

Temperature-Dependent Chemical and Physical Microstructure of Li Metal Anodes Revealed through Synchrotron-Based Imaging Techniques

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The Li metal anode has been long sought-after for application in Li metal batteries due to its high specific capacity (3860 mAh g^{-1}) and low electrochemical potential (-3.04 V vs the standard hydrogen electrode). Nevertheless, the behavior of Li metal in different environments has been scarcely reported. Herein, the temperature-dependent behavior of Li metal anodes in carbonate electrolyte from the micro- to macroscales are explored with advanced synchrotron-based characterization techniques such as X-ray computed tomography and energy-dependent X-ray fluorescence mapping. The importance of testing methodology is exemplified, and the electrochemical behavior and failure modes of Li anodes cycled at different temperatures are discussed. Moreover, the origin of cycling performance at different temperatures is identified through analysis of Coulombic efficiencies, surface morphology, and the chemical composition of the solid electrolyte interphase in quasi-3D space with energy-dependent X-ray fluorescence mappings coupled with micro-X-ray absorption near edge structure. This work provides new characterization methods for Li metal anodes and serves as an important basis toward the understanding of their electrochemical behavior in carbonate electrolytes at different temperatures.

Li metal is an ideal anode candidate for next-generation battery systems due to its high specific capacity, low electrochemical potential, and light weight. However, the use of Li metal anodes has been hindered by its high chemical reactivity toward liquid electrolytes, unstable solid electrolyte interphase (SEI), large volume fluctuations, and dendrite formation.^[1–4] In recent years, several strategies have been proposed to combat the issues associated with Li anodes and to stabilize the SEI layer. Methods including the design of 3D current collectors, electrolyte modification, and thin-film coatings have been shown

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to significantly improve the stability and cycle life of Li metal anodes.^[5–13] While some success has been realized through the use of various protection techniques, almost all of the testing has been done at room temperature conditions. Moreover, the Li metal anode is a critical component of several next-generation battery systems including Li-S, Li-O2, and solid-state batteries. The interactions between Li metal and the various electrolytes in these systems is critical to their performance and several factors can affect the chemical and physical phenomena observed during electrochemical cycling. Parameters such as the type of Li salt, electrolyte composition, and current collectors have been shown to impact SEI formation and Li nucleation morphology.^[14-16] Several studies have set out to observe the relationships between electrode geometry, current densities, voltage profiles, and the plating/stripping behavior of Li anodes at room temperature.^[17-21] However, until recently, there

has been a lack of fundamental understanding on the electrochemical behavior of Li metal anodes in different temperature regimes.^[22–26] For the practical application of Li metal batteries, the system will need to function in both high and low temperature environments. Thus, it is important to take a step back and understand the fundamental kinetic, thermodynamic, and physical behavior of Li metal anodes under these conditions before proper protection techniques can be designed to stabilize the Li surface.

Recently, Cui and co-workers explored the temperaturedependent behavior of Li metal in ether-based electrolytes.^[22,23] Surprisingly, it was found that the electrodeposition of Li on a Cu surface could exhibit higher Coulombic efficiency (CE) at elevated temperatures due to the stabilizing organic/inorganic bilayer formed from electrolyte decomposition. Although the chemical reactivity of the electrolyte is expected to increase at high temperatures, it was revealed by cryogenic electron microscopy that the formed SEI consisted of a polymeric inner layer with a crystalline Li_2O exterior, which can improve CE. Cui and co-workers hypothesized that the organic components of the SEI formed at 20 °C are partially soluble in the electrolyte, resulting in poor anode passivation whereas the thicker and more ordered SEI formed at 60 °C could act as a more mechanically robust and stabilizing layer.

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Carbonate-based electrolytes also serve as an important system for high voltage LMBs.^[26] From an electrochemical standpoint, carbonate electrolyte components have a significantly higher electrochemical stability window compared to their ether counterparts.^[27] Thus, while ether electrolyte may be suitable for Li metal systems such as Li-S, which have low voltage cathodes, all 4 V class cathodes such as LiCoO2 and LiNi_xMn_yCo₂O₂ are incompatible with ether-based systems and require carbonate electrolytes in order to achieve adequate cycle life and stability. Nevertheless, the behavior of Li metal anodes in carbonate electrolyte can be expected to differ significantly from ether and ester-based electrolytes.^[27] Carbonate electrolyte components are thermodynamically unstable against Li metal, more so than their ether counterparts, and suffer from significantly lower CE during electrochemical cycling.^[28] Li metal in carbonate systems corrode due to both chemical and electrochemical reactivity, which can affect cycle life, deposition morphology, and SEI formation. While the recent emergence of Li metal anodes and the development of protection techniques for them has given rise to many studies that utilize carbonatebased electrolytes,^[8,29] there still remains many questions about the electrochemical behavior of Li metal anodes when they deviate from room temperature testing conditions. Therefore, it is of the utmost importance to understand the fundamental effects of temperature on Li metal anodes in carbonate electrolyte and reveal the challenges in various conditions in order to better design targeted protection techniques for both high and low temperature Li metal battery applications.

In this study, we aim to elucidate the (electro)chemical behavior of Li metal in carbonate electrolyte under different thermal conditions from the micro to macroscale with advanced characterization techniques. We further highlight the importance of testing methodology and show how different methods can lead to drastically different conclusions. Different electrochemical methods are used to evaluate Li anode performance and it is shown that thin Li anodes, in contrast to the conventional Cu anodes, are required for more realistic Coulombic efficiency estimates in real Li metal batteries. We further utilize advanced synchrotron-based characterization techniques for the first time to reveal both the chemical and physical microstructure of Li metal anodes cycled under different temperatures. Using energy-dependent X-ray fluorescence (XRF) mappings, the inhomogeneous chemical composition of the SEI is visualized and is further coupled with micro-X-ray absorption near edge structure (micro-XANES) to provide nondestructive information on SEI components present on the surface and at depth. This work serves as an important basis toward a fundamental understanding of practical Li metal anodes in carbonate electrolyte systems and will provide insight for the design of future Li protection techniques.

Symmetrical cell cycling and Coulombic efficiency measurements are the most common characterization techniques used to evaluate the electrochemical performance of Li metal anodes. Throughout this study, we use a current density and capacity of 1 mA cm⁻² and 1 mAh cm⁻² since these are the most common testing conditions found in literature.^[30–36] **Figure 1**A displays the symmetrical cell cycling of Li electrodes with a thickness of ~400 μ m cycled at 0, 25, and 60 °C (referred to as 400 μ m Li||400 μ m Li). As expected, due to the differences in temperature, the overpotential increases significantly as the testing temperature decreases toward 0 °C. For the cells cvcled at 0 °C, an overpotential of ~200 mV can be observed in the initial stage of cycling (Figure 1A). In comparison, the cells cycled at 25 and 60 °C possess overpotentials of \approx 100 and 40 mV, respectively. However, as the cycling time progresses, it can be observed that the cells cycled at 60 °C begin to rapidly fail after 175 h. This finding is in contrast with the previously reported results on ether-based electrolytes, where cells cycled at 60 °C have significantly higher CE compared to those cycled at 20 °C.^[22,23] The reason for the enhanced cycling performance in ether electrolytes was attributed to the formation of a passivating SEI layer.^[22] In contrast, the chemical reactivity of carbonate components such as dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) cannot be inhibited, leading to constant decomposition of electrolyte on the Li metal surface at high temperatures. Furthermore, it has been previously reported that several of the SEI components formed are soluble in electrolyte at high temperatures, leading to continuous dissolution and reformation of the SEI.^[37]

