

MECHANISMS OF LITHIATION IN CARBON AND SILICON ANODES
FOR LITHIUM-ION BATTERIES

by

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DEDICATION

To Grandma Sue, who taught me to love life without reservation.

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ABSTRACT

As the demand for energy increases globally, advanced energy storage materials must be developed to support renewable energy conversion technologies. Lithium-ion batteries (LIBs) are among the most promising energy storage methods technologies for mobile applications, but the mechanisms governing their operation and degradation remain incompletely understood. This thesis presents investigations of carbon- and silicon-based LIB anodes and compares their strengths and weaknesses for energy storage applications. First, we report an ultrafast alternative to graphite for high-power demand applications: a “herringbone” molecular crystal of hexa-peri-hexabenzocoronene (HBC). The unique lithiation mechanism of HBC is revealed via electrochemical, structural, and operando techniques, unveiling the structural origin of its pseudocapacitive character. Second, we report a cost-effective and high-capacity $\text{SiO}_x/\text{Gr}||\text{NMC811}$ battery system for high energy-density applications. Advanced electrochemical characterization techniques including in-situ electrochemical dilatometry were employed to the understand its impressive electrochemical stability for such a high energy density cell. This work reveals a hidden degradation mechanism that is masked by continuous lithium-ion emission into the system over the course of aging. Third, we will briefly discuss a new methodology developed for the compositional analysis of Si/C composite anodes, a recently commercialized technology for mobile LIB applications. This thermal gravimetric method reveals distinct silicon environments that render important implications for the composite electrochemistry. Altogether, these three reports provide new mechanistic insights into how lithium is inserted into carbon and silicon anodes, how its transport rate can be increased, and how its degradation can be prevented over the course of aging.

CHAPTER ONE

INTRODUCTION

Overview

This dissertation is the culmination of research on underlying function and degradation mechanisms in electrode materials for lithium-ion batteries (LIBs). While some data may be presented on cathode materials, particularly in **Chapter 5**, this body of work primarily focuses on the synthesis and characterization of next-generation anode materials comprised of carbon and silicon. Further study involving specific considerations of the cathode in modern lithium-ion battery formulations can be found in the **Appendix**. This dissertation contains specialized and novel aspects of both synthesis and electrochemistry of anode materials, with their background and methods detailed independently in **Chapters 2** and **3**, respectively.

A central theme of this work is the coupling of modern characterization techniques with advanced energy storage materials. By probing lithiation over multiple electrochemical testing regimes, we determine where lithium resides, how it is inserted and transported within the host, and what structural and interfacial changes accumulate during battery operation. Together, these form a mechanistic framework for lithiation in relevant carbon- and silicon- containing anode materials for LIBs.

Chapter 4 details the synthesis, characterization, and electrochemical analysis of hexa-peri-hexabenzocoronene (HBC) and select derivatives thereof. We present four heat-treated variants of HBC with different structures and lithium-ion storage properties, including a columnar hexagonal HBC molecular crystal (h-HBC), recrystallized herringbone HBC (r-HBC), gently

polymerized HBC (p-HBC), and carbonized HBC (c-HBC). Through electrochemical kinetic analysis, we show that certain structures of HBC (especially the r- and p-HBC variants) exhibit ultra-fast lithiation kinetics via intercalative pseudocapacitance, at lower potentials than have been demonstrated for other crystalline pseudocapacitive materials.¹⁻⁴ Furthermore, we demonstrate that these lithiation kinetics originate from specific sites prevalent within the herringbone structure of r-HBC, as elucidated by *operando* X-ray diffraction experiments. Finally, we demonstrate that the herringbone edge site and π - π lithiation mechanisms of r- and p-HBC exhibit comparable energy density characteristics to graphite together with increased rate-capability and power density characteristics, uncovering a class of crystalline hydrocarbon materials with great potential for high-power energy storage applications.

