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Influence of Lithiophilic Substrate on Lithium Metal Batteries at Low Temperature

A Thesis submitted in partial satisfaction of the requirements
for the degree Master of Science

in

Materials Science and Engineering

by

Kangwoon Kim

Committee in charge:

Professor Zheng Chen, Chair
Professor Renkun Chen
Professor Ping Liu
Professor Tod A. Pascal

2022

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University of California San Diego

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ABSTRACT OF THE THESIS

Influence of Lithiophilic Substrate on Lithium Metal Batteries at Low Temperature

by

Kangwoon Kim

Master of Science in Materials Science and Engineering

University of California San Diego, 2022

Professor Zheng Chen, Chair

Lithium metal batteries (LMBs) are an emerging technology that promises to provide high energy density that could compensate for the energy loss of lithium-ion batteries (LIBs) at low temperatures. However, tip-driven growth during lithium deposition remains a problem for LMBs at low temperatures, which should be mitigated for improved cyclability and safety. Tailoring lithium metal nucleation with lithiophilic substrates has shown effectiveness in improving cycling performance at room temperature, but the investigation at low temperatures is limited. For this work, promoting homogeneous lithium nucleation by implementing a

lithiophilic substrate, lithiated graphite (LiC_6), the adverse effects of low temperature on Li cycling were alleviated in a model electrolyte. This lithiated graphite substrate provided 4.2% and 4.5% higher measured coulombic efficiency for Li cycling compared to copper at -20°C and -40°C , respectively, which demonstrated higher specific capacity and improved cyclability for 2x excess $\text{Li}||\text{N}_{0.6}\text{M}_{0.2}\text{C}_{0.2}\text{O}_2$ full cells.

INTRODUCTION

The market for Li-ion batteries (LIBs) is continually growing and has become an inseparable part of consumer electronics and electric vehicles today. However, conventional LIBs using graphite as an anode face severe energy density loss at temperatures below 0°C, which substantially limits their low-temperature applications^[1-4]. One of the major reasons for this phenomenon is increased internal resistance and slow kinetics^[4]. To address the issues at low temperatures, lithium metal batteries (LMBs) are considered to be a possible alternative, which could compensate for the energy density loss due to the high specific capacity of lithium metal (3860 mAh g⁻¹)^[5]. With the capability to provide high specific energy, LMBs could enable the operation of high energy density applications such as electric aviation, space exploration, and autonomous electric transportation.

While lithium metal would be the ideal anode material if successfully employed, it still faces significant limitations at low temperatures. Regardless of operating temperature, the highly reactive nature of lithium continuously causes side reactions when the Li surface is exposed to the electrolyte, leading to the growth of solid electrolyte interphase (SEI) and dead lithium formation during cycling, resulting in high internal resistance and low coulombic efficiency (CE)^[6-10]. At low temperatures, it is known that charge transfer impedance, specifically Li⁺-desolvation, limits the operation of LMBs, though recent electrolyte developments have alleviated many complications associated with dendritic growth^[11-15]. Cui and co-workers have also proposed that Li nucleation on Cu at low temperature is met with a high nucleation barrier, causing inhomogeneous lithium deposition^[16-19]. This inhibited growth could lead to deposition at a narrow range of nucleated sites that causes dendrite formation, which leaves lithium more vulnerable to continual side reactions^[17,19,20,21,22,23]. Despite this, it is still relatively unclear if the nucleation

stage of Li metal growth at reduced temperatures plays a significant role in determining performance.

To control the initial nucleation morphology and particle size, studies have shown that lithiophilic substrates are capable of lowering the nucleation barrier to induce homogenous growth and increase cycling reversibility at room temperature^[18,24,25,26,30]. Yan et al. proposed gold nanoparticles encapsulated inside the carbon nanospheres and Zuo et al. coated a thin silver layer on lithium to induce homogeneous lithium deposition, which resulted in increased cycle life and stability^[18,30]. Of these lithiophilic substrates, lithiated graphite is a well-discussed material, where Liu and co-workers showed its viability in solid-state lithium batteries, and Dahn and co-workers utilized graphite as a substrate in hybrid lithium-ion/metal batteries^[27-29]. Graphite allows lithium to plate when additional capacity is added to fully lithiated particles^[29]. The lithiated graphite particles are known to be highly lithiophilic with their superior electrical conductivity and chemical stability, which would serve as a stable root for lithium plating and stripping^[27,29]. By casting a thin layer of graphite with minimal capacity, we hypothesized that the lithium metal homogeneity and reversibility could be improved at reduced temperatures.