The Li symmetric cell cycling at 25 °C exhibits the typical cycling behavior found in most reported studies. Dasgupta and co-workers thoroughly studied the plating/stripping mechanism of Li metal symmetric cells by optical microscopy and revealed the relationships between voltage profiles and physical phenomena.^[38] The gradual increase in overpotential during prolonged cycling is attributed to the formation of a thick dead Li layer, where the long and tortuous pathway for Li ion diffusion results in increased resistance. The mode of failure under these conditions are usually due to fractal short-circuits upon reaching a critical dead Li layer thickness.^[38,39] The prolonged cycle life of the symmetrical cells cycled at 25 °C compared to that observed at 60 °C is likely due to the accelerated consumption and degradation of electrolyte at high temperature as well as possible morphological effects that will be discussed later.

It is expected that lower temperatures will lead to higher overpotentials due to greater charge-transfer resistance and sluggish Li-ion-transport kinetics through the electrolyte. Moreover, the formation of dendrites at 0 °C should be much more severe compared to 25 and 60 °C according to the Sand's time model, which describes the time for the onset of Li dendrite formation due to mass transport limitations

$$\tau_{\rm Sands} = \pi D \left(\frac{C_0 e}{2J}\right)^2 \left(\frac{u_{\rm a} + u_{\rm c}}{u_{\rm a}}\right)^2 \tag{1}$$

where *D* is the diffusion coefficient, *J* is the effective electrode current density, *e* is the electronic charge, C_0 is the initial cation concentration, and u_a and u_c are the mobilities of anions and cations, respectively.^[40] Interestingly, the cycling lifetime of Li metal symmetric cells cycled at 0 °C differs greatly from the aforementioned results. While it may be expected that the Li symmetrical cells cycled at lower temperature would fail prematurely due to dendrite formation, short-circuiting is not observed for 400 μ m Li||400 μ m Li cells cycled at 0 °C. In fact, the cycling life is significantly prolonged compared to cells cycled at 25 and 60 °C, and the onset of overpotential increase







Figure 1. Electrochemical cycling of Li metal anodes at 0, 25, and 60 °C with different testing formats. A) 400 μm Li||400 μm Li cells, B) Cu||400 μm Li symmetrical cells, and C) 50 μm Li||400 μm Li cells.

is extended. It is apparent that other factors are playing a role in the cycle life.

The Li symmetrical cells were further tested at a high current density of 5 mA cm⁻² (1 mAh cm⁻² capacity) to observe any differences in the electrochemical behavior at different temperatures. It can be seen that when the current density is high, the diffusion limitation at low temperature causes significantly higher overpotentials and eventual premature failure due to short-circuits after about 35 h (Figure S1, Supporting Information). Thus at exceedingly high current densities, while parasitic side reactions may be slowed to the low temperature, dendrite growth and propagation cannot be inhibited. Meanwhile, a similar situation is observed for Li symmetrical cells cycled at 25 and 60 °C where the cycle life is shortened due to fractal short circuits, as indicated by the unstable voltage profiles. Therefore, it can be concluded that at high current densities, the Li metal anode rapidly fails due to dendrite formation regardless of the cycling temperature, and the primary difference is the large difference in initial overpotential due to changes in Li ion mobility. However, at a reasonable current density of 1 mA cm⁻², the cells fail more gradually due to dead Li build up and side reactions with electrolyte.

In order to better understand why the battery does not fail due to dendrite formation at 1 mA cm^{-2} , two types of short-circuit

tests were conducted; 1) an "unrestricted" growth-type symmetric cell with an o-ring in place of a separator and 2) continuous Li plating in symmetric cells with conventional polypropylene separators. The scenario for case (1) is displayed in Figure S2A in the Supporting Information, where the time for the cells to short-circuit due to dendrite formation in the "unrestricted" cells is in agreement with that predicted based on the Sand's time model (60 °C > 25 °C > 0 °C). In contrast, Figure S2B in the Supporting Information shows the cells using conventional polypropylene separator (restricted growth) and reveals that none of the cells short-circuit within a reasonable time frame and eventually fail due to exhaustion of the Li counter electrode. Therefore, it can be concluded that the relative trend for the effect of temperature on short-circuit time can be estimated based on the Sand's time model in cells with unrestricted growth, but in more practical cell configurations (with polypropylene separator), these models may fail to predict the effect of mechanical suppression. The driving force for Li penetration through the separator must exceed the competing mechanical suppression effects, however, under the most commonly tested conditions in literature (1 mA cm⁻², 1 mAh cm⁻²), the diffusion limitation is not enough to cause cell failure.^[41] Nevertheless, the mode of failure cannot be solely determined by symmetrical cells with thick electrodes where the



excessive Li reservoirs remove the possibility of failure due to Li consumption. While the 400 µm Li||400 µm Li symmetric cells may indicate that Li metal can actually achieve longer cycle life at 0 °C compared to 25 and 60 °C, the results of Coulombic efficiency measurements in Cull400 µm Li cells reveal a drastically different conclusion. CullLi cells are the predominant testing format for Coulombic efficiency measurements in literature and are often used to extrapolate efficiencies to real Li anodes.[31,42-44] In the case of the cell cycled at 25 °C, a Coulombic efficiency ranging between 75% and 85% can be observed before rollover at 70 cycles (Figure 1B). In contrast, the cells cycled at 0 and 60 °C both show significantly lower efficiencies from the beginning, rapidly decaying from ≈80% to ≈50% within 30 cycles. Moreover, the poor Coulombic efficiency and quick performance degradation observed in the Cull400 µm Li cells cycled at 0 °C is in stark contrast to the performance displayed in 400 µm Lill400 µm Li cells. There is a clear discrepancy in the performance of these Li metal anodes under different temperatures according to the 400 µm Li||400 µm Li and Cu||400 µm Li testing methods, and conducting one without the other may lead to incorrect assumptions about modes of failure. The performance difference between the two testing methods could possibly be attributed to the thick Li used in 400 μ m Li||400 μ m Li cells, where a large excess Li reservoir can compensate for low Coulombic efficiency and enable artificially prolonged cycle life in the absence of short circuits. However, the Coulombic efficiency measurements in Cull400 µm Li cells are dependent on Li plating and stripping on a Cu surface, and previous reports have shown that Li nucleation behavior and morphology are sensitive to substrate effects.^[45] While Cu current collectors are conventionally used for measuring the Coulombic efficiency of Li metal plating and stripping of Li-containing anodes in Li metal batteries, factors such as pit formation and subsequent cycle nucleation sites may have dramatic effects on cell efficiency. Thus, Coulombic efficiency measurements utilizing the CullLi format may not be representative of a real Li anode due to different SEI formation and plating/stripping morphology. It should be noted that the CullLi testing format may provide accurate CE results for anodefree Li batteries, but other methods of CE measurements may yield more accurate results for Li anode-containing batteries if the CE can be measured directly on a bulk Li surface.