Chapter 5 pivots from carbon to silicon anode materials for LIBs. While silicon-based anodes promise much higher specific capacity than carbon, they face significant challenges in stability. In this work, we analyze an electrochemical analog of silicon, partially oxidized silicon (SiO_x), with the goal of understanding and improving stability while retaining high capacity. We specifically explore the underlying degradation mechanisms of $\text{SiO}_x/\text{Graphite}$ ($\text{Gr}||\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) full-cells in both two-electrode and three-electrode formats. This work reveals an anomalous activation process in the SiO_x anode by harvested electrode analysis, generally not observed because of concomitant silicon electrode degradation. By comparing the capacity fade in the cell from degradation mechanisms with the capacity gained by the cell due to prelithiation effects, we uncover an electrode potential shift effect for this system which “masks” the performance fade experienced by the $\text{SiO}_x/\text{Gr}||\text{NMC811}$ cell over the course of aging.

In **Chapter 6**, we combine carbon and silicon to study commercially relevant high-energy density silicon-carbon composite (Si/C) anodes. Three systematic series of Si/C composites were synthesized by chemical vapor deposition (CVD) of silane (SiH_4) onto carbon scaffolds under inert conditions, then passivated with acetylene (C_2H_2). We show that the structural and textural properties of the carbon scaffold dictate the morphology of the resulting silicon phase. High-porosity scaffolds with small pore sizes promote the growth of nano-silicon environments (Type I Si) whereas non-porous scaffolds promote the growth of bulk silicon environments (Type II Si); in general, both types are present in most Si/C composites and can be quantified using a novel thermogravimetric method presented herein. Finally, we correlate these distinctly identifiable silicon types with their electrochemical properties, showing that the presence of Type I Si is desirable for higher electrochemical stability.

These three complementary studies of state-of-the-art carbon and silicon materials are summarized and integrated in **Chapter 7** by discussing the interplay of synthetic conditions, materials properties, and their resulting electrochemical applications. We proceed to delineate between the strengths and weaknesses in all three anode systems in terms of cost efficacy, energy density, rate capability, and electrochemical stability to conclude on the contributions of this work to the next-generation LIB anode material landscape.

Objectives:

The objectives of this work are as follows:

1. To elucidate the lithiation mechanism and origin of pseudocapacitance in crystalline molecular hydrocarbons.

2. To characterize hidden electrochemical degradation mechanisms and their chemical markers in NMC811||SiO_x full cell systems.
3. To develop diagnostics for understanding the effects of carbon scaffold choice on the structural and electrochemical properties of Si/C composites.

This work addresses these objectives through systematic high-temperature synthesis techniques followed by complementary electrochemical, materials, and *operando* characterization techniques.

In **Chapter 4**, we demonstrate the structural distinctions between synthesized HBC analogs through powder X-ray diffraction (XRD), Raman spectroscopy, 2-point electrical probe conductivity, and CHO combustion analysis. By constant current/constant voltage (CCCV) cycling, we demonstrate the rate capabilities of different HBC crystal structures. The crystallographic lithiation sites for certain analogs of HBC are elucidated by *operando* synchrotron energy dispersive X-ray diffraction (EDXRD), which in turn are correlated with high diffusion coefficient regions in the voltage profile by galvanostatic intermittent titration technique (GITT). We then employ a combination of pseudocapacitive analyses by cyclic voltammetry (CV) and stepped-potential electrochemical impedance spectroscopy (SPEIS) to show that the rate-capable sites in the herringbone structure of HBC exhibit pseudocapacitive characteristics by potential-dependent Bode and Randles-Ševčík analyses.

Chapter 5 assesses an NMC811||SiO_x/Gr full cell system in both two- and three-electrode cell configurations. As silicon is a high-expansion anode material, we measure its expansion during cycling by *in-situ* electrochemical dilatometry (ECD). After cycling, electrolyte reduction product buildup on the anode is explained via complementary microscopic and spectroscopic techniques

such as cross-sectional scanning electron microscopy (SEM), plasma focused ion beam (PFIB) tomography, and cryogenic scanning transmission electron microscopy (cryo-STEM). We then identify and quantify such reduction products by voltage profile shift analysis of the three-electrode cells and harvested-cell voltage profile analysis of the two-electrode cells.

