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Authors

Zeng, Yuqiang
Chalise, Divya
Fu, Yanbao
et al.

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Operando spatial mapping of lithium concentration using thermal wave sensing

Yuqiang Zeng,[1] Divya Chalise,[1,2] Yanbao Fu,[1] Joseph Schaadt,[1,2] Sumanjeet Kaur,[1] Vince Battaglia,[1] Sean D. Lubner,[1,*] Ravi S. Prasher[1,2,3,**]

[1]Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

[2]Department of Mechanical Engineering, University of California, Berkeley, CA, 94720, USA

[3]Lead Contact

*Correspondence: slubner@lbl.gov

**Correspondence: rsprasher@lbl.gov

SUMMARY

The development of battery sensing techniques is crucial for safe, reliable, and fast operation of lithium-ion batteries (LIBs). There is a growing realization that the spatially averaged chemical information provided by existing battery diagnostic tools is insufficient for understanding degradation of LIBs. Here we report the use of thermal waves for *operando* probing of the local lithium concentration as a function of depth inside battery electrodes. The dependence of the thermal conductivity of electrodes on lithiation is used for lithium detection for the first time. A proof-of-concept study of graphite anodes demonstrates that thermal wave sensing provides spatial information of lithium concentration comparable to experimental results using synchrotron X-ray diffraction. Therefore, a valuable battery sensing technique based on thermal waves is developed for studying the lithium concentration and the degradation of electrodes during fast charge which may lead to much cheaper and faster sensing techniques as compared to synchrotron-based techniques.

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INTRODUCTION

Li-ion batteries (LIBs) are essential in a wide range of applications from electric vehicles to grid energy storage.[1,2] Significant progress has been made on the development of LIBs towards higher energy density and faster charge rate in past decades.[3,4] However, the increasing energy density and charge rate causes in- and through-plane chemical heterogeneities in batteries,[4,5] *e.g.*, nonuniform Li plating in the lateral direction of the electrodes[6] and large Li^+ concentration gradients across the electrodes during fast charge.[7–10] That means the measured bulk state of charge (SOC) can significantly underestimate the local SOC near the anode surface at high rates. The locally high SOC relates to a locally low anode potential which is favorable to lithium plating and causes accelerated aging of the electrode surface. Further, the gradient of intercalated Li^+ ion concentration results in a gradient of electrode overpotential and thus polarization of the cell. The cut-off voltage can be reached at a lower bulk SOC as the cell polarization increases with the charge rate. As a result, the capacity of the cell cannot be sufficiently used, and the real charge rate is reduced.

Understanding these heterogeneities calls for the development of *operando* techniques that can provide spatially resolved chemical information in LIBs. Recently, many novel characterization methods have been used to monitor changes inside batteries.[7,8,11–18] Spatially, these methods can be classified as local and global measurement techniques. To acquire the spatial distribution of a parameter, local measurements typically require multiple internal sensors (*e.g.*, temperature[11,15] and optical[13] sensors) or scanning multiple points or regions (*e.g.*, X-ray[7,8] and neutron[18] diffraction methods). Global measurement techniques can be useful in specific applications, *e.g.*, pressure measurements for detecting the growth of solid electrolyte interphase (SEI),[16] ultrasonic scanning to observe electrolyte wetting in batteries,[14] and ultrasonic time-of-flight analysis for probing physical changes in the anode.[17] However, these methods are unable to provide spatially resolved property maps as a function of depth through the electrodes. More importantly, unlike the previously reported simple methods for measuring temperature,[11,13,15] SEI growth,[16] lithium plating,[12] and electrolyte wetting,[14] there is no easy probe for measuring the lithium distribution through the 10s of microns thick electrodes. So far *operando* spatially resolved lithium distribution has been obtained using either synchrotron (X-ray[7,8]) or neutron[18] sources. The time required to conduct experiments using X-ray or neutron is very large (including scheduling) which limits widespread use and inhibits conducting multiple experiments to understand the impact of various parameters. Thus, there is a critical need to develop simple sensors for *operando* measurements of Li concentration.

The lack of simple sensors to monitor this lithium concentration profile is partly due to the high reversibility of the lithium intercalation/deintercalation process in reliable and efficient LIBs, which typically implies a weak signal related to the process. For example, the change of volume and color are two well-known phenomena resulting from the lithiation of graphite anodes.[19,20] However, it is challenging to quantify the lithium concentration profile from measuring these phenomena and without dissecting the cell. Another signal not exploited by the electrochemical community is the variation of thermal conductivity related to electrochemically induced structure/phase transitions.[21–27] Specifically, previous studies of lithium cobalt oxide[23,26] and

graphite[21,22] demonstrated the dependence of the thermal conductivity of electrode materials on the degree of lithiation/delithiation. This suggests the possibility of determining the lithium concentration distribution in battery electrodes by spatially mapping their thermal conductivity. Thermal waves are a natural choice of excitation to use for mapping thermal transport properties as they can lead to *operando* measurements.[28] Thermal wave analysis is a well-established approach for measuring the thermal conductivity (k) of microscale and bulk materials, and the depth to which thermal waves penetrate into a sample during measurement can be controlled using their frequencies.[29–33]

Here, we report a benchtop thermal wave-based measurement scheme to measure lithium concentration distributions as a function of depth through the thickness of battery electrodes. A proof-of-concept study of graphite anodes in $Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2$ (NMC532)/graphite Li-ion pouch cells demonstrates that our method provides the through-plane spatial distribution of lithium concentration with resolution and accuracy comparable to energy-dispersive X-ray diffraction (EDXRD).[7] The methodology developed in this work, not limited to graphite anodes, is universally applicable for probing lithium concentration distributions in battery electrodes. In the rest of this paper, we will first present the physical mechanisms linking lithium concentration to thermal conductivity and explain how thermal waves can be used to measure these properties. We will then describe how our technique is performed in practice, and conclude by presenting the results of our measurements of graphite anodes inside operating LIBs subjected to different charging rates.

