**Photoacoustic Imaging of Lithium Metal Batteries**

Huihui Liu,†§ Yibo Zhao,†§ Jiasheng Zhou, † Ping Li, † Shou-Hang Bo,‡† and Sung-Liang Chen*†‡§

†University of Michigan-Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, China  
‡State Key Laboratory of Advanced Optical Communication Systems and Networks, Shanghai Jiao Tong University, Shanghai 200240, China

Supporting Information

**ABSTRACT:** To better understand and overcome the lithium (Li) dendrite problem in Li metal batteries, great efforts have been made to reveal dendrite growth processes using various imaging modalities. However, because of being almost invisible to electrons and X-rays, directly imaging Li metal with the required contrast and spatial and temporal resolutions has always been the challenge. Here, we show that, by exploiting photoacoustic effect, microscale-resolution three-dimensional structure of Li protrusions inside the glass fiber separator of a Li/Li liquid electrolyte symmetric cell can be clearly visualized with high contrast within minutes by photoacoustic microscopy, demonstrating the potential for observing dendrite growth.

**KEYWORDS:** battery imaging, lithium batteries, dendrites, photoacoustic imaging, photoacoustic microscopy, three-dimensional imaging

Lithium (Li) ion batteries are ubiquitous in present-day technological applications, ranging from portable devices and electric vehicles to grid-scale stationary energy storage. Li ion batteries are composed of positive and negative electrodes (two Li reservoirs with different concentrations) which are separated by a polymeric membrane, i.e., a separator. The separator is immersed in Li ion conducting liquid electrolyte which permits only Li ion shuffling between the positive and negative electrodes during battery cycling. Simultaneously, electrons flow through the external circuit powering electronic devices.

With an increasing demand for higher-energy batteries, it is now a common consensus that the graphite anode in Li ion batteries must be replaced with the most energy-dense Li metal in the next-generation Li metal batteries.1,2 Ironically, the Li metal anode was the choice when the first rechargeable Li battery was invented in the 1970s.2 Soon afterward, however, safety hazards associated with the Li metal anode were identified, which halted the development of Li metal batteries. The problem is inhomogeneous deposition (during charge) and stripping (during discharge) of Li metal, which forms protrusions into the separator (commonly referred to as dendrites in literature) instead of smooth deposits, leading to a short circuit and even an explosion of Li metal batteries.3 The microstructure of such Li metal protrusions can be mossy, whisker-like, or dendritic, and it is a complex function of cycling duration, rate, temperature, and electrolyte concentration, to name a few characteristics. Solid-state batteries utilizing a mechanically strong and nonflammable solid-state electrolyte have been proposed as a promising solution to suppress dendrite growth of Li metal. However, recent studies have shown that metal dendrites can still grow through the grain boundaries of a solid electrolyte and eventually lead to electrolyte crack and a short circuit of the battery.4 It is therefore of uttermost importance to develop a quantitative understanding of Li metal dendrite growth in conventional liquid electrolyte and current solid-state electrolyte settings, and to identify conditions under which smooth Li deposition of tens of micrometers in thickness can be achieved.

Imaging technologies have been demonstrated as a powerful tool to study dendrite growth.5−17 For example, scanning and transmission electron microscopy has been widely used to acquire images of Li dendrites with high resolution and high quality.13−15 While electron microscopy shows the potential to provide the insight into the formation of dendrites, demanding sample preparation is required. Therefore, it is highly challenging for observation in situ, which is essential to track the dynamic evolution of Li metal dendrites during the charge and discharge cycles. Three-dimensional (3D) images of subsurface structures underneath Li metal dendrites were observed with X-ray tomography with resolution on the order of a micrometer.17 However, more than a thousand images were collected with a series of data processing steps required, which restricts the temporal resolution of this technique, limiting its use to ex situ observations only. We further note that Li metal is visible neither to electrons nor to X-rays because Li...
possesses the third lowest electron density of all chemical elements (just above hydrogen and helium), making the observation of bulk Li metal through electron and X-ray microscopy impossible. Only the surfaces of Li metal which are composed of decomposition products resulting from the side reaction between Li metal and the electrolyte (e.g., LiF and Li$_2$CO$_3$) can be visualized. Neutron depth profiling and neutron radiography have been shown to be important tools to probe spatial distribution of Li metal, track inactive Li, and study Li dendrite growth in operando during cycling, providing fundamental insights into the plating and striping behavior of Li metal. Nevertheless, neutron sources and spatial resolution of neutron imaging are both limited. Magnetic resonance imaging (MRI) was utilized to noninvasively observe and quantify Li metal microstructures. However, Li is inherently insensitive to MRI (e.g., much less than that of proton), limiting both the spatial and temporal resolution of $^6$Li and $^7$Li MRI. Optical microscopy (OM) offers one possible route to in situ imaging of dendrites with high temporal resolutions, yet only two-dimensional (2D) images can be obtained. Finally, because of limited penetration depth, most of these techniques discussed above cannot directly visualize Li dendrite growth within the separator or solid-state electrolyte membrane, an important area to precisely locate the positions and patterns of short circuits caused by metal protrusions.

