




Protocol for quantifying inactive lithium in anode-free lithium batteries by mass spectrometry titration

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Quantifying inactive lithium during cycling is essential for understanding the failure mechanisms of lithium-metal batteries. Although many quantitative studies of lithium-metal failure have been reported, insufficient attention has focused on the reproducibility of the data or the reliability of the analysis. Here, we propose a complete mass spectrometry titration protocol and show how to accurately quantify inactive lithium, showing that quantitative results with high repeatability can be achieved. We believe that this protocol can be extended to other alkali-metal battery systems, facilitating more reliable and accurate battery research.

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Lithium metal has been considered as the key anode material for the next generation of high specific energy batteries because of its high capacity and low electrochemical potential¹. However, its commercialization is hindered by rapid capacity attenuation. At present, it is generally believed that the main reason for the capacity attenuation of lithium-metal batteries (LMBs) is the formation of a large number of inactive lithium during the cycles². The inactive lithium is composed of Li⁺ compounds in the solid electrolyte interface (SEI) and metallic dead Li metal (Li⁰) wrapped by SEI, which both change dynamically with the cycles³. Therefore, accurate quantitative research on various forms of inactive lithium throughout the battery cycles is the key to deeply understand the failure mechanism of LMBs and realize their commercial application. However, due to the confusing morphologies and unstable characteristics of inactive lithium, there is a lack of effective diagnostic tools to distinguish and quantify it. Recently, Meng et al. developed titration gas chromatography (TGC) technique and quantified the contribution of dead Li metal to the total amount of inactive lithium, which confirmed that dead Li metal is the main source of capacity loss⁴. Based on the concept of titration, mass spectrometry titration (MST) technique is also exploited to quantify the dead Li metal and SEI components due to the high sensitivity of mass spectra to different gases, and several groups have reported relevant studies. Firstly, Bryan D. McCloskey et al. developed a highly sensitive MST method to quantify inactive lithium, carbonate-containing SEI, and lithium carbide (Li₂C₂) on cycled graphite electrodes, evaluated the beginning and degree of lithium plating⁵. After that, MST technique was also applied to the lithium-metal system, Cui et al. proved that the existence of lithium hydride (LiH) in the inactive lithium of practical LiCoO₂/Li battery, and believed that the gradual accumulation of LiH was one of the most critical sources of Li anode pulverization and failure⁶. Alex et al. also studied the effect of fluoroethylene carbonate (FEC) additives on lithium-metal anode and completed the quantitative detection of dead Li metal and SEI products in Li||Cu battery system⁷. Therefore, MST technique is a powerful tool for the identification and quantification of inactive lithium. Furthermore, our recent work using in-situ solid-state nuclear magnetic resonance (NMR) technique shows that the existence of LiH is the reason for the deviation of the quantitative results of inactive lithium by TGC and MST technique⁸. Therefore, the combination of multiple technologies is essential for the accurate quantification of inactive lithium.

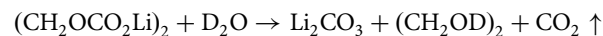
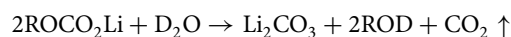
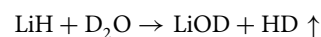
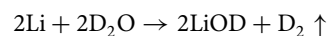
Recently, anode-free batteries (AFBs) have attracted wide attention, it can be also applied to evaluate various strategies for enhancing the performance of LMBs, as their coulombic efficiency is limited almost entirely by the single efficiency of lithium plating and stripping, allowing a more realistic assessment of the electrochemical properties⁹. Therefore, AFBs is an ideal model system to quantitatively study the failure mechanism of lithium metal in different electrolytes on the electrode. In the last several years, the reproducibility of scientific research has attracted widespread concern, which significantly affects the authenticity of research results¹⁰. However, although many quantitative studies on lithium-metal failure have been proposed, there is still a lack of much attention to the reliability and reproducibility of the quantitative results. Preciseness and transparency are the guarantees of reproducibility. Therefore, there is an urgent need for a set of reliable quantitative research procedures, otherwise, it is difficult to ensure the accuracy of quantitative results, and thus affect the analysis and interpretation of failure mechanisms and may lead to wrong understanding, let alone expanding the quantitative results to the practical battery system.