RESULTS AND DISCUSSION

Thermal wave sensing for probing lithium concentration distribution

Intercalation and deintercalation of lithium ions affect the crystal lattice structure and phonon properties of the host material, and thus its thermal conductivity (Figure 1A). This phenomenon has been theoretically and experimentally investigated in various materials for the purpose of tuning thermal conductivity.[21–26] Here, focus will be given to previous studies of common electrode materials used in LIBs, *i.e.*, lithium-intercalated graphite (Li_xC_6)[21,22] and lithium-intercalated layered transition-metal oxides (Li_xTMO_2),[23] especially Li_xCoO_2.[26] Prior Molecular Dynamics (MD) simulations predicted an anisotropic effect of lithium intercalation on the thermal conductivity of Li_xC_6, *i.e.*, the in-plane k decreases monotonically with the degree of lithiation, while the through-plane k decreases first and then increases with the amount of intercalated Li^+ ions.[21,22] As Li^+ ions are intercalated into the van der Waals gaps between graphite layers, the phonon lifetime is suppressed and the phonon group velocity along the in-plane direction is reduced, and thus the in-plane k decreases monotonically. However, the phonon group velocity along the through-plane direction increases dramatically with the degree of lithiation, which dominates over the suppressed phonon lifetime on the through-plane k at high lithiation states. As for the k of Li_xTMO_2, an *in-situ* measurement demonstrated a ~31.5% decrease of the k of Li_xCoO_2 with the delithiation from $Li_{1.0}CoO_2$ to $Li_{0.6}CoO_2$.[26] Recently, quantum calculations by Feng *et al.* attributed the decrease of k to the reduced phonon velocities and increased phonon scattering rates along with the delithiation of Li_xTMO_2.[23]

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These studies show that the thermal conductivity of Li_xC_6 and Li_xTMO_2 is a strong function of the degree of lithiation/delithitaion. Previously, the focus of this type of finding was the electrochemical tunability of thermal conductivity. However, the finding also reveals that the lithiation/delithiation state can be calculated from the measured thermal conductivity using a calibrated relationship between these two parameters. Thus, the task of measuring lithium concentration can be replaced by measuring thermal conductivity.

Figure 1B illustrates the use of thermal waves for measuring the spatial distribution of thermal conductivity, and hence lithium concentration, in battery electrodes. A surface sensor on top of the electrode stack undergoes periodic Joule heating, resulting in temperature oscillations that diffuse into the battery as thermal waves. The thermal penetration depth (δ_d) is $\propto 1/\sqrt{\omega}$ where ω is the frequency of AC current used for producing the periodic joule heating and thermal waves.[29] δ_d can be controlled by adjusting ω. Therefore, thermal waves can be localized near the sensor for high ω or allowed to extend to the bottom of the battery for low ω, providing spatial resolution for the measurements. The sensor simultaneously functions as a resistive heater (to produce thermal waves), and a resistive thermometer (to record the resulting signal). The thermal wave signals across a wide range of frequencies (*e.g.*, $0.05 – 100$ Hz) are rich with information about the thermal transport properties in all the subsurface layers and interfaces. Thermal wave analysis is well-established for measuring the spatial maps of thermal conductivity of microscale materials.[29–33] The measured map of local thermal conductivity is then converted into a map of local intercalated Li^+ ion concentration using a pre-calibrated quantitative relationship between these two properties.

Measurement protocol and data analysis
A typical procedure consists of fabricating sensors on top of the electrode stack, calibrating the temperature coefficient of resistance (α) of the sensor (Note S1), calibrating the relationship between the thermal conductivity and lithium concentration of the electrode, and then extracting the spatial distribution of thermal conductivity and lithium concentration from a thermal wave measurement spanning a range of frequencies (details in the experimental procedures). Prior to the sensor deposition, a thin electrically insulating layer (parylene and alumina) is used to passivate the current collector (CC) of the electrode, so that the sensors are electrically decoupled from the battery (Figure 1B). Powering these sensors with AC current at frequency ω generates temperature oscillations (at frequency 2ω), which we can calculate from the measured voltage oscillations at frequency 3ω ($V_{3\omega}$) using α (see experimental procedures on why the voltage has a frequency of 3ω).

In traditional thermal wave analysis, the data is analyzed by fitting it to an analytical thermal model that divides the sample geometry into discrete layers. Each layer is described by a collection of parameters (*e.g.*, depth, thickness, k, heat capacity), any of which can optionally be included as free parameters in the fitting process. Thus analysis of the frequency-dependent response, $V_{3\omega}(\omega)$, can yield the thermal conductivity at different distances from the sensor.[31–33] In our case, we wish to extract a complete k profile (to then be converted into a Li concentration profile). One approach would be to virtually sub-divide the anode into many discrete layers and separately fit k of each imaginary sub-layer, resulting in k as a function of depth (*i.e.*, k for each consecutive sub-layer). However, simultaneously fitting this many free parameters to a single dataset would make our

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measurement uncertainties unacceptably large. Instead, we leverage the fact that lithium diffusion and intercalation is a process well-defined by Newman-type models,[34–36] and is therefore subject to certain constraints during fast charge. Applying these constraints allows us to extract a full Li concentration profile from the data from only 2 free parameters in the fitting procedure (details in the experimental procedures).

To link this thermal conductivity profile with an intercalated Li^+ concentration profile, the dependence of the thermal conductivity of electrodes (k_{elec}) on lithiation or state of charge (SOC) is previously calibrated by performing thermal wave measurements at different SOCs, produced by charging at a slow rate of 0.1C (details in the experimental procedures). Such a slow charge rate ensures an approximately uniform lithium concentration distribution across the electrode, necessary for a reliable calibration.[7,9,10]

Proof-of-concept study of graphite anodes
To experimentally validate our technique, we performed a proof-of-concept study of graphite anodes in NMC532/graphite Li-ion pouch cells. Figure 1C shows the schematic of a pouch cell with an embedded sensor and thermal waves for measuring Li^+ ion concentration gradients across the graphite anode (see Figure S1 for the assembled pouch cell with sensors). Here we use z to represent the thickness across the anode (Figure 1C) with $z = 0$ for the electrode surface near the separator and $z = 70$ μm for the surface near the Cu CC (the anode is 70 μm thick). Note that the embedded sensor, which is located within the pouch but on the outside of the electrode stack, does not affect the battery electrochemistry. This is demonstrated in Figure 1D by the cells with and without sensors having nearly identical 1C cycling performance in 100 cycles.