CHAPTER 1: INVESTIGATION OF LITHIUM MORPHOLOGY

The morphology of plated lithium has been shown to vary based on the lithiophilicity of the substrate, which effectively modulates the nucleation barrier^[18,32]. There has been an effort to minimize this barrier to facilitate the growth and induce homogenous growth with larger particle size distribution^[16-17]. Lithiophilic substrates such as graphite, Si, Au, and Ag have been proposed to significantly reduce Li metal nucleation energy due to their intrinsic solubility with Li, forming alloys or intercalation compounds^[18,24,30]. On the other hand, Cu is known to be highly insoluble with lithium and therefore displays nucleation energy barriers significantly higher than the aforementioned lithiophilic substrates^[18]. At lower temperatures, Li⁺ desolvation is known to severely limit Li plating performance, which could exacerbate dendritic growth in the case of inhomogeneous nucleation. (Figure 1a). Despite the Li⁺ desolvation barrier at low temperature, we propose that the more homogenous nucleation behavior of lithium on lithiated graphite would still promote larger particle growth (Figure 1b).

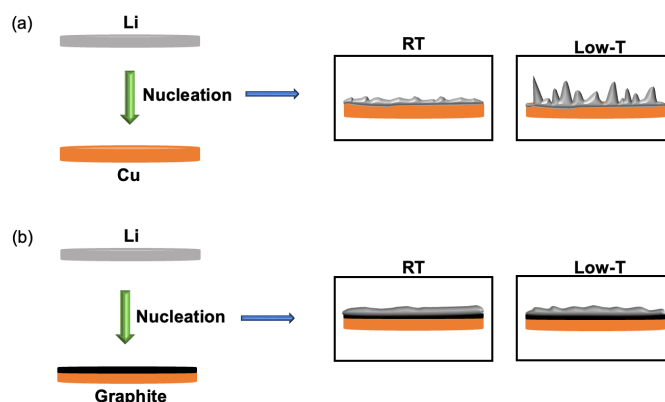


Figure 1) Schematic of the temperature-dependent nucleation morphology of lithium plated on **a)** Cu and on **b)** graphite.

To elucidate the effect of the lithiophilic substrate on initial nucleation and subsequent performance, Li/Cu and Li/Graphite cells were compared in the carbonate-based electrolyte, 1 M lithium hexafluorophosphate in a 3:7 (volume) mixture of ethylene carbonate (EC) and ethyl

methyl carbonate (EMC), hereby referred to as Gen 2, with a 5% FEC additive. We elect to include the 5 % FEC additive due to the inherent reactivity between Gen 2 and Li metal, which leads to untenable cycling efficiencies even at room temperature (Figure S1) [33,34].