Photoacoustic imaging is based on the photoacoustic effect that light absorbed by a material can be converted into heat and the subsequent thermoelastic expansion to generate an acoustic wave. In the past 20 years, this has been extensively explored in the biomedical imaging field to reveal a wide variety of endogenous or exogenous absorbers. Since light is highly absorbed by most metals, we anticipate that Li metal can be visualized and quantified by photoacoustic imaging. In this paper, for the first time, we demonstrate that photo-acoustic imaging can be exploited to map Li protrusions in Li metal batteries in 3D. A home-built photoacoustic microscopy (PAM) system is used to successfully observe the microstructure of Li protrusions inside the separator of a Li/Li liquid electrolyte symmetric cell. Although we image Li metal to demonstrate the utility of photoacoustic imaging, the obtained results suggest that photoacoustic imaging can potentially be a new tool to realize real-time imaging of Li as well as other metals, such as sodium and magnesium. We believe that PAM can also be extended to image Li metal dendrite growth in solid-state batteries. The imaging technique is also cost-effective and easy to operate.

The details of the Li/Li cell sample fabrication, packaging, and charging can be found in Supporting Information. The PAM imaging system used in this work was also described in Supporting Information. The lateral and axial resolutions of our PAM system were 3.3 μm (Figure S2c) and 26 μm (Figure S2d), respectively. The damage threshold of the Li/Li cell was calibrated to be >86 nJ, and the penetration depth in the cell by PAM was estimated, as elaborated in Supporting Information.

Several imaging experiments were demonstrated to show the PAM’s ability in studying Li protrusions. First, coregistered PAM and OM imaging of the Li-deposited electrode, the side with Li deposition after charging the Li/Li cell, was conducted for comparison of the two imaging modalities. The Li/Li cell sample was prepared, which was charged under a current density of 0.5 mA/cm$^2$ for 15 h. To facilitate image coregistration of PAM and OM, some markers were made on the top surface of a sample holder (Figure 1a) by using an ink pen. Li was deposited along the +Y direction upon electrochemical charging (Figure S1d). Figure 1 shows PAM maximum amplitude projection (MAP) (XY) and OM images of the Li/Li cell sample. The markers can be clearly seen in Figure 1b,c. Note that Figure 1c,e was taken by 5× and 20×.
objectives, respectively. As can be seen, by comparing coregistered PAM and OM images in Figure 1b,c, PAM enables much higher contrast. In addition, by comparing coregistered PAM and OM images in Figure 1d,e, PAM provides a larger depth of focus (DOF). Further, Figure 1f shows the 3D rendering image of Figure 1d, demonstrating the 3D imaging capability of PAM. By contrast, OM suffers from low contrast, limited DOF, and no depth information.

Next, to demonstrate the imaging capability of PAM in visualization of Li protrusions from the Li-deposited electrode toward the glass fiber separator (GFS) of the Li/Li cell, the cross-sectional sidewall surface of one Li/Li cell sample before and after charging at a current density of 1 mA/cm² for 15 h was imaged. Figure 2 shows the PAM MAP (XY) images at two representative regions around the Li-deposited electrode of the Li/Li cell sample. As can be seen, before charging, a thin layer of the Li metal electrode with relatively uniform thickness was observed. By contrast, after charging, protrusions of Li metal from the Li-deposited electrode toward the GFS can be clearly identified. The fusion image shows the PAM image after charging overlaid with that before charging, providing a better comparison. The results suggest that Li protrusions after charging can be revealed by PAM. As can be observed in Figure 2, the thickness of the thin layer of the Li electrode before and after charging remained almost the same, which is considered to be plausible. In addition, Li protrusions were concentrated in certain areas of the Li-deposited electrode, demonstrating the inhomogeneous nature of Li deposition. The above-mentioned characteristics were observed in both of the two representative regions in Figure 2.