First, a relationship (calibration step) between the amount of intercalated Li^+ ions and the thermal conductivity of anode (k_{anode}) is obtained by charging the cell at 0.1C which enables uniform Li concentration in the anode. With the calibrated relationship, we use our technique to measure the Li concentration profiles of a cell charged to different SOCs at a rate of 1C. The obtained lithium distributions are then qualitatively verified using optical characterizations, and then quantitatively validated by comparing to prior studies using EDXRD.[7] The comparisons demonstrate that our method measures the through-plane spatial distribution of local lithium concentration with resolutions and accuracies comparable to the experimental results using EDXRD.[7]

k_{anode} vs. **SOC calibrated at 0.1C**
Figure 2A shows how the raw $V_{3\omega}(\omega)$ data changes with the SOC of the battery. Note that the data is normalized to $V_{3\omega}(\omega)$ at a SOC of 0. The peaks (~10 Hz to ~100 Hz) occur at the frequencies with greatest sensitivity to k_{anode}, implying that the decrease in k_{anode} dominates the change in the measurement (Note S2). By fitting to the data after 0.1C charging (see a representative best fit in Figure S2), we quantify the relationship k_{anode} vs. SOC and observe a ~25% decrease of the k_{anode} when the cell is charged from SOC = 0 to 100% (Figure 2B). In addition, we simultaneously extract the thermal conductivity of the electrical insulating layer (0.15 ± 0.006 W/m-K) and the combined thermal interface resistance between the separator and electrodes ((3.81 ± 0.47) × 10^{-4} m^2K/W), which agrees well with the previous *operando* thermal measurements by Lubner *et al.*[28] Other parameters used in the model can be found in Table S1.

To understand the dependence of k_{anode} on SOC and further validate our measurements, we model the anode as a simple composite of just graphite particles wetted by electrolyte, since the graphite constitutes 91.83 wt% of the anode (Table S2). We first use the Bruggeman model to back calculate the effective thermal conductivity of the graphite particles (k_p) from the measured thermal conductivity of electrolyte and k_{anode} (Figure S3A),[28,38,40] so that we can compare our measured dependence of k_p on lithiation to predictions from the literature. In order to compare the relative change of k_p, we designate k_p measured at a SOC of 0 to be $k_{p,ref}$ and examine the relative change $k_p/k_{p,ref}$ (Note S3). Prior MD simulations predicted an anisotropic effect of lithium intercalation on the thermal conductivity of Li_xC_6.[21,22] To compare with the effective thermal conductivity of graphite particles from our measurements, we approximate the graphite particles in this study as polycrystals with randomly oriented grains (Figure 2C) and relate the predicted anisotropic thermal conductivity tensors[21,22] to the effective thermal conductivity of graphite particles using an approximate solution by Mityushov and Adamesku (Note S3).[37] Note that a quantitative understanding of the dependence of k_p on the degree of lithiation is beyond the scope of this work due to the complex nature of real graphite particles. Therefore, we compare our measurements of the variation of $k_p/k_{p,ref}$ with the concentration of intercalated Li^+ ions to the same variation predicted by prior atomistic simulations. Figure 2D shows that the experimentally determined $k_p/k_{p,ref}$ *vs.* x agrees qualitatively with the trend predicted by the analytical solution and MD simulation results. Both the measurements and calculations demonstrate that the effective thermal conductivity of graphite particles decreases nearly monotonically with the degree of lithiation, which depends mainly on the high in-plane k. Yang *et al.* validated the formulation by Mityushov and Adamesku[37] by using a detailed finite element analysis and similar to our findings concluded that the effective k is most sensitive to the highest directional thermal conductivity.[39]

Nonuniform lithium concentration distribution measured at 1C

As a feasibility study of using thermal waves for measuring the Li^+ ion distribution, we charge the same cell to different bulk SOCs via 0.1C and 1C charge rates, respectively, and compare the response (Figure 3A). In Figure 2A for 0.1 C the relative *increase* in $V_{3\omega}$ with respect to SOC = 0 in the 10 Hz – 100 Hz range signified increased Li concentration in the anode for increasing SOC. In contrast in Figure 3A, the relative *decrease* in $V_{3\omega}$ in the 10 Hz – 100 Hz range signifies *decreased* Li concentration in the anode near the Cu CC when moderately charging (1C) to an apparent bulk (average) SOC compared to slow charging (0.1C) to the same apparent bulk SOC. In the data analysis, we divide the anode into 10 equal sub-layers (see Figure 1C) with each sub-layer thickness (7 μm) close to the diameter of the graphite particles (5-10 μm), *i.e.*, each sub-layer consists of approximately a single layer of graphite particles.

Figure 3B shows the extracted distribution of k_{anode} across the anode corresponding to bulk SOC = 30%, 50%, and 70%, respectively. Accordingly, the local SOC for each sub-layer can be obtained based on the k_{anode} *vs.* SOC relationship calibrated at 0.1C (Figure 2B), resulting in Figure 3C. As the cell is charged to higher bulk SOCs, a steep concentration gradient develops and the local SOC can deviate significantly from the bulk SOC even at a moderate charge rate like 1C. For example, the difference between the local SOC adjacent to the separator and the average bulk SOC is 8.3%, 10.6%, and 17.9% after 1C charging to bulk SOCs of 30%, 50%, and 70%, respectively. To further confirm the Li concentration gradient, the cells charged to 70% SOC by 0.1C and 1C

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were then disassembled in a glove box and the lithiated anode was sealed in a chamber for optical characterizations (Figure S4). Figure 3D presents the cross-sectional view of the pristine anode and the anodes charged to the same bulk SOC by 0.1C and 1C. The uniform color in the pristine (SOC = 0) anode and the anode lithiated at 0.1C to SOC = 70% demonstrates the homogeneity of the sample and of the degree of lithiation, respectively. In contrast, the strong color gradient observed in the anode charged at 1C to SOC = 70% qualitatively verifies the steep Li concentration gradient measured by our sensor, *e.g.*, the gold color at the electrode surface (left) indicates the highly lithiated graphite particles.[20] These observations are further supported by the top view of the samples (Figures 3E-G).

As a final confirmation, the well-established pseudo-2D (P2D) model developed by Newman and coworkers[34–36] allows a quantitative comparison of the lithium spatial distribution between this work and a previous study using EDXRD.[7] Note that the graphite electrodes in both works are from the same facility and have nearly identical properties except for the coating thickness. Thus, it is meaningful to have a quantitative comparison between the two studies using the similar graphite electrodes and the same electrolyte. Here, the computation is done using a validated P2D solver built by Higa *et al.*[41] and more details can be found in Note S4. Figures 4 show the good agreement between the simulation and experimental results in both studies and thus quantitatively validate our method for measuring lithium spatial distributions *operando*.

Current limitations and future applications of thermal wave sensing
As summarized in a recent review,[42] different global methods have been developed to detect the plated Li metal from a global signal of the entire cell. While these global techniques lack spatially resolved through-plane information that is critical for understanding early degradation of LIBs, they do provide accessible and practical solutions to quantify the total amount of plated Li or qualitatively confirm the occurrence of Li plating. From this perspective, our thermal wave sensing technique involving sensor fabrication is not as simple as some global methods requiring no extra cell components. Furthermore, currently the sensor was implemented on a single layer cell where we expect the sensitivity of the through-plane thermal conductivity and thus SOC to be high. For commercial multi-layer cells, the sensitivity will be reduced due to the presence of multiple layers. In this scenario, it may be possible to extract the parameters of interest by separately measuring the thermal conductivity of other layers such as the cathode; however, this needs to be validated. Also, the measurement sensitivity for the global techniques such as acoustic-based techniques is based on total plated Li as compared to graphite capacity (> 1% of the graphite capacity[42]), whereas our technique is local and the sensitivity is dependent on how much Li has intercalated into the graphite (even if it has not plated). Based on the noise level (Figure S1C), our technique can detect through-plane spatial concentration dependence as long as SOC is > 1.5%.