In order to determine the real reason behind the observed differences, we have adopted a model proposed by Zhang and co-workers to measure the Coulombic efficiency of Li on a Li metal surface.^[46] This method utilizes a quasi-symmetric cell with a thin Li electrode (50 μ m) on Cu foil coupled with a thick Li counter electrode, which acts as a Li reservoir with a large excess of Li. The 50 µm Li||400 µm Li cell is then cycled under the same conditions as the 400 μ m Li||400 μ m Li cell until all of the Li is exhausted on the 50 μm Li electrode and the cell voltage rapidly increases to 1 V. From this testing method, the average Coulombic efficiency over the number of cycles to failure can be estimated in a more accurate environment compared to the Cull400 µm Li testing method. Figure 1C displays the cycling performance of the Coulombic efficiency cells with the 50 µm Lill400 µm Li cell format. Surprisingly, the trend in cycle life and Coulombic efficiency is not the same as that found in Cull400 µm Li cells and instead mirrors the cycling stability found in the 400 µm Lill400 µm Li cells. The average Coulombic

efficiencies of Li metal at 0, 25, and 60 °C are ≈85%, 79.4%, and 73.5%, respectively. It is clear that the substrate plays a critical role in cycle life and stability, especially when exposed to environments with different temperatures. The difference between Cull400 µm Li and 50 µm Lill400 µm Li Coulombic efficiency measurements highlight the need to conduct measurements on a Li metal surface in order to obtain more accurate results in a realistic environment. These results imply that the prolonged cycle life observed in 400 µm Lill400 µm Li symmetric cells with thick electrodes cycled at 0 °C is due to both an enhanced Coulombic efficiency and a lower tortuosity pathway for Li ions through the dead Li layer, as indicated by the more gradual increase in overpotential over time compared to those cycled at higher temperatures. While the initial overpotential of Li metal anodes cycled at 0 °C is higher due to poor diffusion kinetics at low temperatures, the cycle life may be enhanced if failure due to premature short-circuits can be avoided.

Electrochemical impedance spectroscopy (EIS) was used to further understand the evolution of the Li metal anodes in 400 μ m Lill400 µm Li format over the first 10 cycles at 0, 25, and 60 °C. Figure S3 in the Supporting Information depicts the Nyquist plots of the symmetrical cells after the 1st, 2nd, 3rd, 5th, 7th, and 10th cycles. Two semicircles are observed in all cells, which can be attributed to the SEI layer at the high frequency region and the charge transfer resistance in the medium frequency regime. As expected from the temperature dependency of Li ion diffusion kinetics, the overall impedance associated with the cells increases along with a decrease in testing temperature. For the case of 400 µm Li||400 µm Li cells cycled at 25 °C (Figure S3B, Supporting Information), a gradual increase in the SEI resistance can be observed along with a subtle change in charge transfer resistance. The relative change in SEI resistance from the 2nd to 10th cycle is even more pronounced for cells cycled at 60 °C, which can be attributed to the inability of Li metal to form a stable interphase in carbonate electrolyte at elevated temperatures. It is interesting to note that the SEI and charge transfer resistance after the 1st cycle is initially greater than that found in subsequent cycles, possibly caused by the dissolution and re-formation of SEI components formed through chemical reactions after the initial resting period (6 h). The Nyquist plots of 400 µm Lill400 µm Li cells cycled at 0 °C display very different characteristics with the semicircle attributed to charge transfer resistance being reduced significantly over the initial 10 cycles (Figure S3A, Supporting Information). Moreover, the SEI resistance, while larger than that found at 25 and 60 °C, appears to be more stable and undergoes little change in the initial cycling period. The decrease in charge transfer resistance may be due to the formation of high surface area dendrites, which lower the overall impedance.

The nucleation and growth of Li metal is a critical factor affecting the overall electrochemical performance and Coulombic efficiency of the battery system. **Figure 2**A–K displays scanning electron microscopy (SEM) images of Li metal plating on a bulk Li surface at 0, 25, and 60 °C for different charging capacities (0.1–1 mAh cm⁻²). We identify four primary stages of growth applicable to all temperature testing conditions:

1) Nucleation: In an ideal system, the initial stages of Li plating are expected to follow the classical model according to the following equation

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$$r_{\rm crit} = 2\gamma V_{\rm m} / F |\eta_n| \tag{2}$$

where $r_{\rm crit}$ is the critical nuclei radius, γ is the surface energy of the Li–electrolyte interface, V_m is the molar volume of Li, F is Faraday's constant, and $\eta_{\rm n}$ is the nucleation overpotential. Thus, an increase in overpotential (lower temperature) is expected to lead to smaller nuclei formation. In the early stages of Li plating (0.1 mAh cm⁻²), there are subtle differences in Li deposit morphology that can be identified (Figure 2A,E,I). At the microlevel, it can be observed at 0 and 25 °C that dendritic-like morphological features form sporadically on the Li surface. From the macroscopic level, SEM images reveal fewer island features at low temperature (Figure S4A, Supporting Information) however those present are larger in size compared to the Li deposition at 25 °C (Figure S4E, Supporting Information). In contrast, at 60 °C, the initial nucleation stage gives rise to a combination of smaller rod-type and particle-like morphologies with irregular shapes in addition to inhomogeneous island deposition with respect to size and location (Figure 2I and Figure S4I, Supporting Information). The irregular deposition at 60 °C is believed to be highly influenced by the instability of the SEI, which is supported by the EIS results. From an electrochemical standpoint, it is expected that higher overpotentials should result in smaller nuclei due to slower diffusion kinetics. However, other factors such as chemical reactivity, homogeneity, and composition of the nucleation surface are not taken into consideration and thus actual observations may deviate greatly from theoretical predictions. In particular, carbonate-based electrolytes are significantly less stable against Li metal compared to etherbased electrolytes, potentially leading to nonideal conditions. Moreover, the traditional nucleation theory does not take into consideration the activity of the nucleation sites after the initial plating, which may vary from site-to-site due to localized differences in charge transfer kinetics. Thus, a careful interplay between classical theory and chemical/temperature-dependent effects can lead to different nucleation phenomena.

2) Densification: While previous reports have focused on the nucleation of Li metal in different systems at the nanolevel,^[45,47] few studies have looked at the subsequent stages of Li deposition. We find that after the initial nucleation stage, a densification process occurs. Early stages of Li deposition usually occur in a direction perpendicular to the bulk Li surface due to the kinetics and mass transport of Li ions directed toward the electrode. Dendrite formation typically occurs due to the formation of concentration gradients at the surface and a resulting Li ion depletion zone caused by sluggish transport kinetics, leading to dendrite propagation in an attempt to instigate charge neutrality.^[48] Nevertheless, for sufficiently

low current densities, the dendrite propagation through the separator can be inhibited due to effects such as stack pressure, small pore size, and tortuous pathways. Thus, upon reaching this barrier, we find that Li begins to grow in the void spaces initially formed during the nucleation stage until a densified structure is formed, as seen after plating of Li to 0.25 mAh cm⁻² (Figure 2B,F,J). Figure S5 in the Supporting Information depicts a lower magnification SEM image of Li metal at this stage of plating where clearly defined dense regions are surrounded by porous dendritic Li. While many studies may observe Li plating in an "unrestricted" growthtype environment, the lack of pressure can cause significant effects on dendrite propagation or morphology. With coin cells sealed under realistic crimping pressures, the force is enough to inhibit the dendrite penetration through the separator and instead leads to infill of the unoccupied void space before growth in a more unrestricted lateral direction.