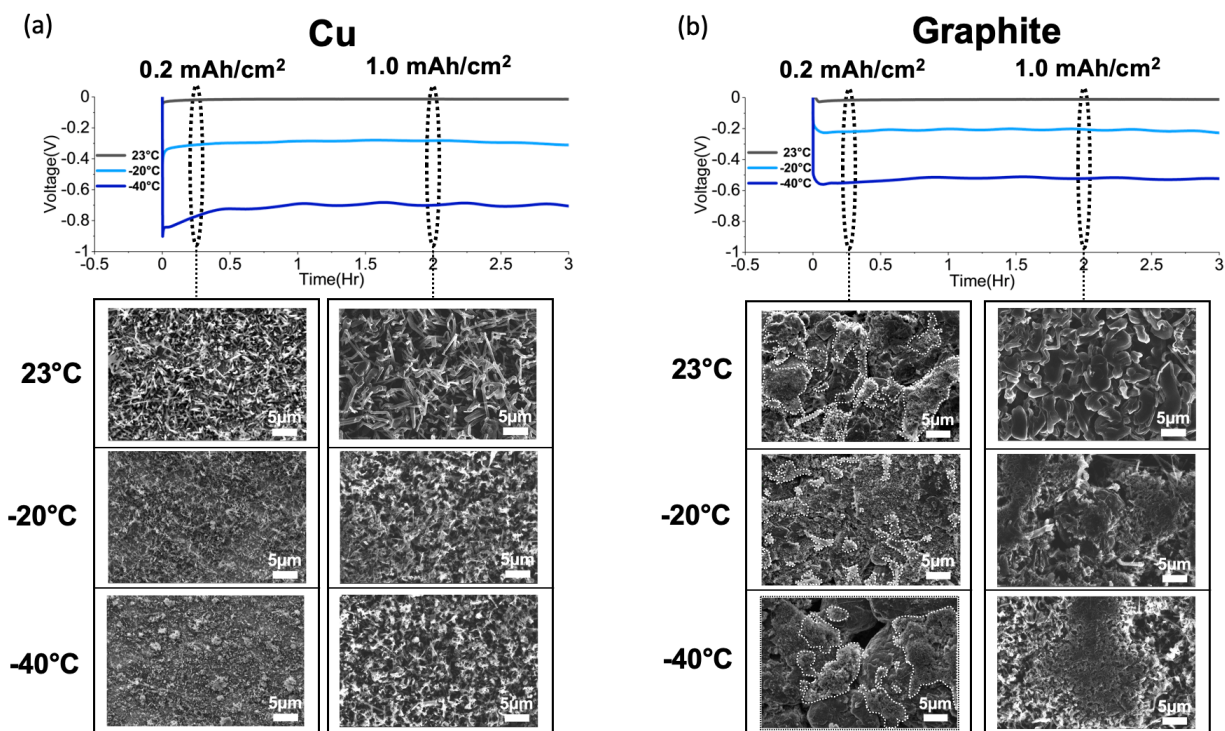


Figure 2) Nucleation barrier and Li metal characterization plated on **a)** Cu and on **b)** graphite based on temperature at 0.2mAh/cm² and 1mAh/cm² in Gen2 w/ 5%FEC.

The lithiophilic substrate effect is clear in the beginning phase of lithium plating, where the difference in nucleation barrier and polarization is much larger for lithium plated on copper (Figure 2a,b). Scanning electron microscopy (SEM) was taken at different points of Li growth, 0.2 mAh/cm² and 1 mAh/cm² to view the initial nucleation sites and the growth based on said nucleation behavior as a function of temperature. The morphology of lithium plated on copper is highly dendritic, which is evident at both the investigated capacities at all temperatures as shown in figure 2a. The particle size faces a significant reduction as the temperature decreases down to -40°C, which signifies a tendency towards tip-driven growth and an increased surface area to

volume ratio that would expose more area of lithium deposits to the electrolyte, causing greater side reactions and formation of dead lithium. On the other hand, lithium growth on lithiated graphite at room temperature appears to be very granular with evidently larger particle sizes than copper, as shown in figure 2. At low temperatures, lithium deposited on graphite appears to maintain its larger particle size distribution relative to Cu, where the grown Li also tends to form intimate contact with the lithiated graphite underneath. It is also notable that at 0.2 mAh/cm^2 , lithium deposits are observed to be more granular when deposited on lithiated graphite compared to Cu. We also find that lithium growth on lithiated graphite is not limited to the deposition on the top surface, but also throughout individual lithiated graphite particles, which is evident from the cross-sectional SEM image and energy-dispersive X-ray spectroscopy (EDX) analysis at room temperature shown in figure S2.