In this work, we discuss how to accurately quantify the inactive lithium in AFBs and propose an integrated and explicit operation process of MST technique for quantifying inactive lithium. We emphasize some issues that require special attention in the process of preparation before titration, establishment and validation of standard curves, specific titration operation, etc. Based on such an experimental protocol proposed in this paper, other researchers can also quantify inactive lithium correctly and reproducibly. Furthermore, the protocol can be also expanded to other alkali-metal battery systems, to get a comprehensive and reliable understanding of the failure mechanisms of the batteries.

Results and discussion

Quantification of inactive lithium by MST method. MST installation in turn consists of carrier gas cylinder, mass flow controller (MFC), sealed titration container, cold trap device and mass spectrometer (Hiden Analytic Ltd.). The installation and procedure of MST are shown in Fig. 1. During the test, put the sample into a sealed titration container and inject deuterium-oxide (D₂O) as titrant. The generated gas passes through the cold trap with the carrier gas, and then enters the mass spectrometer for analysis. Multi ion mode (MID) is used to record ion currents with different m/z values (corresponding to different gases). The carrier gas used in this paper is 99.99% high purity argon with a flow rate of 0.8 mL min⁻¹.

The basic principle of MST technique used in the analysis of inactive lithium is the reaction products of inactive lithium and D₂O are quite different:



This paper mainly discussed the quantitative determination of dead Li metal and LiH in inactive lithium by the changes of D₂ (m/z = 4) and HD (m/z = 3) signals during titration.

First of all, it is necessary to ensure the stability of the instrument and working environments. For example, the whole experiment should be carried out in a thermostatic (e.g. ~25 °C) and dehumidified room, and the vacuum of the mass spectrometer is relatively stable (about 2×10^{-6} torr). Before titration, the U-tube in the cold trap needs to be washed with absolute ethanol several times and dried thoroughly in the oven. This ensures that there are no impurities and vapors in the titration unit. The carrier gas flow rate is consistent (0.8 mL min⁻¹) throughout all tests. After connecting the gas path each time, the empty headspace vessel must be tested first, until the content of argon carrier gas is constant and the content of other gases (like N₂, O₂ and CO₂, etc.) is reduced to a sufficiently low value (less than 5×10^{-15}), and then other samples can be replaced for titration test. If an empty vessel is not tested in advance, various impurity gases and unstable argon carrier gas that may exist in the titration gas path will affect the accuracy of quantitative results. In addition, there must be enough dry ice in the cold trap, and the top is stuffed with cotton balls to ensure sufficient condensation effect. This fully cooled condition guarantee removing the low-temperature evaporation gas components contained in the total gas before it enters the mass spectrometer and ensures an unobstructed gas path. Otherwise, the continuously purged carrier gas may bring in a large amount of steam into the mass spectrometer, resulting in the blockage of the gas path and even the mass spectrometry capillary (Fig. 2a). It will