- Island growth: The next stage of growth involves lateral 3) propagation of Li deposition stemming from the initial nuclei sites. As the densified Li deposits begin to fill, the active surface area decreases and the Li flux begins to cause Li deposition parallel to the bulk Li surface leading to growth of Li islands, as seen in Figure S4C,G,K in the Supporting Information. It can be inferred from the lateral growth that the energy barrier associated with subsequent Li deposition on these new Li islands is less than that required to form new nucleation sites. Dendrite formation at 0 and 25 °C begin to propagate laterally, repeating the cycle of densification and continue to grow outward from the center of the Li islands. At the micro-level, the Li metal anodes cycled at 25 and 60 °C begins to form globular features of irregular size and shape, with those formed at 60 °C being the largest (Figure 2G,K).
- 4) Convergence: The final stage of Li deposition involves the convergence of macroscopic Li islands. Island growth progresses to the point where the spatial distribution of Li deposits converge to form interconnected networks (Figure S4D,H,L, Supporting Information). At the macroscopic level, the initial Li deposition at 25 °C has the most uniform Li coverage while that observed at 0 °C has more active Li islands of smaller size, however it tends to have areas in which few islands have grown and the uncycled Li surface is exposed. The Li islands observed at 60 °C are more inhomogeneous and randomly dispersed with several islands having nonradial geometries, suggesting that the chemical reactivity of carbonate electrolyte at high temperature plays a role in directing macroscopic growth patterns. The region of island convergence at the microscale can be observed in Figure 2D,H,L for 0, 25, and 60 °C, respectively. At 0 °C, small dendritic Li features can be seen to converge until the merging zone is densified. A similar phenomenon is observed for the case of 25 °C however larger particles are identified. In contrast, the Li morphology at 60 °C differs significantly from the other cases and large rod-shaped particles of varying size are packed together across a poorly defined interface. Given the relatively large particle size of the Li deposits at 60 °C, it is likely that the poor Coulombic efficiency observed in Li metal anodes at this temperature is caused by both SEI formation as well as large isolated Li deposits that become electrochemically inactive in subsequent cycles.

Further SEM images of the Li anodes after 30 cycles reveal the long-term effects of cycling Li in carbonate electrolytes under different temperature conditions. The exterior surface of Li metal after 30 cycles at 0 °C appears to be microporous with Li filaments seen in some regions (Figure S6A, Supporting Information). In contrast, the cell cycled at 25 °C possesses large cracks throughout the surface with large granular-like deposits that are interconnected and flattened at the outermost surface (Figure S6B, Supporting Information). At 60 °C, the Li surface is rough and consists of particles of irregular shape and size (Figure S6C, Supporting Information). It quickly becomes apparent that the influence of temperature has a dramatic effect on not only the initial nucleation morphology, but can also affect the long-term plating/stripping behavior. It is possible that some of the large particles observed at 60 °C are electronically isolated from the electroactive Li surface due to thick SEI layers caused by electrolyte decomposition, which suggests that the poor Coulombic efficiency of Li cycled at elevated temperature is attributed to the formation of inactive Li deposits rather than purely from chemical reactivity and continuous SEI formation.

While ex situ SEM imaging can provide information on surface morphology at different stages of cycle life, several other factors such as cell disassembly and exposure to ambient environments during sample transfer can have adverse effects on the surface.^[47] Observation of Li metal in its native environment is more practical and can reveal information that cannot be obtain by ex situ analysis. There have been several publications recently on the use of in situ SEM to observe dendrite growth and morphology in solid-state systems with sulfide, oxide, or polymer-based electrolytes.^[49-52] The nonvolatile nature of these systems allows for direct observation of the physical changes of the battery system during electrochemical cycling. Nevertheless, the high vapor pressure and volatility of carbonate and ether electrolytes make in situ observation unfeasible without highly specialized cell designs or the use of ionic liquids. Alternatively, synchrotron X-ray computed tomography is a nondestructive technique that can be used to visualize the evolution of morphological features in 3D space. Typically, X-ray tomography utilizes the absorption contrast between different materials to identify different morphological features. However, the hard X-rays required to penetrate through the cell for imaging (19 keV in this case) leads to low absorption contrast between low Z elements such as Li, C, and O. Nevertheless, the phase contrast of materials can enable visualization of Li metal and differentiation between its reacted phases.[53,54] Phasecontrast imaging can be achieved in-line using a coherent synchrotron X-ray source-a technique known as propagation-based phase contrast imaging. Here, we observe Li metal anodes in LillLi cells at different stages of cycling at 0, 25, and 60 °C to reveal the influence of temperature on macroscopic morphology evolution in 3D space through nondestructive characterization. The cell configuration used for characterization is displayed in Figure S7 in the Supporting Information. Figure 3A-C shows the gradual formation of cycled Li layers after 10 and 20 cycles where the highlighted blue, green, and red regions correspond to cycled Li deposits at 0, 25, and 60 °C, respectively. The same cells were used for each stage of imaging. The "cycled" Li layer possesses different phase contrast than the



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Figure 3. Synchrotron X-ray computed tomography images of Li||Li symmetrical cells cycled at 0, 25, and 60 °C. A) Li||Li cell in the pristine state and after 10 and 20 cycles at 25 °C. C) Li||Li cell in the pristine state and after 10 and 20 cycles at 25 °C. C) Li||Li cell in the pristine state and after 10 and 20 cycles at 60 °C. Reconstructed images are taken from representative regions of the cells. Highlighted regions with blue, green, and red color represent the cycled Li layers at 0, 25, and 60 °C, respectively.

uncycled bulk Li due to incorporation of decomposed organic electrolyte species. It should be noted that the dead Li cannot be directly differentiated from the cycled Li due to similar phase contrast caused by SEI reaction products encapsulating the Li deposits. Nevertheless, distinct differences can be observed between cells cycled ten times at a current density and capacity of 1 mA cm⁻² and 1 mAh cm⁻², respectively. Uneven Li deposits can be found dispersed throughout the symmetrical cells after 10 cycles at 0 and 60 °C. On average, larger island formations are found at 60 °C whereas the cell cycled at 0 °C cell displays regions of converged islands with a thinner cycled Li layer. In contrast, the cell cycled at 25 °C shows a much more uniform cycled Li layer with more pronounced island-like Li deposits dwelling in large-scale pits. There is a clear difference in macroscopic morphology when cycled at different temperatures, even in the subsurface regions, which could not be observed through traditional SEM characterization.