In addition, it is worth noting that the through-plane lithium concentration provided by this technique is a local average of Li concentration at a particular depth in the porous electrode with contributions from Li_xC_6 at different lithiation stages. With the lithium diffusivity in graphite (0.5 ± 0.34 × 10^{-8} cm^2/s) from a recent work,[43] the estimated solid diffusion penetration depth of Li at 600 mins (0.1C), 60 mins (1C), and 10 mins (6C) is 134.9±59.0 μm, 37.0±13.0 μm, and 16.1±6.3 μm, respectively. Considering the size of graphite particles (~8 μm) in our work, approximate

equilibrium behavior is expected at slow and moderate charge rates as the graphite particle size is much less than the diffusion length of Li. At extremely fast charge rates, the densely lithiated stage and lightly lithiated stage may coexist in a particle when the particle size is much larger than the diffusion length.[43] In this scenario, the measured average lithium concentration at each depth in the porous electrode may not reliably indicate the appropriate effective lithiation phase as the surface concentration on individual graphite particles may be much larger than their average Li concentration. This may lead to the onset of lithium plating locally at lower average SOC than measured by the thermal wave sensor.

The methodology developed here can potentially be applied to investigate lithium distributions and lithium plating during extreme fast charging. The through-plane lithiation heterogeneity is expected to increase with the charge rate.[6] For high-rate (> 1C) studies, high-frequency thermal waves (10 – 100 Hz) can be used for sensing with a higher temporal resolution, *e.g.*, the period of a thermal wave at 10 Hz is 0.1 s and the measurement can be done in seconds. Further work is in progress on investigating the signature of Li plating at higher C rates such as 6C. As the k of Li metal (85 W/m-K) is much higher than that of electrodes (~1 W/m-K), Li formed at the interface likely reduces the thermal contact resistance between the electrode and the separator and can be modeled as an interfacial layer. This phenomenon can be potentially harnessed for higher C rates but more studies are needed.

It is expected that the lateral heterogeneity of Li will increase at significantly high C rates.[6] To capture lateral heterogeneity, multiple sensors distributed laterally will be needed, and there must be no interference of thermal signatures from each sensor's thermal waves. The typical guidance is to keep the distance between any two sensors greater than 2 times their penetration depth if they use common frequencies,[29] or else if they are spaced closer than this they must use different frequencies that also have no common harmonics. Because we choose thermal wave frequencies such that their thermal penetration depth is roughly the same as the electrode thickness and because the thermal waves propagate in all directions, then for electrodes with isotropic thermal conductivity the minimum lateral spatial resolution of each individual sensor is approximately equal to the electrode thickness (~70 μm in our case).

Further, this technique can be potentially applied to measure the lithiation/delithiation and structural change of cathodes given the dependence of the thermal conductivity of Li_xTMO_2 cathode materials on the degree of lithiation/delithiation (Figure 1A). Overall, this work opens the door to battery diagnostics using thermal wave sensing.

Conclusions

Li plating, identified as a major concern for fast charge, typically occurs in charging conditions such as high charge rate, overcharging, and low temperature.[4,5,44,45] However, these local SOC measurements confirm that Li plating conditions can be locally met even when the cell is charged by a moderate rate (*e.g.*, 1C) to a moderate bulk SOC (*e.g.*, 70%). The occurrence of Li plating depends on the rate of lithium intercalation and deposition. From the intercalation reaction rate described by the Butler-Volmer equation, a locally high SOC relates to a low intercalation rate as

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the corresponding exchange current density increases with SOC first and then decreases at relatively high SOCs. As a result, the rate of Li deposition can exceed the intercalation rate, leading to Li plating, since the exchange current density of deposition does not vary with SOC. Further, the locally high SOC, *i.e.*, a great x in Li_xC_6, indicates a locally low anode potential and tends to cause a negative overpotential which makes Li plating thermodynamically possible.

As predicted in simulations and observed in experiments, the lithium concentration heterogeneity across the electrode can create conditions conducive to Li plating near the anode surface earlier than indicated by global measurements. Although we demonstrate a case study at a moderate charge rate of 1C, the concentration heterogeneity is expected to increase with the charge rate and bulk SOC. Thus, local Li plating will tend to occur at an even lower bulk SOC during faster charging. Avoiding this scenario requires being able to monitor the spatial distribution of local SOC during charging, especially near the anode surface adjacent to the separator. With this local SOC information, the charge current can be adjusted once the local SOC reaches a cut-off value which may trigger local Li plating. We anticipate that the Li detection capability of thermal wave sensing can be of significance in the development of smart battery sensing and fast charge protocols, as well as future research seeking to elucidate the impact of different parameters on Li concentration distributions and Li plating In particular future endeavors on placing the thermal wave sensor on the casing of the cell rather than on the surface of the electrode can lead to a completely non-invasive Li detection sensing technology.

In summary, we have presented a simple benchtop technique to measure spatially mapped lithium concentration distributions as a function of depth through the thickness of battery electrodes in operating cells. Our technique leverages the strong relationship between the local concentration of intercalated Li^+ ions and thermal conductivity. The scheme enables thermal wave sensing to monitor the lithium concentration profile *operando* during rapid charging. A proof-of-concept study of graphite anodes charged at 1C quantitatively demonstrates that our method provides local maps of lithium concentration through the anode with resolution and accuracy comparable to experimental results using EDXRD. Compared to the higher cost, inconvenience and time summing aspects of X-ray-based methods, our thermal wave sensing technique enables this type of study with a simple and more accessible setup. In addition, this study displays how thermal metrologies can be used to probe subsurface structures based on structure-dependent thermal conductivity, enabling simple probes for a variety of situations. The methodology developed in this work can be universally applied to electrode materials where thermal conductivity is a function of structure or phase of the material.

EXPERIMENTAL PROCEDURES

Resource availability
Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the Lead Contact, Ravi S. Prasher (rsprasher@lbl.gov).

Materials availability

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This study did not generate new unique materials.

Data and code availability
The datasets presented in this study are available from the Lead Contact upon reasonable request.