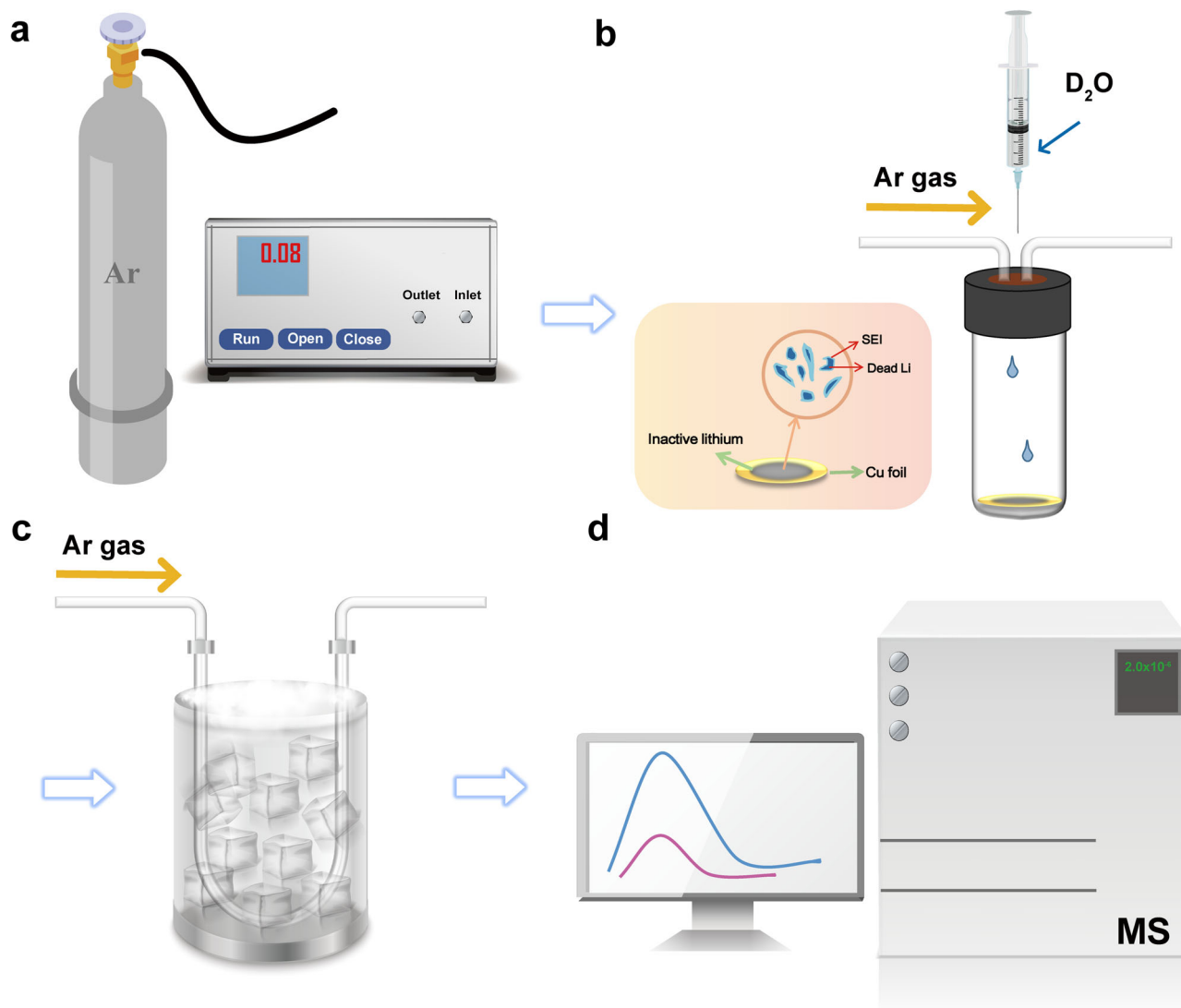


Fig. 1 Schematic illustration of mass spectrometry titration system for quantification of inactive lithium. **a** Carrier gas cylinder and mass flow controller. **b** The sealed titration gas analysis installation. **c** Condensing installation. **d** The mass spectrometer.

not only cause significant deviation of quantitative results but also damage the mass spectrometry instrument.

By building up the standard curve, the direct relationship between the area of D_2 and HD gas obtained by MID curve integration and the amount of Li metal and LiH in the titrated sample can be established. Here we use the external standard method to protract the standard curve. Commercial lithium metal with a mass of 0.11 mg to 0.82 mg and commercial LiH powder with a mass of 0.18 mg to 3.69 mg were carefully weighed in a glove box filled with argon atmosphere using a five-digit balance (10^{-5} g), and then titrated with D_2O for MST tests. It's worth noting that the quality of lithium metal and LiH should be evenly selected near the amount range of inactive lithium of the batteries we want to test. Therefore, it is suggested to titrate the first cycle and completely failed battery samples in advance to estimate the selected range of mass points. After titration of a series of lithium metal and LiH powders with known weight, the signal area of D_2 and HD is integrated after the signals of D_2 and HD are completely attenuated. Note that the signal of each gas shall be normalized with argon baseline gas. Thus, a series of data points of integral signal area with sample quality are obtained, and these data points are linearly fitted to receive the standard curves