The cycled Li layers begin to rapidly grow and recognizable features become more pronounced after 20 cycles. In the case of cells cycled at 60 °C (Figure 3C), the cycled Li layer is unevenly formed throughout the Li metal surface with irregular deposit size and shapes. This observation is in line with the belief that the chemical reactivity of carbonate electrolytes at high temperature causes destabilization of the SEI and subsequent dissolution of soluble components, leading to inhomogeneous Li plating/stripping. Additionally, the thickness of the cycled Li layer appears to be less than that observed in the cell cycled at 25 °C. Moreover, taking into consideration the thickness of these layers, the longer cycle life of Li anodes in symmetrical cells at 25 °C, and the fact that they typically fail due to dead Li formation, it is probable the cells cycled at 60 °C do not simply fail due to the formation of a thick and tortuous dead Li layer but also degradation of the electrolyte itself. The cell cycled at 25 °C for 20 cycles (Figure 3B) displays distinct large-scale pit features (≈150 µm wide) where the Li is seen to redeposit. The homogeneous layer formed at 25 °C and the growth of macroscopic pits indicate the possibility of the electroactive Li preferentially plating/stripping along the edge regions of preformed pits underneath the cycled layer, which could not be observed by other methods such as SEM. In contrast, the cell cycled at 0 °C (Figure 3A) shows a thinner cycled Li layer that is not as homogeneous as its 25 °C counterpart. Moreover, the large-scale pit features and Li islands are not observed, indicating different cycling behavior at 0 °C. Upon closer inspection, small-scale pits can be seen on a similar scale to that found for the cell cycled at 25 °C for 10 cycles, which may suggest Li metal cycled at 0 °C will eventually form larger pits with extended cycling.

The layer-by-layer morphological differences over extended regions of interest can also be observed in Movies S1–S3 in the Supporting Information, which show the top-down view of reconstructed layers of Li metal after 20 cycles at 0, 25, and 60 °C, respectively. The movies depict $\approx 6.1 \times 4.4$ mm areas of the electrodes and display individual layers of the tomograms with 3.6 µm pixel size as they progress through the bulk Li layer, through the cycled Li layer, followed by the separator layer at a rate of 4 frames per second. Movie S1 in the Supporting Information of the Li metal cycled at 0 °C reveals irregularly shaped Li islands submerged beneath a relatively smooth and compact cycled Li layer. In contrast, the cell cycled at 25 °C



shows well defined "tree-like" growth where the initial Li deposition sites grow outward and expand until they converge and form a smooth film at the cycled Li-separator interface (Movie S2, Supporting Information). The island shape, size, and dispersion are more uniform at 25 °C compared to that found at 0 °C. At an elevated temperature of 60 °C, the Li metal deposition morphology appears quite different and porous in nature with localized regions of inhomogeneous Li deposits (Movie S3, Supporting Information). It is possible that the chemical reactivity of Li toward the carbonate electrolyte leads to the gradual consumption of the inactive Li on the surface leading to the formation of porous surface features compared to the more smooth interface found between the cycled Li and separator layers in cells cycled at 25 and 0 °C. Further investigation into the density and porosity of these cycled Li layers should be considered to gain a better understanding of mass transport to the electroactive surfaces.

Energy-dependent XRF mapping is a chemically selective spectroscopic imaging technique that exploits unique absorption features specific to different chemical species in XANES spectra. The incident energy used for XRF mapping can be fine-tuned to enable selective excitation of core level electrons to unoccupied orbitals, subsequently inducing fluorescence attributed to different chemical species if the incident energy resonates around "fingerprint" spectral features. By controlling the excitation energy resonance around certain near-edge features, fluorescence mapping of the SEI components with chemical sensitivity can be obtained. Upon mapping at different energies, unique features or hotspot differences between the maps can be attributed to different chemical species. For the first time, we have exemplified energy-dependent X-ray fluorescence resonance mapping coupled with micro-XANES to study the Li metal anode. All electrodes were transferred to the beamline without exposure to air though the use of an anaerobic sample holder (Figure S8, Supporting Information). The F references used for this work are displayed in Figure S9 in the Supporting Information. Figure 4A-C shows XRF mappings at 691.3 and 694.0 eV, which are associated with energies below and at the peak of the F 1s \rightarrow unoccupied 2p state whiteline transition of LiF, respectively. The mappings at 694.0 eV display hotspots associated with decomposition of Li salts and the formation of LiF. In all mappings, the intensity of the fluorescence counts was normalized to the maximum counts found at either energy where yellow color represents high counts and blue corresponds to low counts. For the case of Li metal after 10 cycles at 0 °C, very distinct regions of LiF hotspots can be observed in the mapping at 694.0 eV (Figure 4A). It can be seen the LiF formation in the SEI is inhomogeneously dispersed throughout the surface, and the localized hotspots may be a result of regions with severe dendrite growth or high surface area Li deposits. The mapping at 691.3 eV has significantly weaker overall counts, which can be attributed to the formation of other fluorinated species. It is possible that some reduced PF_x or more complex PO_xF_y -type bonding structures are formed as a result of other side reactions between SEI components.^[55] The XRF mappings of Li metal cycled at 25 and 60 °C tell different stories than their 0 °C counterpart. At 25 °C, the LiF distribution is found to be more homogeneous than the cell cycled at 0 °C, however, there are still small regions where the distribution of fluoride species differs (Figure 4B). Particularly in the bottom region of the XRF

mappings at 25 °C, areas of low F counts appearing as dark blue islands in the XRF map taken at 691.3 eV suggest the lack of reduced PF_x or PO_xF_y -type fluorine structures. Nevertheless, the same regions in the mappings at 694.0 eV clearly show the excitation and fluorescence of F-containing species specific to this energy level. At 60 °C, there are few differences in the spatial distribution of different F species, but the overall F distribution appears to be more even compared to the Li metal anodes cycled at lower temperature. This suggests that the chemical decomposition of carbonate electrolyte at 60 °C occurs more readily than at lower temperatures and more F-containing species are present in the SEI, however, it may not be beneficial toward the overall electrochemical performance since the reaction rate and consumption of Li salts may lead to faster cell failure. The higher F counts in the XRF maps at 60 °C further supports the findings of poor Coulombic efficiency at high temperatures and degradation of electrolyte as likely failure modes for high temperature Li metal anodes in carbonate electrolyte.

To better understand the SEI composition of Li metal cycled at 0, 25, and 60 °C, micro-XANES spectroscopy was employed in multiple regions to explore the electronic structure of fluorine- and oxygen-containing species. Moreover, measurements in total electron yield (TEY) and fluorescence yield (FLY) modes were utilized to observe differences in composition in the nearsurface region (2-10 nm) and the bulk, respectively, of each point. The coupling of energy-dependent XRF mapping with TEY and FLY mode micro-XANES provides the opportunity to explore the physical location of different SEI components on a large scale along with the ability to provide depth-sensitive information in a nondestructive manner, unlike tradition X-ray photoelectron spectroscopy characterization methods. The fluorine species found in the SEI should arise from the decomposition of the LiPF₆ salt—the sole fluorine component in the tested electrolyte. The primary decomposition product of LiPF₆ is LiF and PF₅, which may undergo further reaction to form further reduced PF_x , $Li_x PO_y F_z$, $PO_x F_y$, or small amounts of fluorinated hydrocarbons under certain conditions.^[55] Figure 4D displays the F K-edge XANES in regions I and II of Li metal after 10 cycles at 0 °C with a beam size of \approx 20 µm. Region I is within a region of the SEI that is representative of the bulk distribution, as seen in the XRF maps in Figure 4A. The TEY and FLY spectra share several common spectral features with key peak at 693.9 and 702 eV likely associated with a mixture of PF_xO_v and LiF, with LiF found to be more present in the near surface region.^[56] Further absorption features are observed at energies lower than that of LiF and at 695.3 eV, and may be attributed to other salt reduction products. In contrast, region II is in the center of the hotspot seen in the energy-dependent XRF mappings and confirms that the region is primarily LiF, as confirmed by both TEY and FLY measurements. The F K-edge spectra of region III is not shown as the F content was too low to accurately determine composition. In contrast, Li metal cycled at 25 °C yields different composition in both the surface and bulk compared to that found in Li cycled at 0 °C. Figure 4E shows that the F species in the SEI are homogeneous at all depths with little variation between the tested regions. The F K-edge spectra indicate the F species are primarily LiF with a small contribution from another species as indicated by the broadening of the edge jump region located at 692.2 eV. Upon increasing the cycling temperature to 60 °C the SEI is found