Preparation of cells
We used the electrodes from Argonne's Cell Analysis, Modeling and Prototyping (CAMP) Facility (Table S2 for properties provided by CAMP). We first coated a layer of parylene (~400 nm) on the Cu CC using a vacuum deposition system (SCS Labcoter 2). An adhesion promoter A-174 Silane was used for the parylene coating. A 100 nm Al_2O_3 layer was deposited via atomic layer deposition (Cambridge Nanotech Fiji200) as a surface of higher adhesion with the metallic sensors. For the sensors, we first deposit a 10 nm Cr adhesion layer followed by a 120 nm Au layer, deposited onto the Al_2O_3 layer through a shadow mask using a Mbraun thermal evaporator system. Electrical connections to outside the battery were realized by attaching 50 μm diameter electrically insulated copper wires to the sensor contact pads using silver epoxy (EPO-TEK® H20E adhesive). On top of the sensors, we attached a 2 mm polyethylene foam for thermal insulation, which is compatible with the battery electrolyte. On the backside electrode (the surface of Al CC), we attach a 2 mm thick Al plate to enhance signal sensitivity and to act as a heat spreader. More details can be found in our prior work.[28]

Electrochemical tests
The pouch cells were tested by MPG2 potentiostat (Bio-Logic) in a thermoelectric temperature chamber (TestEquity TEC1). All the tests were performed around room temperature (23 °C). The nominal capacity (32 mAh) of the cell was calculated based on the coating loading of cathode. The 3 formation cycles were performed at a charging rate of 0.1C, and were operated in the 3-4.1 V range to form the solid electrolyte interphase on the graphite anode. After formation, the cells were cycled in the 3-4.2 V range for a higher degree of lithiation at 1C charging rates. Figure S5 shows the electrochemical performance of the cell with sensors.

Thermal wave measurements
The AC current passing through the sensors was provided by a Keithley 6221 AC current source, and the corresponding signal was acquired using an Amtek 7279 Lock-in Amplifier. Sensors typically have an electrical resistance of ~11 Ohms and were powered by 50 mA RMS of current. ~1 K of AC surface temperature rise of the sensor is sufficient for accurate measurements. To collect the information across the full thickness of the stack, the frequency of the applied current is varied from 50 mHz to 100 Hz. To collect data at each frequency, it takes several periods to allow the signal to stabilize and another several periods to gather sufficient data points for analysis. Typically, the data collection for each frequency can be done in 10 periods, *e.g.*, 1 sec for getting a 10 Hz signal. The total measurement time can be reduced significantly when only a few signals at representative frequencies are needed. For example, since the frequency needed to resolve the through-plane thermal conductivity and lithium distribution of battery electrodes is in the range of 10 to 100 Hz, the time required to conduct this frequency sweep is a few seconds (< 10s). High signal-to-noise ratios of 10^3 to 10^4 were obtainable due to the frequency domain nature of the measurement, the high lock-in amplifier time constants (corresponding to very narrow bandwidths) used in our measurements, and the ambient thermal noise shielding from the

isothermal temperature chamber (Figure S1C). Note that the thermal wave signal at a particular frequency depends only on heating occurring at that same frequency, and thus is unaffected by all other thermal or electrical signals associated with cycling the battery or other external stimuli. A constant compression pressure (~5 psi) was applied on the cell for a good contact between cell components during cycling. While the applied pressure does not affect the sensor itself, it can change the contact of electrodes and interfaces and thus the generated signal (Figure S1D), *e.g.*, higher pressures might improve the contact and charging performance. Extracting the SOC distribution requires a sensor calibration done under the same cycling conditions, including pressure.

Thermal wave analysis

An expression is developed for the periodic heat conduction through our multilayered stack based on Feldman's algorithm.[46] The expression relating the frequency-dependent average surface temperature (T_0) to the measured $V_{3\omega}$ is[30]

$$V_{3\omega} = -\frac{1}{2}\alpha R_0^2 I^3 \left[\mathrm{Re}\left\{\frac{T_0}{q}\right\} + i\,\mathrm{Im}\left\{\frac{T_0}{q}\right\} \right] \tag{1}$$

where q is the total heat generated by the sensor. Note that since the current has a frequency ω, the temperature rise has a frequency of 2ω due to joule heating. Since the electrical resistance of the sensor increases linearly with temperature it has a frequency of 2ω which results in the voltage having a frequency of 3ω as it is given by $V = IR$. Therefore, this technique is also widely known as 3ω technique. $\mathrm{Re}\{\frac{T_0}{q}\}$ and $\mathrm{Im}\{\frac{T_0}{q}\}$ corresponds to the in-phase and out-of-phase thermal response, respectively. We use an analytical model of T_0 in the literature to fit the measured $V_{3\omega}$.[31–33] The parameters to be determined are the thermal conductivity of the insulating layer between the sensor and current collector (k_{ins}), the thermal conductivity of the electrode near the sensor (k_{elec}), and the total thermal interface resistance between the separator and electrodes (TIR_{s-e}). As typically done in these multilayer models, the separator-electrodes interfaces are modeled as a layer with vanishing thickness (1 nm) and vanishing heat capacity (10^{-3} kJ/m^3-K). For the k of the electrode layer far away from the sensor, we use the value from *ex situ* measurements in all the data fitting since our single-side sensor has a poor sensitivity to this term, meaning it will have only a small effect on the measured values of other parameters of interest (see Note S2). The uncertainty of the measured thermal transport properties and SOC is analyzed by considering the errors that propagate from uncertainties of the parameters used in data fitting (see Table S1).

Calibration of k_{elec} *vs.* SOC

At a slow charge rate (*e.g.*, 0.1C), modeling studies predicted that Li$^+$ ions are uniformly distributed across the electrode.[11,12] Thus a bulk thermal conductivity, k_{elec}, is used for the electrode layer near the sensor. We simultaneously fit three parameters in the model, *i.e.*, the thermal conductivity of the electrical insulation layer (k_{ins}) between the sensor and Cu CC, k_{elec}, and the total thermal interface resistance (TIR_{s-e}) of the separator-anode and separator-cathode interfaces. As the cell is charged to various SOCs, the k_{elec} changes since the phase of lithium intercalated compounds varies with the amount of intercalated Li$^+$ ions. Here we assume the k_{ins} and TIR_{s-e} does not change with the SOC in a cycle as the intercalation/deintercalation happens in the

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electrode. The deintercalation/intercaltion of Li$^+$ ions in the opposite electrode can affect its thermal conductivity, but the sensor has a poor sensitivity to this layer (Note S2). For simplicity we use the same k for the electrode layer far away from the sensor at all SOCs.