CHAPTER 2: HALF CELL PERFORMANCE EVALUATION

The effect of lithiophilic substrate on cell performance was evaluated by determining the average coulombic efficiency (CE) in the accurate method proposed by Adams et al., which for our purposes allows for the determination of CE without concerns for the reversibility of the graphite substrate^[35]. For the cell design, the mass loading of the active material was constrained to 1.3 mg cm^{-2} to minimize the effect of the capacity of graphite while serving the role of the lithiophilic substrate. To ensure full lithiation of the graphite substrate, the Li||graphite cell was discharged at 0.1 mA/cm^2 until the voltage reached 0.01V. After the voltage reached 0.01V, lithium was plated and stripped at 0.5 mA/cm^2 on top of the lithiated substrate. The formation cycle for Li was conducted at room temperature and graphite was fully lithiated before formation cycles and before testing at RT, -20°C , and -40°C . To more vividly demonstrate the lithiophilic substrate effect, the active material to super P to binder ratio of 8:1:1, 90:5:5, and 96:2:2 was compared to observe the effect of increased lithiated graphite particles. It was revealed through SEM imaging that for the 8:1:1 ratio, regions of super P and polyvinylidene fluoride (PVDF) were exposed as opposed to graphite particle-dominated regions in 90:5:5 and 96:2:2 ratios as shown in Figure S3a. We believe that the exposed regions without graphite particles would reduce overall deposition homogeneity, which was confirmed through the half-cell electrochemical performance data at room temperature where the 96:2:2 ratio showed superior performance to other ratios with measured CEs of 95.9 %, 94.1 % for 8:1:1, and 94.2 % for 90:5:5 (Figure S3b). At -20°C and -40°C , graphite with 96:2:2 ratio showed CEs of 92.1 %, and 86.2 %, respectively, while copper showed 89.4% and 81.9%, respectively (Figure 3).

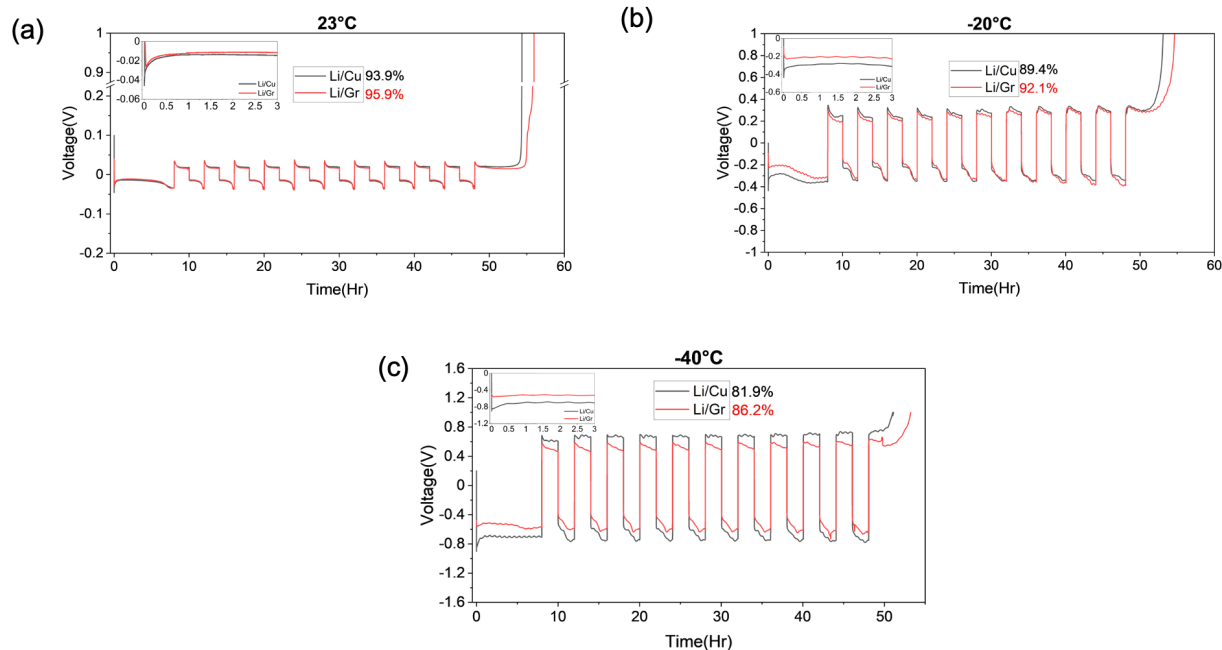


Figure 3) Li metal plating and stripping cycles for CE determination at **a)** room temperature, **b)** -20°C, **c)** -40°C. The capacity of lithiated graphite was not considered during the CE measurement.