Figure 4. Synchrotron energy-dependent XRF mappings and micro-XANES measurements of the Li metal SEI at 0, 25, and 60 °C. XRF mappings of the Li metal surface after 10 cycles at A) 0 °C, B) 25 °C, and C) 60 °C with incident energies of 691.3 and 694.0 eV. D–F) F K-edge micro-XANES at regions I–III of Li metal cycled at 0, 25, and 60 °C, respectively. G–I) O K-edge micro-XANES at regions I–III of Li metal cycled at 0, 25, and 60 °C, respectively.

to change once again to form SEI layers of different but still homogeneous composition. Regions I–III of Figure 4F present spectral features similar to that observed in region I of Li cycled at 0 °C, suggesting that certain electrolyte components may have preferential decomposition products at both high and low temperatures. However, unlike Li cycled at 0 °C, the homogeneity of the reaction products may be attributed to the high chemical reactivity of the carbonate electrolyte and lower activation barrier toward decomposition. The oxygen K-edge spectra taken over three separate regions further reveal the unique composition and distribution of organic and inorganic SEI components at the micro-level. Previous reports on SEI composition include oxygenated species such as Li₂O, Li₂CO₃, LiOH, and various alkyl Li components.^[4,37,57] Key fingerprint features can be observed in the XANES spectra at \approx 531.3, 532.3, 533.8, 536.6, 539.3, and 543.5 eV corresponding to various transitions from the O 1s to unoccupied 2p states. In all cases where Li metal is cycled at 0, 25, or 60 °C, the resulting O K-edge XANES



reveals the presence of many of these components, however, the spatial distribution and relative quantity of the species differs greatly. Li_2CO_3 appears to be the predominant component with the relative ratio of other species differing depending on operating temperature.

O K-edge XANES of Li metal cycled a 60 °C at various points reveals the presence of various organic and inorganic species within the surface and bulk (Figure 4I). The well-defined peak present at 533.8 eV is related to the π^* transition of Li₂CO₃. The relative density of states associated with this transition is found to be more prominent in the FLY signals compared to the TEY signals in the corresponding regions, indicating the inorganic Li₂CO₃ species is preferentially formed on the innermost SEI or in SEI layers found deeper in the dead Li layer. Moreover, the peak at 531.3 eV can be attributed to the σ^* transition of C-O-H-type molecular structures from organic polymeric species formed in the SEI layer.^[57,58] Regions I and III show strong features associates with this type of structure present in the near surface region (TEY) with diminishing contribution from these species in the bulk at the same points (FLY). The feature observed at 536.6 eV may also be related to Li-O-R structures with a similar bonding environment, providing more evidence that at 60 °C, lithiated organic oxygen species are formed more prevalently in the surface SEI compared to at depth. Furthermore, the presence of LiOH is found throughout the surface and subsurface. Identification of Li2O with both TEY and FLY measurements is convoluted by the coexistence of other inorganic oxygen species such as Li₂CO₃, which have nearly overlapping spectral features, nevertheless, the spectral feature at 544.5 eV may be used to distinguish the two inorganic compounds.^[57,58] Broadening of the peak at 533.8 eV may also be a result of Li₂O contributions and alkyl carbonate species.

The spectral features within the O K-edge XANES of the Li metal anode cycled at 0 °C display clear variations between composition in the near-surface and subsurface SEI layers (Figure 4G). A broad peak at 544.5 eV is present in all the three regions on the surface, as indicated by the TEY measurements. However, the fluorescence from the electronic transitions associated with this peak is attenuated in the FLY signals, suggesting that Li₂O is found more prevalent in the near surface region rather than within the bulk dead Li layers. Moreover, the peak at 533.8 eV attributed to the π^{\star} (C=O) orbital of Li₂CO₃ is more distinct in the FLY spectra compared to the TEY spectra, which indicates the preferential formation of carbonates at depth in the SEI. Other organic oxygen-containing species such as polyolefins are not as prominent at 0 °C with only small amounts being observed on the surface of region I. However, unlike Li metal cycled at 25 and 60 °C, displays strong contributions from a spectral feature located at 532.3 eV, which may be related to C-O-H structures. The Li₂O is primarily observed in regions II and III in both TEY and FLY spectra, indicating that this reaction product has a more homogeneous spatial distribution.

The chemical sensitivity of the O 1s edge features reveal the relative concentration of certain oxygen-containing species observed at 25 °C is an intermediate of that found at 0 and 60 °C (Figure 4H). As a general trend, the contribution from the spectral feature at 531.3 eV, which may be attributed to polymeric -C-C-O- type bonding, increases from 0 up to 60 °C.

This is also supported by the dampening of the feature at 536.6 eV as compared to that observed in the case of Li metal cycled at 60 °C. Other inorganic species such as Li_2CO_3 are common in the SEI formed at 25 °C, as indicated by the features present at 533.8 and 539.3 eV. However, the relative intensity of the peak at 533.8 eV compared to that at 539.3 eV is increased in the FLY measurements of all regions, which may indicate the formation of more Li_2O deeper within the cycled Li layers. The spectral feature at 533.8 eV overlaps with a transition of Li_2O while that found at 543.5 eV does not, which allows for differentiation in the relative ratios of these oxide components.

To highlight the advantages of XANES over other spectroscopic techniques, the O 1s XPS of Li anodes cycled under the same conditions were compared (Figure S10, Supporting Information). The results of the Li metal SEI at 0, 25, and 60 °C are consistent with the TEY micro-XANES results and indicate the presence of more Li₂O on the surface at low temperatures and more organic alkyl carbonate species formed at high temperatures. The peak located at ≈531.9 eV may be attributed to Li₂CO₃ species and is present regardless of testing temperature. However, the similarity in binding energy and peak shapes in XPS make it difficult to determine the composition of the SEI with absolute certainty. Moreover, the surface sensitivity of XPS prevents characterization of the SEI beyond the escape depth of the photoelectron, while the fluorescence X-rays measured by XANES in FLY mode provide nondestructive depth information and can build a more complete picture of the SEI evolution. These facts coupled with the unique fingerprint spectral features induced by the core level excitation of electrons to unoccupied states in XANES provide significant advantages over traditional XPS characterization of the Li metal SEI.