Constraints from Newman models

Lithium intercalation is a process well-defined by Newman-type models,[34–36] and thus it is subject to the following constraints during fast charge: (i) the local SOC decreases monotonically with z, (ii) the second derivative of SOC with respect to z is nonnegative, and (iii) the SOC distribution is unlikely to have abrupt changes and thus obeys some type of smoothness restriction. Further, the bulk SOC can be easily measured and thus the average of the SOC distribution is known. These constraints can be easily converted to restrictions of k_{elec} based on the calibrated k_{elec} *vs.* SOC relationship. As for the smoothness of SOC(z), the SOC(z) can be simply approximated as a second-order polynomial with the defined constraints, which originates from the fact that Newman models are built on partial differential equations involving second-order space derivatives.[34–36]

Multilayer analysis for obtaining the k_{elec} distribution

For simplicity, we define the normalized SOC*, k^*, and z^* as $SOC^*(z^*) = SOC(z^*)/\int_0^{L_{elec}} SOC(z^*)dz^*$, $k^*(z^*) = k(z^*)/\int_0^{L_{elec}} k(z^*)dz^*$, and $z^* = z/L_{elec}$, respectively. L_{elec} is the thickness of the electrode where the lithium concentration distribution needs to be measured. Approximate $SOC^*(z^*)$ as a second-order polynomial $az^{*2} + bz^* + c$ with parameters a, b, and c to be determined, and convert the SOC distribution constraints based on Newman models to $SOC^*(z^*)$: (i) $2az^* + b \leq 0$ and (ii) $a \geq 0$. The smoothness is satisfied as the polynomial is a smooth function. Further, the normalized function $SOC^*(z^*)$ must have $\int_0^{L_{elec}} SOC^*(z^*)dz^* = 1$ and thus $\frac{a}{3} + \frac{b}{2} + c = 1$. These constraints can be reorganized as: $b \leq 0$, $0 \leq a \leq -\frac{b}{2}$, and $c = 1 - \frac{a}{3} - \frac{b}{2}$. To such a constrained 2-parameter fitting problem, we use two free parameters (u_1 and u_2) in the fitting procedure and meet the constraints by having $a = |u_1^2 - \frac{u_2^2}{2}|$, $b = -u_2^2$, and $c = 1 - |\frac{u_1^2}{3} - \frac{u_2^2}{6}| + \frac{u_2^2}{2}$. Based on the calibrated k_{elec} *vs.* SOC relationship, $k^*(z^*)$ can also be expressed in 2 free parameters. With all the parameters expressed in two free parameters, extracting the distribution is simplified to a two-parameter fitting problem which can be easily done as in prior works.[31–33]

The electrode is divided into multiple sub-layers for data fitting based on Feldman's algorithm.[46] The average of $SOC^*(z^*)$ for each sub-layer can be calculated from the SOC^* distribution. Take the example of dividing the electrode into 10 sub-layers, the average $SOC^*(z^*)$ of the first sub-layer is expressed as $\frac{\int_0^{0.1}(az^{*2}+bz^*+c)dz^*}{0.1} = \frac{a}{300} + \frac{b}{20} + c$. The expression for other sub-layers can be derived likewise.

Optical characterizations

The cells were charged to SOC = 70% at charging rates of 0.1C and 1C, respectively. The lithiated anodes were then extracted from the charged cells in a glove box and sealed in a chamber for optical characterizations outside the glovebox using a Hitach microscope (Figure S4). The optical

images were taken within an hour, ensuring anode contact to oxygen or moisture was sufficiently low. We observed that the color of the electrodes disappeared after ~2 days due to the leakage.

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AUTHORS CONTRIBUTIONS

Y.Z., S.D.L. and R.S.P. conceived the idea. Y.Z., D.C., Y.F., J.S., and S.K. contributed to sensor and cell preparation. Y.Z., D.C., S.D.L., and R.S.P. contributed to the analysis of thermal conductivity and lithium distribution. Y.Z. and D.C. contributed to the characterization of electrodes. Y.Z., S.D.L., V.B., and R.S.P contributed to writing.

DECLARATION OF INTERESTS

The authors declare no competing financial interests.

REFERENCES

1. Dunn, B., Kamath, H., and Tarascon, J.M. (2011). Electrical energy storage for the grid: A battery of choices. Science (80-.). *334*, 928–935.

2. Cano, Z.P., Banham, D., Ye, S., Hintennach, A., Lu, J., Fowler, M., and Chen, Z. (2018). Batteries and fuel cells for emerging electric vehicle markets. Nat. Energy *3*, 279–289.

3. Howell, D., Cunningham, B., Duong, T., and Faguy, P. (2016). Overview of the DOE VTO advanced battery R&D program.

4. Ahmed, S., Bloom, I., Jansen, A.N., Tanim, T., Dufek, E.J., Pesaran, A., Burnham, A., Carlson, R.B., Dias, F., Hardy, K., et al. (2017). Enabling fast charging – A battery technology gap assessment. J. Power Sources *367*, 250–262.

5. Liu, Y., Zhu, Y., and Cui, Y. (2019). Challenges and opportunities towards fast-charging battery materials. Nat. Energy *4*, 540–550.

6. Tanim, T.R., Paul, P.P., Thampy, V., Cao, C., Steinrück, H.G., Nelson Weker, J., Toney, M.F., Dufek, E.J., Evans, M.C., Jansen, A.N., et al. (2020). Heterogeneous Behavior of Lithium Plating during Extreme Fast Charging. Cell Reports Phys. Sci. *1*.

7. Yao, K.P.C., Okasinski, J.S., Kalaga, K., Shkrob, I.A., and Abraham, D.P. (2019). Quantifying lithium concentration gradients in the graphite electrode of Li-ion cells using: Operando energy dispersive X-ray diffraction. Energy Environ. Sci. *12*, 656–665.

8. Finegan, D.P., Quinn, A., Wragg, D.S., Colclasure, A.M., Lu, X., Tan, C., Heenan, T.M.M., Jervis, R., Brett, D.J.L., Das, S., et al. (2020). Spatial dynamics of lithiation and lithium plating during high-rate operation of graphite electrodes. Energy Environ. Sci. *13*, 2570–2584.

9. Hasan, M.F., Chen, C.-F., Shaffer, C.E., and Mukherjee, P.P. (2015). Analysis of the Implications of Rapid Charging on Lithium-Ion Battery Performance. J. Electrochem. Soc. *162*, A1382–A1395.