To investigate the interplay between these substrate effects and electrolyte chemistry, tests were also performed in a localized high concentration electrolyte, 1M LiFSI BTFE/DME 3:1, which produces CE over 99% at room temperature on Cu. The average coulombic efficiency for Li/Cu was 98.1%, 99.0%, and 98.3% at room temperature, -20°C, and -40°C, respectively. For graphite, the average CE was 98.1%, 99.1%, and 98.6% at room temperature, -20°C, and -40°C, respectively as shown in figure S4. It is evident that the lithiophilic substrate is not as effective in highly efficient electrolytes. Although the reduced nucleation barrier of the lithiated graphite substrate would indicate that the deposition is more homogenous, we propose that the reduced reactivity of the electrolyte renders such effects less influential on overall performance.

CHAPTER 3: DISCUSSION OF FULL CELL OPERATION

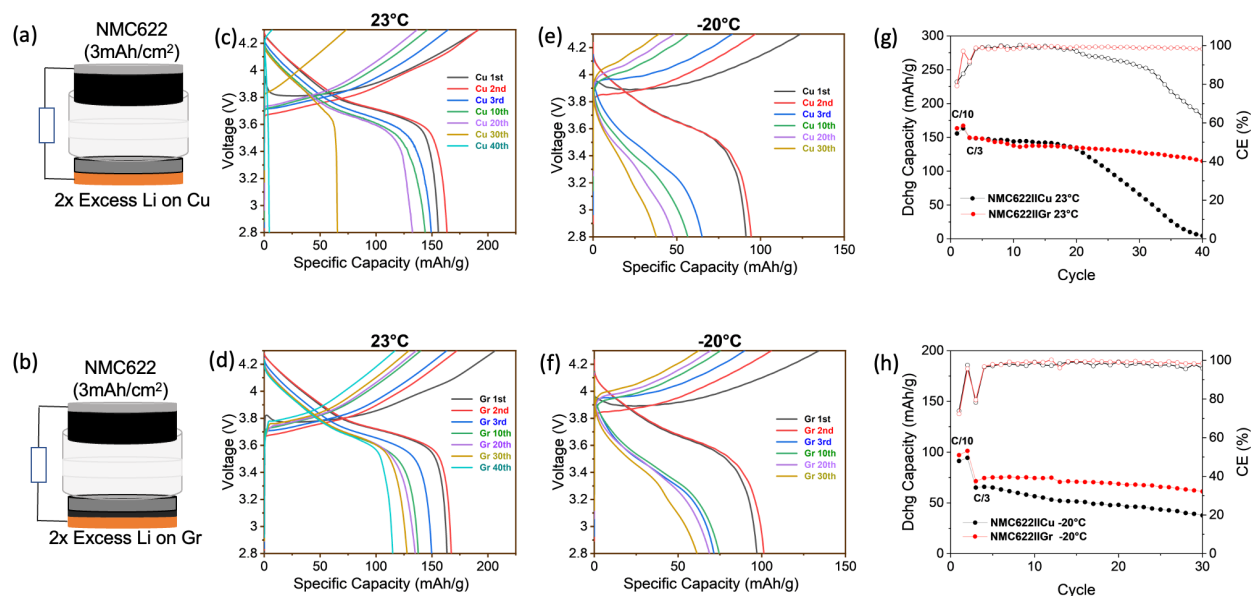


Figure 4) 2x Li||NMC622 full cell performance at room and low temperature in Gen2 +5%FEC. Schematics of the full cells on a) Cu and b) graphite. Room temperature charge and discharge profiles of the full cells on c) Cu and b) graphite. -20°C charge and discharge profiles of the full cells on e) Cu and f) graphite. All voltage profiles include two C/10 conditioning cycles. Cycling performance comparison of full cells on Cu and graphite at g) room temperature and h) -20°C. Full cells were cycled C/5||C/3 for charge||discharge. Full cells were charged and discharged once at C/10 at room temperature before transferring to low temperature.

To investigate the practical influence of the lithiophilic substrates on lithium metal cycling, 2x excess Li||LiN_{0.6}M_{0.2}C_{0.2}O₂ (NMC622) full cells were assembled and tested at room temperature and -20°C (Figure 4 a,b). As employing lithiophilic substrate was shown to be effective in reactive electrolytes, the test was performed in Gen 2 + 5 % FEC. Evidence of the lithiophilic substrate effect was revealed in the full cell comparison, where the full cell with lithium plated on Cu showed rapid capacity loss beginning on the 20th cycle, corresponding to exhaustion of the excess Li anode reservoir. On the other hand, full cell operation with the graphite substrate showed 85.3% capacity retention at the 30th cycle at room temperature. At -20°C, the full cell with lithium plated on Cu showed greater capacity fade in the initial cycle, suggesting larger side reactions caused by tip-driven growth of lithium on Cu. While the subsequent cycles retain