(Fig. 3). The results show that the quality of lithium metal and LiH is linearly correlated with the area of D_2 and HD ($R^2 = 99.3\%$, $R^2 = 99.9\%$), indicating that MST system is effective for their quantification. In addition, repeated experiments must be performed to verify the accuracy of the standard curves. More importantly, because the standard curve is made by external standard method, thus it could be affected by the working status of the instruments. For example, the instrument stability, ionization efficiency and the signal response of the mass spectrometer; the sensitivity of the analyzer; the ash deposition caused by long-time high vacuum state, etc. These unexpected changes of the instruments will lead to the deviation of the standard curve. The standard curve of lithium metal before calibration is shown in Fig. 2b. When the vacuum degree of mass spectrometry changes greatly, we use the same method to calibrate the lithium-metal standard curve. It can be seen that the data point obtained from the calibration experiment is no longer on the previously made standard curve. Therefore, we remade the standard curves, as shown in Fig. 2b. There is still a strong linear relationship between the integral area and the quality of the standard sample, but the slope of the standard curve has a change that cannot be ignored. Therefore, we strongly recommend checking the working status of

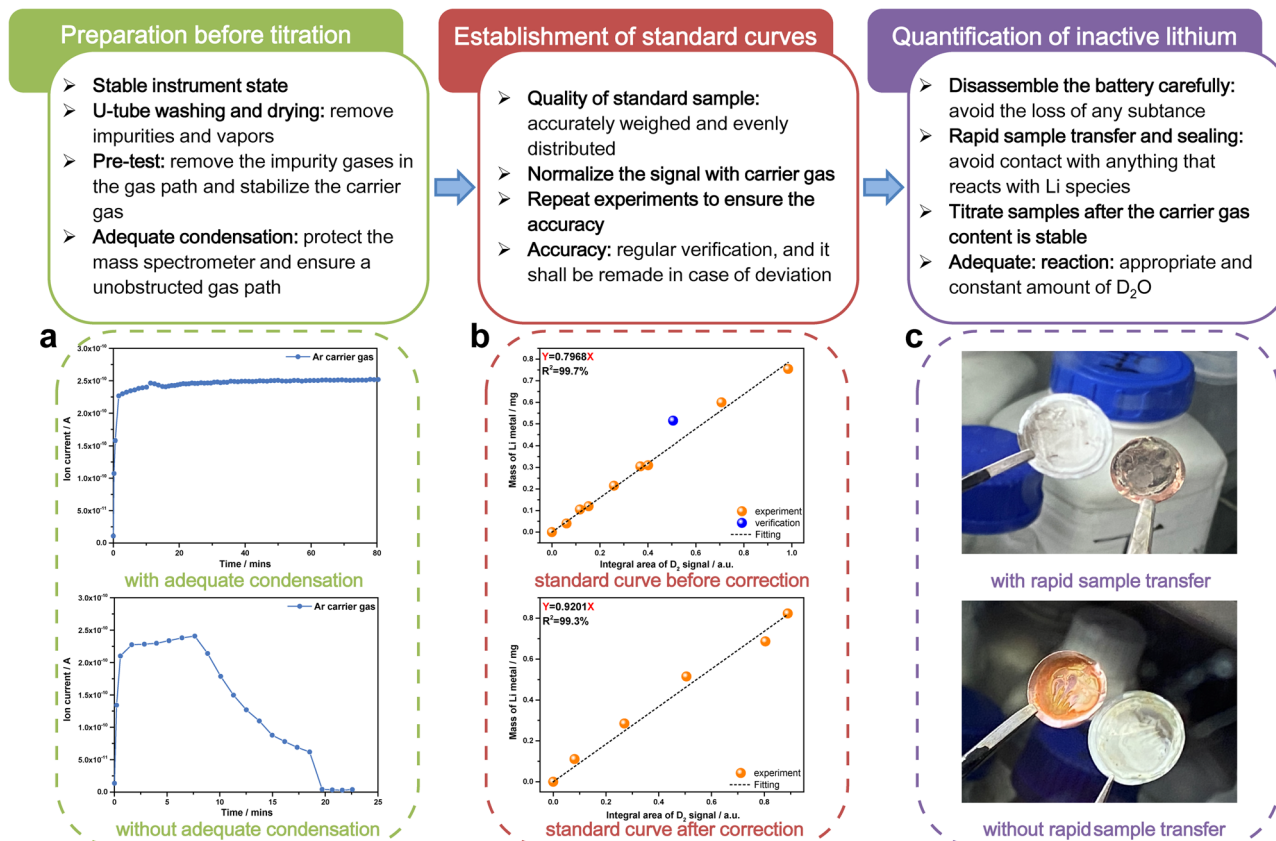


Fig. 2 All points for attention and a complete protocol for reproducible MST results. **a** With/without adequate condensation. **b** The Li metal standard curve before/after correction. **c** With/without rapid sample transfer.

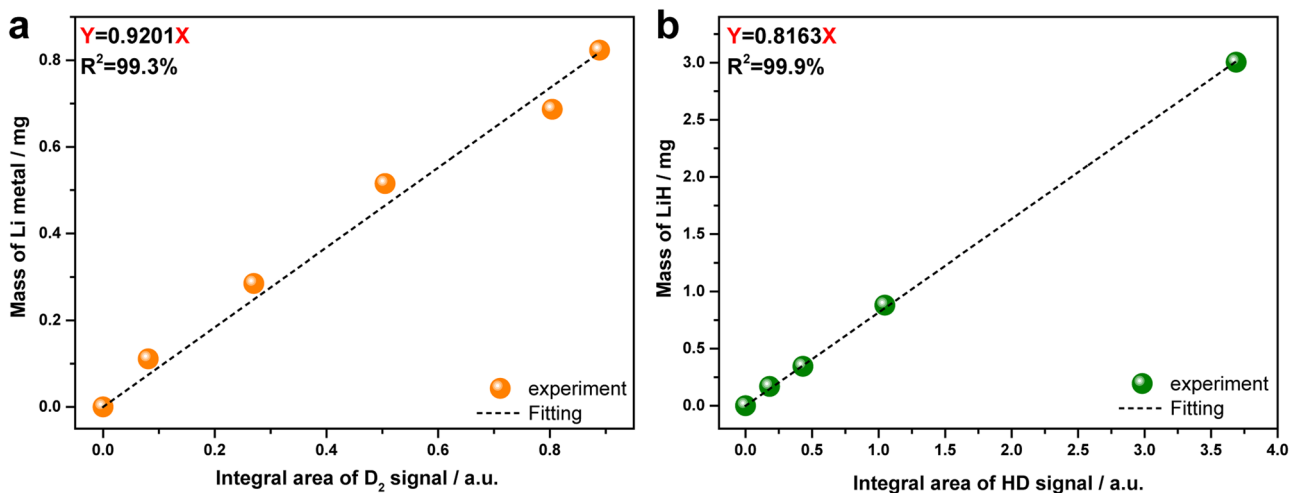


Fig. 3 The quantitative titration standard curves. **a** The calibration curve of mass of Li metal and corresponding integral area of D_2 signal. **b** The calibration curve of mass of standard LiH and corresponding integral area of HD signal.

the mass spectrometers frequently, such as the vacuum level and baseline signal, etc., and the standard curves should be calibrated periodically and the instrument needs to be recalibrated again in case of large deviations.