To summarize, the SEI formed on the Li metal anode differs significantly depending on the temperature at which it is cycled. Moreover, we are able to show that the composition is not only different between electrodes cycled at 0, 25, and 60 °C, but can also vary significantly within individual electrodes depending on the area of measurement. The use of energy-dependent XRF mappings coupled with micro-XANES is able to visualize the local variations in SEI formation that would be otherwise looked over by tradition testing methods such as XPS, which typically take average measurements over a large area. Additionally, the use of TEY and FLY modes of measurement is used as nondestructive tools to reveal that the surface and subsurface chemical compositions differ greatly. Our results indicate that at 0 °C, according to TEY and FLY modes of measurement, the chemical composition of F-containing species is more homogeneously dispersed at the surface and at depth, but has isolated regions where the bulk composition may differ significantly from neighboring regions. This is in contrast to Li anodes cycled at 25 and 60 °C where the spatial distribution of F species is more uniform across the entire surface, but still differ in chemical composition in the near-surface regions and at depth. Micro-XANES further reveals strong differences in composition of organic species across the electrodes and at different depths when cycled at different temperatures. Li₂CO₃ is found be the predominant reaction product and forms preferentially deeper in the SEI layer along with other inorganic components, and the ratio of carbonate to other organic species differs depending on the operating temperature. These advanced characterization

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techniques will prove useful for further studies on Li metal anodes to show how certain conditions or protection techniques will affect SEI composition and homogeneity in quasi-3D space.

Understanding the behavior of Li metal anodes operating under different conditions is of the utmost importance for the development of next-generation Li metal batteries. We have thoroughly studied the influence of temperature on Li metal anodes cycled in carbonate electrolytes, which has been poorly understood until now. The trends in electrochemical behavior of Li metal anode cycled at 0, 25, and 60 °C in carbonate-based electrolyte are shown to be significantly different from recent reports on Li metal anodes in ether electrolyte, and we show that testing methodology is critical to interpreting modes of failure at different temperatures. Low temperatures are shown to increase Coulombic efficiency and extend cycle life through lower chemical reactivity in the absence of short-circuits, whereas it is believed that higher temperatures lead to unstable SEI formation, poor Coulombic efficiency, and electrolyte degradation. Moreover, the mechanism of Li nucleation and growth at the microlevel was studied by SEM and synchrotron-based X-ray tomography to reveal the effect of thermal conditions on the initial and early stages of cycling in symmetric cells. Furthermore, energy-dependent XRF mapping coupled with micro-XANES was used for the first time to study the Li metal SEI to show differences in spatial distribution and composition at the micro-level at 0, 25, and 60 °C. This work provides valuable insight into the electrochemical behavior of Li metal anodes in carbonate systems and offers new characterization methods for the study of Li metal batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbonate electrolytes, electrochemical behavior, failure modes, Li dendrites, Li metal anodes $% \left({{{\left({{L_{\rm{s}}} \right)} \right)}_{\rm{s}}} \right)$

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- [1] Z. A. Ghazi, Z. Sun, C. Sun, F. Qi, B. An, F. Li, H. M. Cheng, Small 2019, 15, 1900687.
- [2] D. Lin, Y. Liu, A. Pei, Y. Cui, Nano Res. 2017, 10, 4003.
- [3] Y. He, X. Ren, Y. Xu, M. H. Engelhard, X. Li, J. Xiao, J. Liu, J. G. Zhang, W. Xu, C. Wang, Nat. Nanotechnol. 2019, 14, 1042.
- [4] C. Fang, J. Li, M. Zhang, Y. Zhang, F. Yang, J. Z. Lee, M. H. Lee, J. Alvarado, M. A. Schroeder, Y. Yang, B. Lu, N. Williams, M. Ceja, L. Yang, M. Cai, J. Gu, K. Xu, X. Wang, Y. S. Meng, *Nature* **2019**, *572*, 511.
- [5] Y. Sun, Y. Zhao, J. Wang, J. Liang, C. Wang, Q. Sun, X. Lin, K. R. Adair, J. Luo, D. Wang, R. Li, M. Cai, T. K. Sham, X. Sun, *Adv. Mater.* **2019**, *31*, 1806541.
- [6] L. Liu, Y. X. Yin, J. Y. Li, S. H. Wang, Y. G. Guo, L. J. Wan, Adv. Mater. 2018, 30, 1706216.
- [7] K. R. Adair, C. Zhao, M. N. Banis, Y. Zhao, R. Li, M. Cai, X. Sun, Angew. Chem., Int. Ed. 2019, 58, 15797.
- [8] H. Wang, Y. Liu, Y. Li, Y. Cui, Electrochem. Energy Rev. 2019, 2, 509.
- [9] P. Zou, Y. Wang, S. W. Chiang, X. Wang, F. Kang, C. Yang, Nat. Commun. 2018, 9, 464.
- [10] Y. Xu, T. Li, L. Wang, Y. Kang, Adv. Mater. 2019, 31, 1901662.
- [11] X. Wang, J. Zhuang, M. Liu, C. Wang, Y. Zhong, H. Wang, X. Cheng, S. Liu, G. Cao, W. Li, *J. Mater. Chem. A* **2019**, *7*, 19104.
- [12] H. Duan, W.-P. Chen, M. Fan, W.-P. Wang, L. Yu, S.-J. Tan, X. Chen, Q. Zhang, S. Xin, L.-J. Wan, Y.-G. Guo, Angew. Chem., Int. Ed., https://doi.org/10.1002/anie.202003177.
- [13] H. Duan, J. Zhang, X. Chen, X.-D. Zhang, J.-Y. Li, L.-B. Huang, X. Zhang, J.-L. Shi, Y.-X. Yin, Q. Zhang, Y.-G. Guo, L. Jiang, L.-J. Wan, J. Am. Chem. Soc. 2018, 140, 18051.
- [14] X. Wang, R. Kerr, F. Chen, N. Goujon, J. M. Pringle, D. Mecerreyes, M. Forsyth, P. C. Howlett, Adv. Mater. 2020, 32, 1905219.
- [15] A. Mauger, C. M. Julien, A. Paolella, M. Armand, K. Zaghib, *Materials* **2019**, *12*, 3892.
- [16] A. Mauger, C. M. Julien, A. Paolella, M. Armand, K. Zaghib, Mater. Sci. Eng., R 2018, 134, 1.
- [17] Q. Li, T. Yi, X. Wang, H. Pan, B. Quan, T. Liang, X. Guo, X. Yu, H. Wang, X. Huang, L. Chen, H. Li, *Nano Energy* **2019**, *63*, 103895.
- [18] C. von Lüders, J. Keil, M. Webersberger, A. Jossen, J. Power Sources 2019, 414, 41.
- [19] E. Kazyak, R. Garcia-Mendez, W. S. LePage, A. Sharafi, A. L. Davis, A. J. Sanchez, K.-H. Chen, C. Haslam, J. Sakamoto, N. P. Dasgupta, *Matter* **2020**, *2*, 1025.
- [20] J. Sanchez, E. Kazyak, Y. Chen, K.-H. Chen, E. R. Pattison, N. P. Dasgupta, ACS Energy Lett. 2020, 5, 994.
- [21] K.-H. Chen, A. J. Sanchez, E. Kazyak, A. L. Davis, N. P. Dasgupta, Adv. Energy Mater. 2019, 9, 1802534.
- [22] J. Wang, W. Huang, A. Pei, Y. Li, F. Shi, X. Yu, Y. Cui, Nat. Energy 2019, 4, 664.
- [23] K. Yan, J. Wang, S. Zhao, D. Zhou, B. Sun, Y. Cui, G. Wang, Angew. Chem. 2019, 58, 11364.
- [24] Y. Zhu, J. Xie, A. Pei, B. Liu, Y. Wu, D. Lin, J. Li, H. Wang, H. Chen, J. Xu, A. Yang, C. L. Wu, H. Wang, W. Chen, Y. Cui, *Nat. Commun.* 2019, 10, 2067.
- [25] W. S. LePage, Y. Chen, E. Kazyak, K.-H. Chen, A. J. Sanchez, A. Poli, E. M. Arruda, M. D. Thouless, N. P. Dasgupta, J. Electrochem. Soc. 2019, 166, A89A97.
- [26] L. Suo, W. Xue, M. Gobet, S. G. Greenbaum, C. Wang, Y. Chen, W. Yang, Y. Li, J. Li, *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 1156.
- [27] K. Xu, Chem. Rev. 2004, 104, 4304.
- [28] F. Shi, A. Pei, D. T. Boyle, J. Xie, X. Yu, X. Zhang, Y. Cui, Proc. Natl. Acad. Sci. USA 2018, 115, 8529.
- [29] D. Lin, Y. Liu, Y. Cui, Nat. Nanotechnol. 2017, 12, 194.
- [30] J. Lopez, A. Pei, J. Y. Oh, G. N. Wang, Y. Cui, Z. Bao, J. Am. Chem. Soc. 2018, 140, 11735.