stability, the plating and stripping occur at a much lower capacity, which indicates lower active material utilization. At the 30th cycle, full cell operation demonstrated 60.3% and 87.2% capacity retention for the Cu substrate and the graphite substrate, respectively. This leaves the implication that if the electrolyte-electrode interface is manipulated with a lithiophilic substrate, it could alleviate additional parasitic reactions and mitigate the adverse effect of Li⁺ desolvation to a noticeable degree at low temperatures.

CONCLUSION

Lithium deposition was controlled by employing a lithiophilic substrate to determine the influence of homogeneous nucleation at low temperatures, and the effect of substrates in electrolytes with varying reactivity. It was notable that in a reactive electrolyte, the lithiophilic substrate facilitated lithium deposition with granular and homogeneous morphology, promoting a larger particle size distribution. This realizes less surface area of lithium in contact with the electrolyte, which alleviates parasitic reactions. Coulombic efficiency measurements in Li/Cu half cells demonstrated the benefit of this strategy, where the reduction in nucleation barrier due to the lithiophilic substrate enabled less dead lithium formation and enhanced cycling performance. Further impact of the lithiophilic substrate was studied in 2x excess Li||NMC622 full cells to display practical implications of manipulating lithium deposition. Full cells with lithiated graphite substrates demonstrated higher capacity retention at room temperature and delivers greater capacity at low temperature compared to the Cu substrate. Additionally, the findings in less reactive localized high concentration electrolyte revealed less lithiophilic substrate-dependent performance. This suggests that the impact of the lithiophilic substrates would be greater in less Li-compatible electrolytes at all temperatures.

Acknowledgments

The Thesis in full is currently being prepared for submission for publication of the material. Kim, Kangwoon; Holoubek John; Li, Mingqian; Kim, Taehee; Yin, Yijie; Cai, Guorui; Chen, Zheng. The thesis author was the primary author of this chapter.

EXPERIMENTAL

Materials

Graphite electrodes were prepared by mixing superior graphite powder, Super-P, and polyvinylidene fluoride (PVDF, KYNAR 1800) in a ratio of 96:2:2, 90:5:5, and 8:1:1 in N-methyl pyrrolidinone (NMP, sigma) solvent, cast on Cu foil (MTI) and dried in a vacuum oven at 80°C overnight.

$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NMC622) electrodes were prepared by mixing NMC622 powder (Targray), Super-P, and PVDF (KYNAR 1800) in a ratio of 90:5:5 in N-methyl pyrrolidinone (NMP, sigma) solvent, cast on Al foil (MTI) and dried in a vacuum oven at 120°C overnight.

Lithium hexafluorophosphate (LiPF_6), Ethylene Carbonate (EC), and ethyl methyl carbonate (EMC) were purchased from Gotion. Fluoroethylene Carbonate (FEC) was purchased from Tokyo Chemical Industry. The electrolyte was prepared by mixing 1.2M LiPF_6 in EC/EMC (3:7 by volume).

Lithium bis(fluorosulfonyl)imide (LiFSI) was purchased from Kelude. Anhydrous 1,2-dimethoxyethane (DME) was purchased from Millipore-Sigma. Bis(2,2,2-trifluoroethyl) ether (BTFE) was purchased from Synquest, and dried with activated molecular sieves for at least 24 hrs before use. The electrolyte was prepared by mixing 1M LiFSI in BTFE/DME (3:1 by volume).

Characterization

FEI Quanta 250 Scanning Electron Microscope (SEM) equipped with energy dispersive spectroscopy (EDS) was used for characterizing the morphology of deposited lithium on Cu substrate and lithiated graphite substrate at varying temperatures and areal capacities. The samples were obtained from coin cells and washed with DME before analysis.