In order to guarantee the accuracy and reliability of the experimental results, it is of great importance to ensure that the experimental conditions are consistent and the reaction is sufficient and thorough. Before titration, $LiFePO_4 || Cu$ cells after stripping under various conditions are disassembled immediately inside an

Ar-filled glove box. The copper foil and the separator that covered with inactive Li residue should be carefully retrieved and put into the bottom of a headspace vessel, to ensure that the Li species on the surface can fully react with D_2O . At the same time, when taking out the copper foil and separator, it is also necessary to avoid the loss of any substance remaining on the copper surface, leading to inaccurate measurement results. Before taking it out of the glove box, the cap of the headspace vessel must be tightened and carefully sealed with parafilm. While transferring the samples, it should

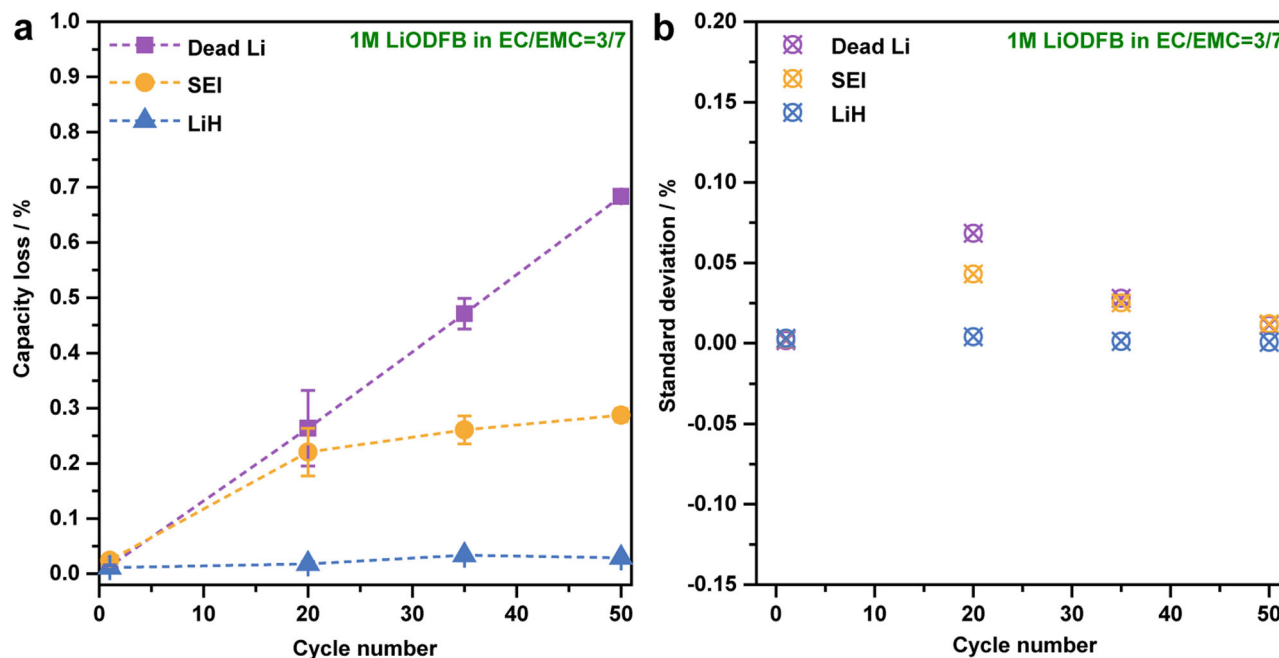


Fig. 4 The quantitative results of inactive Li of the 1M LiODFB in EC/EMC electrolyte. **a** The capacity losses consumed by dead Li metal, SEI and LiH. Error bars indicate the standard deviations of the average values of MST quantitative results. **b** Standard deviation of the quantitative results.

avoid contact with water and other substances that can react with Li species as much as possible (Fig. 2c). Then, two capillaries are quickly inserted into the headspace vessel, with one flushing argon gas (99.99%) as inlet and the other as outlet, and both capillaries should be sealed with wax carefully to prevent air leakage. During titration, after the gas content is stabilized, we use the injector to extract a fixed and excess D_2O (99.9%) into the headspace vessel to react with inactive Li. We usually use 0.2 ml D_2O for titration experiments, which can ensure that the reaction of inactive Li and D_2O can proceed completely, without causing drastic changes in the pressure in the headspace vessel. After titration, the injection site on the cap is carefully sealed with wax again. Then the continuous flow of argon gas carries the D_2 and HD gases released from the titration reaction into the mass spectrometer for detection and analysis.

