface an approved EIS module as these testing tools provide great ease of use during testing. These tools also allow easy scaling since the MSTAT tester is offered in chassis of 4 to 64 channels, the MZTC Multi-Chamber have optional racks, and each EIS module is shared across up to 32 Arbin channels.

Complete Battery Materials Research Solution with EIS and Temperature Control

Arbin's MSTAT system is designed for high performance electrochemical research of battery materials and advanced battery testing. Each channel is an independent potentiostat/galvanostat with built-in voltage reference. The 6-point connection on each channel allows researchers to directly connect the 3E Coin Cell Holder and grants full control of test profiles and data logging. The MSTAT provides true bipolar circuitry to ensure cross-zero linearity with no switching time between charge and discharge when performing dynamic real-world simulations. MSTAT hardware provides both digital and analog voltage control. Digital control maximizes the safety of battery cycling and can handle dynamic device resistance, while analog control enables the fast response and stability necessary for electrochemical applications. These features merely enhance the standard 24-bit resolution and extreme precision.
Arbin can now offer our customers a complete solution from the coin cell housing and holder, to the high precision potentiostat/galvanostat test channels coupled with EIS testing and temperature control.

Electrochemical Impedance Spectroscopy (EIS)
Users can pair third party EIS devices, such as Gamry or Autolab, with the MSTAT system to perform multiplexed EIS experiments measurements up to 2MHz. This will allow for a single EIS channel to run tests on up to 32 Arbin test channels without the need to change cell connections, fully maximizing the duty cycle of EIS station and Arbin tester. Three-electrode testing with a reference electrode is an important method for overcoming the interference caused by the interactions between the WE and CE. The RE provides researchers with data to determine how each component of the cell affects overall battery performance.

MZTC Multi-Chamber

For researchers who require temperature-controlled environments, Arbin also offers a cell-isolating thermal safety chamber comprised of 8 independently controlled mini-chambers. Insulation and protection between each mini-chamber provide greater temperature control and a safe testing environment by isolating each cell or pair of cells. The small, independent mini-chambers ensure a stable and uniform temperature for all cells without temperature fluctuation that oversized chambers suffer. Isolating cells this way provides greater independence to access and monitor the devices under test and prevents a weak or failed cell from affecting others during testing. The 3E Coin Cell+Holder is specially designed to work with Arbin's MZTC Multi-Chamber for users performing thermal testing between 10-60C.

To Learn More: https://www.arbin.com/products/materials-research/
Contact Arbin at: sales@arbin.com.

About Arbin

Arbin Instruments is the leading manufacturer of high-precision battery test equipment. Arbin offers a competitive edge to battery researchers and industry clients who's decision-making is empowered by seeing the smallest changes happening in their batteries.

Arbin was founded in 1991 and headquartered in College Station, Texas, USA. Regional offices are located in China, Germany, Hong Kong, South Korea, and Taiwan to support our global network. www.arbin.com | sales@arbin.com | +1 979 690 2751 (USA)

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