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- [31] Y. Zhao, M. Amirmaleki, Q. Sun, C. Zhao, A. Codirenzi, L. V. Goncharova, C. Wang, K. Adair, X. Li, X. Yang, F. Zhao, R. Li, T. Filleter, M. Cai, X. Sun, *Matter* **2019**, *1*, 12151231.
- [32] H. Zhang, X. Liao, Y. Guan, Y. Xiang, M. Li, W. Zhang, X. Zhu, H. Ming, L. Lu, J. Qiu, Y. Huang, G. Cao, Y. Yang, L. Mai, Y. Zhao, H. Zhang, *Nat. Commun.* **2018**, *9*, 3729.
- [33] S. Li, H. Wang, J. Cuthbert, T. Liu, J. F. Whitacre, K. Matyjaszewski, Joule 2019, 3, 1637.
- [34] M. S. Kim, Sci. Adv. 2019, 5, eaax5587.
- [35] R. Zhang, X. Chen, X. Shen, X.-Q. Zhang, X.-R. Chen, X.-B. Cheng, C. Yan, C.-Z. Zhao, Q. Zhang, *Joule* **2018**, *2*, 764.
- [36] Q. Pang, X. Liang, A. Shyamsunder, L. F. Nazar, Joule 2017, 1, 871.
- [37] E. Peled, S. Menkin, J. Electrochem. Soc. 2017, 164, A1703A1719.
- [38] K.-H. Chen, K. N. Wood, E. Kazyak, W. S. LePage, A. L. Davis, A. J. Sanchez, N. P. Dasgupta, J. Mater. Chem. A 2017, 5, 11671.
- [39] N. Delaporte, Y. Wang, K. Zaghib, Front. Mater. 2019, 6, 267.
- [40] L. Li, S. Li, Y. Lu, Chem. Commun. 2018, 54, 6648.
- [41] X. Zhang, Q. J. Wang, K. L. Harrison, K. Jungjohann, B. L. Boyce, S. A. Roberts, P. M. Attia, S. J. Harris, J. Electrochem. Soc. 2019, 166, A3639.
- [42] E. Cha, M. D. Patel, J. Park, J. Hwang, V. Prasad, K. Cho, W. Choi, Nat. Nanotechnol. 2018, 13, 337.
- [43] J. Fan, Y. Luo, K. Jiang, C. Wang, RSC Adv. 2020, 10, 3145.
- [44] K. Liu, A. Pei, H. R. Lee, B. Kong, N. Liu, D. Lin, Y. Liu, C. Liu, P.-c. Hsu, Z. Bao, Y. Cui, J. Am. Chem. Soc. 2017, 139, 4815.
- [45] K. Yan, Z. Lu, H.-W. Lee, F. Xiong, P.-C. Hsu, Y. Li, J. Zhao, S. Chu, Y. Cui, *Nat. Energy* **2016**, *1*, 16010.

[46] B. D. Adams, J. Zheng, X. Ren, W. Xu, J.-G. Zhang, Adv. Energy Mater. 2018, 8, 1702097.

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www.advmat.de

- [47] A. Pei, G. Zheng, F. Shi, Y. Li, Y. Cui, Nano Lett. 2017, 17, 1132.
- [48] P. Bai, J. Li, F. R. Brushett, M. Z. Bazant, Energy Environ. Sci. 2016, 9, 3221.
- [49] M. Golozar, P. Hovington, A. Paolella, S. Bessette, M. Lagacé, P. Bouchard, H. Demers, R. Gauvin, K. Zaghib, *Nano Lett.* 2018, 18, 7583.
- [50] M. Golozar, A. Paolella, H. Demers, S. Bessette, M. Lagacé, P. Bouchard, A. Guerfi, R. Gauvin, K. Zaghib, *Commun. Chem.* 2019, 2, 131.
- [51] S. Kaboli, H. Demers, A. Paolella, A. Darwiche, M. Dontigny, D. Clément, A. Guerfi, M. L. Trudeau, J. B. Goodenough, K. Zaghib, *Nano Lett.* **2020**, *20*, 1607.
- [52] S. H. Kim, K. Kim, H. Choi, D. Im, S. Heo, H. S. Choi, J. Mater. Chem. A 2019, 7, 13650.
- [53] K. J. Harry, D. T. Hallinan, D. Y. Parkinson, A. A. MacDowell, N. P. Balsara, *Nat. Mater.* **2014**, *13*, 69.
- [54] M. Tripathi, W. N. Su, B. J. Hwang, Chem. Soc. Rev. 2018, 47, 736.
- [55] S. Parimalam, B. L. Lucht, J. Electrochem. Soc. 2018, 165, A251.
- [56] M. Balasubramanian, H. S. Lee, X. Sun, X. Q. Yang, A. R. Moodenbaugh, J. McBreen, D. A. Fischer, Z. Fu, *Electrochem. Solid-State Lett.* 2002, 5, A22.
- [57] S. J. Rezvani, F. Nobili, R. Gunnella, M. Ali, R. Tossici, S. Passerini, A. Di Cicco, J. Phys. Chem. C 2017, 121, 26379.
- [58] S. J. Rezvani, R. Gunnella, A. Witkowska, F. Mueller, M. Pasqualini, F. Nobili, S. Passerini, A. D. Cicco, ACS Appl. Mater. Interfaces 2017, 9, 4570.