After the signal of HD and D_2 is fully attenuated, we can integrate the signal of HD and D_2 (normalized with argon baseline gas) and convert the integral areas into the capacity loss caused by dead Li metal (Q_{dead}) and LiH (Q_{LiH}) respectively through the pre-established calibration curves. All capacities are normalized by the 1st charge capacity, which is assumed as the total active Li. The total irreversible capacity (Q_{total}) is equal to the initial charging capacity minus the current discharge capacity. We assume the rest capacity loss comes from SEI, then the SEI capacity loss (Q_{SEI}) can be calculated as follows: $Q_{SEI} = Q_{total} - Q_{dead} - Q_{LiH}$. The specific calculation method can refer to our previous work⁸.

A complete protocol is summarized in Fig. 2, emphasizing all the key steps to obtain repeatable results in MST experiments and illustrating the necessity of the steps in our protocol with several examples. The protocol proposed in this paper can also be applied to different battery systems, providing some helpful insights for the exploration of their failure mechanisms, such as anode-free sodium metal batteries and graphite-based batteries.

Reproducibility and reliability of MST quantification. Each quantitative result requires at least three independent experiments to obtain the average value and error bars according to

such a complete and clear operation process proposed above. Here, we perform titration tests for $LiFePO_4 || Cu$ batteries assembled with 1M difluoro(oxalato)borate (LiODFB) in EC/EMC = 3/7 electrolyte after completing 1, 20, 35 and 50 cycles and then obtain the distribution and the evolution of dead Li, SEI and LiH respectively (Fig. 4a). It's shown that the unexpected increase of dead Li metal is the main cause of capacity loss in this electrolyte, while the formation of SEI and LiH is inhibited. Figure 4b shows the standard deviation of the quantitative results (calculated according to STDEV.S function). In accordance with our MST operation process, the quantitative standard deviation is small, and the maximum standard deviation is no more than 7%, indicating the high reproducibility of our quantitative results. Using the same operation protocol, the same high reproducibility quantitative result of inactive lithium is also shown in other electrolyte system⁸. In addition, our recent work rigorously and comprehensively compared the reliability of NMR, TGC and MST techniques for the quantification of dead lithium, and fully demonstrated the accuracy of MST technique⁸.

Accurate quantification of inactive lithium. MST technique is demonstrated by its unique capability to identify and quantify some SEI components such as LiH and Li_2C_2 , which is difficult to be well-resolved by routine NMR technique. However, it should be noted that MST also has its inherent limitations. As a destructive means, MST is difficult to conduct real-time analysis of inactive lithium in practical battery systems, and for some battery systems such as the solid-state batteries where the lithium metal/electrolyte interface is buried, destructive titration methods may be difficult to use precisely due to possible interference from solid electrolytes adhered⁸. Although operando NMR is a powerful tool to quantify inactive lithium during cycling, its quantitative range is significantly limited by the skin-depth effects (the penetration depth of the radiofrequency field is limited up to a certain depth). For instance, a 200 MHz solid-state NMR spectrometer, the skin depth of radiofrequency is 14.7 μm ¹¹, then the thickness of deposited lithium metal must be less than this value

supposed the Li can be completely and accurately quantified. Therefore, accurate quantification of inactive lithium requires careful selection or combination of MST and operando NMR techniques according to different cyclic conditions, in order to fully understand the complex failure mechanism of lithium metal.