Electrochemical Testing

CR-2032 type coin cells were assembled using graphite or Cu as the working electrodes, Celgard 2325 membrane as the separator (25 μ m), and lithium foil (500 μ m) as the counter electrodes for Li||Cu and Li||Gr half cells with 75 μ L of electrolyte in an Ar filled glovebox kept at <0.5 ppm O₂ and <0.1 ppm H₂O. For 2x excess Li||NMC 622 full cells, a Li counter electrode was electroplated beforehand in a separate Li||Cu or Li||Gr half-cell, assembled with 3.0 ± 0.1 mAh/cm² NMC622 electrode.

Room temperature and -20°C galvanostatic testing was done on a Neware BTS 4000 system, and -40°C galvanostatic testing was done on an Arbin LBT-10V5A system.

APPENDIX

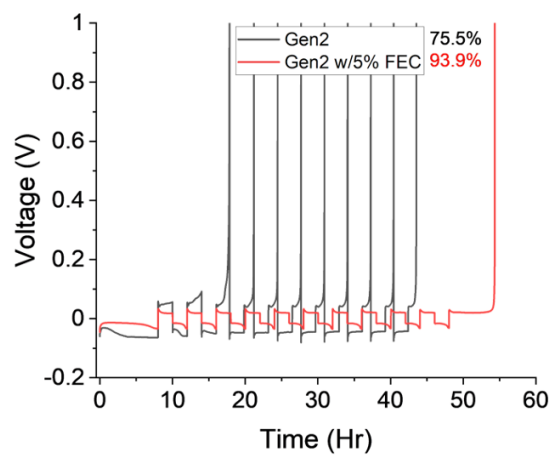


Figure S1) Li||Cu half-cell cycling performance comparison for 1M LiPF₆ EC/EMC 3:7 electrolyte with and without fluoroethylene carbonate (FEC) additive.

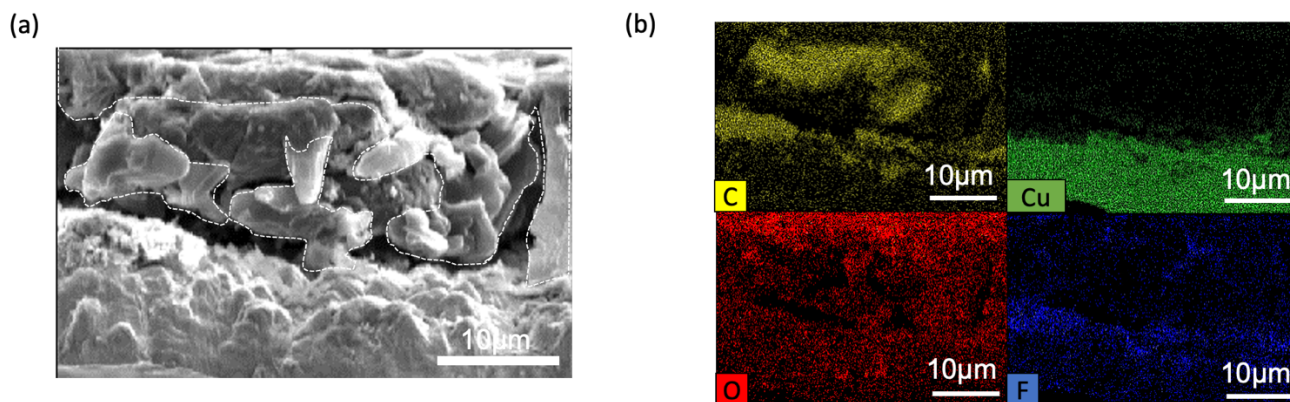


Figure S2) a) SEM image of the cross-section of lithium plated on lithiated graphite. b) EDX image for determining lithium location based on the oxygen signal.