10. Gallagher, K.G., Trask, S.E., Bauer, C., Woehrle, T., Lux, S.F., Tschech, M., Lamp, P., Polzin, B.J., Ha, S., Long, B., et al. (2016). Optimizing Areal Capacities through Understanding the Limitations of Lithium-Ion Electrodes. J. Electrochem. Soc. *163*, A138–A149.

11. Wang, H.H., Zhu, Y., Kim, S.C., Pei, A., Li, Y., Boyle, D.T., Wang, H.H., Zhang, Z., Ye, Y., Huang, W., et al. (2020). Underpotential lithium plating on graphite anodes caused by temperature heterogeneity. Proc. Natl. Acad. Sci. U. S. A. *117*, 29453–29461.

12. Bommier, C., Chang, W., Lu, Y., Yeung, J., Davies, G., Mohr, R., Williams, M., and Steingart, D. (2020). In Operando Acoustic Detection of Lithium Metal Plating in Commercial LiCoO2/Graphite Pouch Cells. Cell Reports Phys. Sci. *1*, 100035.

13. Huang, J., Albero Blanquer, L., Bonefacino, J., Logan, E.R., Alves Dalla Corte, D., Delacourt, C., Gallant, B.M., Boles, S.T., Dahn, J.R., Tam, H.Y., et al. (2020). Operando decoding of chemical and thermal events in commercial Na(Li)-ion cells via optical sensors. Nat. Energy *5*, 674–683.

14. Deng, Z., Huang, Z., Shen, Y., Huang, Y., Ding, H., Luscombe, A., Johnson, M., Harlow, J.E., Gauthier, R., and Dahn, J.R. (2020). Ultrasonic Scanning to Observe Wetting and "Unwetting" in Li-Ion Pouch Cells. Joule *4*, 2017–2029.

15. Zhu, Y., Xie, J., Pei, A., Liu, B., Wu, Y., Lin, D., Li, J., Wang, H., Chen, H., Xu, J., et al. (2019). Fast lithium growth and short circuit induced by localized-temperature hotspots in lithium batteries. Nat. Commun. *10*, 1–7.

16. Louli, A.J., Ellis, L.D., and Dahn, J.R. (2019). Operando Pressure Measurements Reveal Solid Electrolyte Interphase Growth to Rank Li-Ion Cell Performance. Joule *3*, 745–761.

17. Knehr, K.W., Bommier, C., Davies, G., Kim, A., Steingart, D.A., Knehr, K.W., Hodson, T., Bommier, C., Davies, G., and Kim, A. (2018). Understanding Full-Cell Evolution and Non-chemical Electrode Crosstalk of Li-Ion Batteries Understanding Full-Cell Evolution and Non-chemical Electrode Crosstalk of Li-Ion Batteries. Joule *2*, 1146–1159.

18. Siegel, J.B., Lin, X., Stefanopoulou, A.G., Hussey, D.S., Jacobson, D.L., and Gorsich, D. (2011). Neutron Imaging of Lithium Concentration in LFP Pouch Cell Battery. J. Electrochem. Soc. *158*, A523.

19. Schweidler, S., De Biasi, L., Schiele, A., Hartmann, P., Brezesinski, T., and Janek, J. (2018). Volume Changes of Graphite Anodes Revisited: A Combined Operando X-ray Diffraction and in Situ Pressure Analysis Study. J. Phys. Chem. C *122*, 8829–8835.

20. Ohzuku, T., Iwakoshi, Y., and Sawai, K. (1993). Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell. J. Electrochem. Soc. *140*, 2490–2498.

21. Qian, X., Gu, X., Dresselhaus, M.S., and Yang, R. (2016). Anisotropic Tuning of Graphite Thermal Conductivity by Lithium Intercalation. J. Phys. Chem. Lett. *7*, 4744–4750.

22. Wei, Z., Yang, F., Bi, K., Yang, J., and Chen, Y. (2018). Tunable Anisotropic Thermal Conductivity and Elastic Properties in Intercalated Graphite via Lithium Ions. J. Phys. Chem. C *122*, 1447–1455.

23. Feng, T., O'Hara, A., and Pantelides, S.T. (2020). Quantum prediction of ultra-low thermal conductivity in lithium intercalation materials. Nano Energy *75*, 104916.

24. Kang, J.S., Ke, M., and Hu, Y. (2017). Ionic Intercalation in Two-Dimensional van der Waals Materials: In Situ Characterization and Electrochemical Control of the Anisotropic Thermal Conductivity of Black Phosphorus. Nano Lett. *17*, 1431–1438.

25. Zhu, G., Liu, J., Zheng, Q., Zhang, R., Li, D., Banerjee, D., and Cahill, D.G. (2016). Tuning thermal conductivity in molybdenum disulfide by electrochemical intercalation. Nat. Commun. *7*, 1–9.

26. Cho, J., Losego, M.D., Zhang, H.G., Kim, H., Zuo, J., Petrov, I., Cahill, D.G., and Braun, P. V. (2014). Electrochemically tunable thermal conductivity of lithium cobalt oxide. Nat. Commun. *5*, 2–7.

27. Lu, Q., Huberman, S., Zhang, H., Song, Q., Wang, J., Vardar, G., Hunt, A., Waluyo, I., Chen, G., and Yildiz, B. (2020). Bi-directional tuning of thermal transport in SrCoOx with

electrochemically induced phase transitions. Nat. Mater. *19*, 655–662.

28. Lubner, S.D., Kaur, S., Fu, Y., Battaglia, V., and Prasher, R.S. (2020). Identification and characterization of the dominant thermal resistance in lithium-ion batteries using operando 3-omega sensors. J. Appl. Phys. *127*, 105104.

29. Cahill, D.G. (1990). Thermal conductivity measurement from 30 to 750 K: The 3ω method. Rev. Sci. Instrum. *61*, 802–808.

30. Dames, C., and Chen, G. (2005). 1Ω, 2Ω, and 3Ω Methods for Measurements of Thermal Properties. Rev. Sci. Instrum. *76*, 1–14.

31. Tong, T., and Majumdar, A. (2006). Reexamining the 3-omega technique for thin film thermal characterization. Rev. Sci. Instrum. *77*.

32. Borca-Tasciuc, T., Kumar, A.R., and Chen, G. (2001). Data reduction in 3ω method for thin-film thermal conductivity determination. Rev. Sci. Instrum. *72*, 2139–2147.

33. Bauer, M.L., and Norris, P.M. (2014). General bidirectional thermal characterization via the 3ω technique. Rev. Sci. Instrum. *85*.

34. Doyle, M., Fuller, T.F., and Newman, J. (1993). Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell. J. Electrochem. Soc. *140*, 1526–1533.