The importance of reproducibility in quantitative research. The reproducibility of quantitative results seriously affects the correct understanding of the problems of quantitative analysis. In past studies on quantification of the inactive lithium, some researches added error range to quantitative results^{4,7,12,13}, while others did not^{3,6}. Therefore, we strongly suggest that repeated experiments should be carried out and the reproducibility of the results should be properly explained in any quantitative research. Otherwise, it is difficult to believe and evaluate the reliability of the conclusion. If necessary, other techniques can also be used in quantitative research to verify and validate the accuracy of quantitative results again¹³.

Conclusion

In summary, we discuss the critical parameters for quantitative determination of inactive lithium by MST technique, and put forward a set of detailed operation process, according to which we can achieve high reproducibility of quantitative inactive lithium. We believe that the accurate quantification of inactive lithium needs to select or combine a variety of technologies according to different cyclic conditions. We hope that our procedures and insights of accurate quantification of inactive lithium will be beneficial and helpful to reproducible and reliable battery research.

Methods

Electrochemical testing. All the cell assembly/disassembly was carried out in the glove box of argon ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). All the tested coin cells are 2025 type. LiFePO_4 cathode slurry were prepared by mixing 80 wt% active material, 10 wt% polyvinylidene fluoride binder (PVDF) and 10 wt% carbon black. The slurry was then coated on aluminum foil and dried in a vacuum oven at 80 °C overnight. The LiFePO_4 cathode was punched into small disks with a diameter of 14 mm and the areal capacity loading is 2.15 ± 0.15 mA h cm^{-2} . The copper foil was punched into small disks with a diameter of 16 mm and then successively cleaned with HCl, acetone and ethanol to remove the oxide prior to use, and then dried in a vacuum oven at 80 °C. The LiFePO_4 || Cu cell was assembled in an Ar-filled glove box, with a copper foil as anode substrate, one layer of celdgard as separator (19 mm diameter), a LiFePO_4 cathode, and with 50 μl electrolyte. The electrolyte used is 1 M LiODFB in EC/EMC (3:7 by weight). Electrochemical tests were performed on Land CT-20001A, and all the testing temperature was controlled at 30 °C. All cells were cycled within a voltage window between 2.8 V and 3.8 V, with a fixed current density of 0.75 mA cm^{-2} .

Mass spectrometry titration. MST experiments were performed on a mass spectrometer (Hiden Analytical Ltd.). The Cu foils and separators that covered with inactive Li were retrieved from cycled LiFePO_4 || Cu AFBs in the Ar-filled glove box ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm) and placed into a sealed headspace vessel. Then the headspace vessel was connected to the gas path of the mass spectrometry titration system, which had been tested with an empty headspace vessel in advance to ensure the stable argon carrier gas and no impurity gas. One capillary with flushing argon gas (99.99%) as inlet and the other capillary as outlet, were both quickly inserted into the headspace vessel and then sealed with wax. After the gas content was stabilized, fixed and excess D_2O (99.9%, 0.2 ml) was injected into the headspace vessel to react with inactive Li. Then the released D_2 and HD were brought into the mass spectrometer by the continuous flowing argon carrier gas for detection and analysis. After the signals fully attenuated, we integrated the signals of HD and D_2 (normalized with argon baseline gas) and converted the corresponding integral areas to obtain the capacity loss caused by dead Li metal (Q_{dead}) and LiH (Q_{LiH}) respectively through the pre-established calibration curves.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Received: 25 December 2021; Accepted: 12 July 2022;
Published online: 27 July 2022

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Acknowledgements

This research was financially supported by National Natural Science Foundation of China (Grant no. 21935009) and the National Key R&D Program of China (Grant No. 2021YFB2401800).

Author contributions

Y.Y. and M.T. planned the project. Y.Y. supervised the project. Y.X. and M.T. prepared the titration standard curves. M.T., D.Z. and P.S. performed the M.T. experiments. The manuscript was mainly written and revised by M.T., Y.X., D.Z. and Y.Y. All authors approved and revised the final version of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Peer review information *Communications Materials* thanks Feifei Shi and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Primary Handling Editors: Jie Xiao and John Plummer.

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