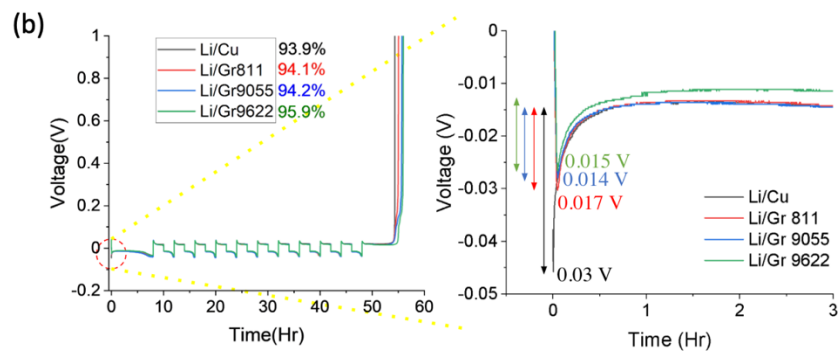
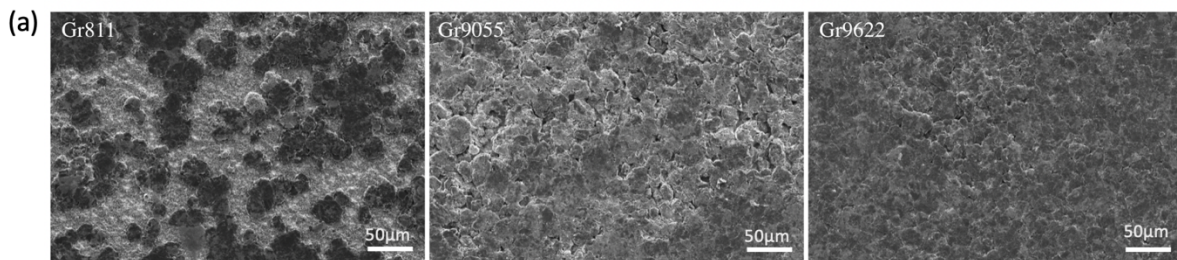


Figure S3) a) SEM image of graphite based on varying active material to super P to binder ratios. b) Lithium metal half-cell cycling performance comparison of substrates with varying active material content.

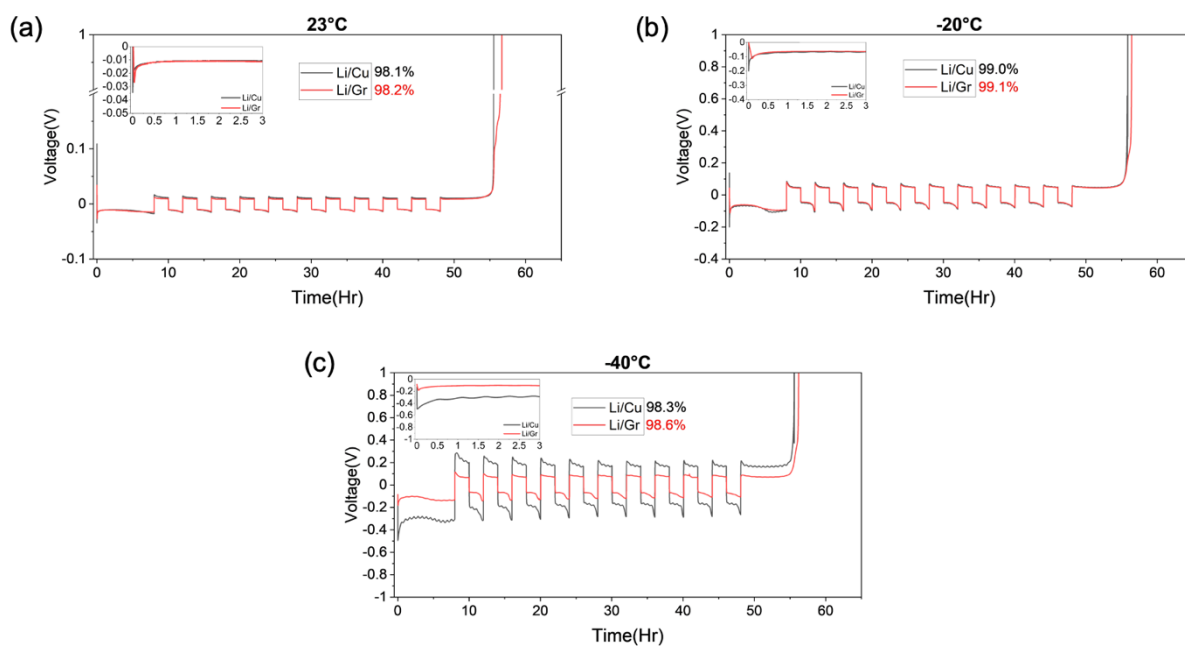


Figure S4) Lithium metal half-cell cycling performance comparison in 1M LiFSI BTFE/DME 3:1 electrolyte at a) room temperature, b)-20°C, c) -40°C.

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