Furthermore, because PAM is able to image Li protrusions, as demonstrated above, we attempted to utilize PAM to study quantitative changes of Li protrusions of the Li/Li cells under different charging current densities. Six Li/Li cell samples were prepared as follows: before charging and after charging under current densities of 0.1, 0.2, 0.3, 0.5, and 1 mA/cm², respectively, for 15 h. Figure 3a shows the PAM MAP (XY) images of the six Li/Li cell samples. As can be seen, Li protrusions grew more and more as the charging current density increases. The Li thickness increased from ~0.11 mm...
for the case of before charging to ∼0.54 mm for that of after charging at a current density of 1 mA/cm². Figure 3b shows a representative 3D rendering image corresponding to the region labeled by the dashed box in the image of 1 mA/cm² in Figure 3a, demonstrating PAM’s ability of 3D examination of Li protrusions inside the GFS. To quantify the Li protrusions under different current densities, the Li ratio, defined as the proportion of the area with Li over the observed area in 2D MAP images, was calculated. The calculation method of the Li ratio and error range is described in Supporting Information. As shown in Figure 3c, the Li ratio increases gradually as increased charging current densities and reaches saturation at a current density of 0.5 mA/cm². For charging current densities <0.5 mA/cm², the trend agrees with an increasing amount of Li deposition as the current density (or areal capacity) increases. However, in Figure 3c, the Li ratio for the case of 0.1 mA/cm² is lower than that for the case “Before”, which is not reasonable. Another abnormal result is that, above 0.5 mA/cm², no substantial increase of the Li ratio was observed as the current density doubled (i.e., from 0.5 to 1 mA/cm²). This may be explained by the two limitations (finite imaging thickness and challenging sample preparation) discussed below, which compromise the accuracy of the quantified results to some degree.

Two limitations of PAM for this quantitative study are noticed (i.e., finite imaging thickness and challenging sample preparation), and possible solutions are discussed. (i) With the current light illumination along the Z direction in PAM (Figure 1a), only the top surface of Li protrusions (i.e., facing the −Z direction) can be visualized due to strong absorption of Li metal. To better quantify volumetric distribution of Li protrusions by PAM, dual-view PAM is a potential solution.28 Furthermore, even with 160 μm penetration depth into the GFS, it is still impossible to image all Li metal contained in the GFS because the typical diameter of a GFS is on the order of centimeters and above. Development of a PAM sectioning tomography system could be considered, which is similar to the idea of micro-optical sectioning tomography to obtain a high-resolution image of a whole mouse brain.30(ii) Six different pristine Li/Li cell samples were used in this study. The sample difference impairs the accuracy of the quantified Li protrusions. To improve the accuracy of quantification, the same Li/Li cell sample should be imaged by PAM before and after charging (the two images denoted as PAMb and PAMa, respectively). By subtracting PAMb from PAMa, more accurate quantification of Li protrusions can be obtained. However, we note the primary challenge associated with sample preparation. To ensure the quality of PAM imaging, a plastic bag with good light penetration was used in our study, yet this compromises the air tightness of the cell to some extent, which results in poor charge/discharge characteristics of the same Li/Li cell sample. In later studies, packaging materials of the cell that compromise the air tightness of the cell to some extent, which results in poor charge/discharge characteristics of the same Li/Li cell sample. In later studies, packaging materials of the cell that

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssem.9b01791.

Sample preparation of the Li/Li cell, PAM imaging system, calibrations of damage threshold and penetration depth, and calculation method of the Li ratio and error range (PDF)

Video of Figure 1f (AVI)

Video of Figure 3b (AVI)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: shouhang.bo@sjtu.edu.cn (S.-H.B.).

*E-mail: sungliang.chen@sjtu.edu.cn (S.-L.C.).

ORCID

Sung-Liang Chen: 0000-0002-0572-5110

Author Contributions

§H.L. and Y.Z contributed equally to this work.

FINANCIAL SUPPORT

We acknowledge financial support from the National Science Foundation of China (NSFC) (61775134) and the Shanghai Sailing Program (18YF1411100).

REFERENCES

(1) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; Meng, Y. S.; Subramanian, V. R.; Toney, M. F.; Viswanathan, V. V.; Whittingham,