35. Thomas, K.., Newman, J., and Darling, R.. (2002). Advances in Li ion Batteries.

36. John Newman, K.E.T.-A., Newman, J., and Thomas, K.E. (2004). Electrochemical systems 3rd ed. (John Wiley & Sons, Inc.).

37. Mityushov, E.A., Adamesku, R.A., and Gel'd, P. V. (1984). Relation between kinetic properties of single crystals and of oriented polycrystalline materials. J. Eng. Phys. *47*, 1052–1056.

38. Bruggeman, D.A.G. (1937). Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. III. Die elastischen Konstanten der quasiisotropen Mischkörper aus isotropen Substanzen. Ann. Phys. *421*, 160–178.

39. Yang, F., Ikeda, T., Snyder, G.J., and Dames, C. (2010). Effective thermal conductivity of polycrystalline materials with randomly oriented superlattice grains. J. Appl. Phys. *108*, 1–12.

40. Wang, B.X., Zhou, L.P., and Peng, X.F. (2003). A fractal model for predicting the effective thermal conductivity of liquid with suspension of nanoparticles. Int. J. Heat Mass Transf. *46*, 2665–2672.

41. Higa, K., Wu, S.-L., Parkinson, D.Y., Fu, Y., Ferreira, S., Battaglia, V., and Srinivasan, V. (2017). Comparing Macroscale and Microscale Simulations of Porous Battery Electrodes. J. Electrochem. Soc. *164*, E3473–E3488.

42. Paul, P.P., McShane, E.J., Colclasure, A.M., Balsara, N., Brown, D.E., Cao, C., Chen, B.R., Chinnam, P.R., Cui, Y., Dufek, E.J., et al. (2021). A Review of Existing and Emerging Methods for Lithium Detection and Characterization in Li-Ion and Li-Metal Batteries. Adv. Energy Mater.

43. Gao, T., Han, Y., Fraggedakis, D., Das, S., Zhou, T., Yeh, C.N., Xu, S., Chueh, W.C., Li, J., and Bazant, M.Z. (2021). Interplay of Lithium Intercalation and Plating on a Single Graphite Particle. Joule *5*, 393–414.

44. Waldmann, T., Hogg, B.I., and Wohlfahrt-Mehrens, M. (2018). Li plating as unwanted side reaction in commercial Li-ion cells – A review. J. Power Sources *384*, 107–124.

45. Liu, Q., Du, C., Shen, B., Zuo, P., Cheng, X., Ma, Y., Yin, G., and Gao, Y. (2016). Understanding undesirable anode lithium plating issues in lithium-ion batteries. RSC Adv. *6*, 88683–88700.

46. Feldman 1999 - Algorithm for solutions of the thermal diffusion equation in a stratified medium with a modulated heating source.pdf.

Figure 1. Concept of thermal wave sensing for lithium detection
(A) Schematic of the lattice expansion due to intercalation of Li$^+$ ions and its impact on the thermal conductivity of common electrode materials (Li$_x$C$_6$[21,22] and Li$_x$TMO$_2$[23,26]).
(B) Frequency-dependent thermal waves for measuring the local thermal conductivity as a function of depth. The thermally probed region is controlled by adjusting the thermal wave frequency, *e.g.*, high frequencies are sensitive to the properties of layers near the sensor and lower frequencies for layers farther away. The measured spatial distribution of thermal conductivity in the electrode can be converted to the lithium concentration distribution based on a calibrated relationship between the thermal conductivity and the amount of intercalated Li$^+$ ions.
(C) A schematic of a NMC532/graphite LIB cell with embedded sensor. The sensor generates thermal waves over a range of frequencies and the measured thermal wave signal contains information about the spatial distribution of Li$^+$ ions throughout the thickness of the graphite electrode. The anode is divided into multiple imaginary sub-layers for thermal wave analysis.
(D) The capacity retention of cells with and without the sensor. The cells were cycled at 1C after formation, and show nearly the same performance in 100 cycles.

Figure 2. Calibration of k_{anode} vs. SOC at 0.1C
(A) Representative raw $V_{3\omega}(\omega)$ data (normalized to $V_{3\omega}(\omega)$ at SOC = 0%), plotted for different SOCs. The increase of $V_{3\omega}$ with SOC indicates the decreased effective k of the cell stack. The peaks (~10 Hz to ~100 Hz) occur at the frequencies with greatest sensitivity to k_{anode}, implying that the decrease of k_{anode} dominates the change.
(B) k_{anode} vs. SOC calibration, measured using 0.1C charging rates for two separate samples.
(C) Representative SEM image of samples' graphite anode particles.
(D) The effective thermal conductivity of lithiated graphite particles extracted from our calibration measurements. The measured $k_p/k_{p,ref}$ vs. x agrees qualitatively with the trend calculated by the analytical solution[37] and MD simulation results.[21,22]

Figure 3. Lithium distribution from the measured k_{anode} profile
(A) Raw $V_{3\omega}(\omega)$ data after 1C charging to three different bulk/average SOCs normalized to raw data after 0.1C charging to the same SOCs. The peaks (~10 Hz to ~100 Hz) occur at the frequencies with greatest sensitivity to k_{anode}, implying that changes in the Li distribution within the anode dominate the change in data with different charge rates.
(B) The k_{anode} profile across the anode. The surface region of the anode ($z = 0$; adjacent to the separator) has a lower thermal conductivity than the region near the Cu CC ($z = 70$ μm), corresponding to a higher degree of lithiation near the surface.
(C) The local SOC distribution calculated from the measured k_{anode} distribution. As the cell is charged to higher bulk SOCs (from 30% to 70%) by 1C, a steep concentration gradient develops and the local SOC deviates significantly from the bulk SOC.
(D-G) *Ex-situ* optical images of pristine (SOC = 0) and lithiated (SOC = 70%) graphite anode show how in the cell charged at 1C, the anode region near the separator has a much higher degree of lithiation (*i.e.*, more gold color) than the regions farther away (cross-section view (D) and top views (E-G)). The same CC and electrode are used in these cells. For electrodes in panel (D), the left side is adjacent to the separator and the right side is adjacent to the current collector. The scale bar in panel (D) is 50 μm, and those in panels (E-G) are 100 μm.

Figure 4. Lithium distribution from our sensor and prior studies using EDXRD
(A and B) The same P2D model is used to predict the lithium distribution for our anodes (A) and those used in an EDXRD measurement from the literature (B).[7] Identical parameters are used for both simulations except for the different coating thicknesses. Shaded areas represent predictions from the simulation results, and points represent experimental measurements from (A) our technique and (B) the previous studies using EDXRD[7]. The shaded modeling results are due to the range of tortuosity assumed (see Table S3).