Chapter 6 focuses on the role of carbon scaffold porosity and crystallinity on the resultant properties of Si/C composites synthesized by CVD. In this work, we use differential thermogravimetric analysis (DTGA) as a method for assessing the quantity and type of silicon deposited on any given Si/C composite through gaussian integration of temporally separable oxidation events. The gaussian decomposition of DTGA is then validated by energy dispersive X-ray spectroscopy (EDS) on the same composites to validate obtained sample composition values. The electrochemical properties of representative Si/C composites and pure silicon samples are explored in half cells to measure the voltage profile shape and cycling stability.

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CHAPTER TWO

BACKGROUND

Battery ApplicationsElectricity Demand and Grid Intermittency

Electrification in the 21st century is reshaping the global energy landscape. The demand for electricity is growing faster than the demand for energy itself (**Figure 1**, left), indicating a relative enrichment of electricity as a global energy source. Grid electrification is driven by the increased relative abundance of renewable energy (38%, **Figure 1**, right), resulting in the largest absolute increase in electricity demand ever recorded in 2024.¹

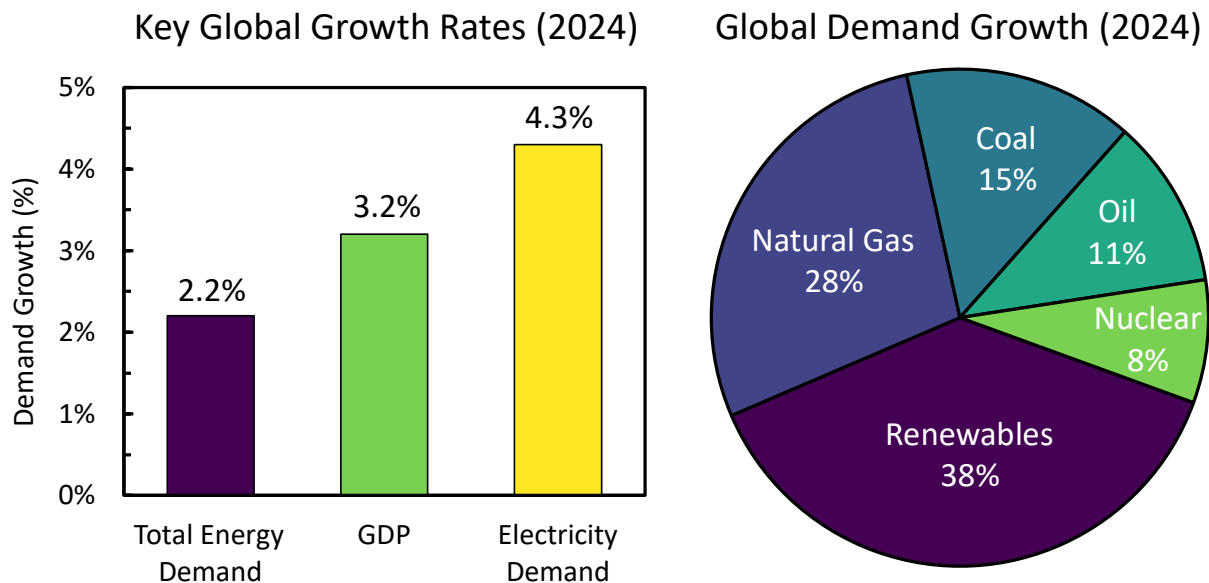


Figure 1. (left) 2024 growth rates of total energy demand (dark purple), gross domestic product (light green), and electricity demand (yellow); (right) global energy demand growth by energy source. Reproduced from [1].

However, integration of renewable energy sources into the grid is accompanied by issues of energy production intermittency. All renewable energy sources (e.g., solar and hydropower) are cyclic in nature and do not produce a constant amount of energy over time. For example, this intermittency results in a greater insufficiency of solar production to meet electricity demand at night than between 9:00 am and 5:00 pm: the infamous “duck curve,” as shown in **Figure 2**. Over the last ten years, technological advancements in solar harvesting technology have decreased the gap between production and demand to nearly zero during peak daylight hours.² However, the efficiency of a solar panel cannot help during periods of darkness, and so another technology is needed to supplement renewables during times of low energy production.

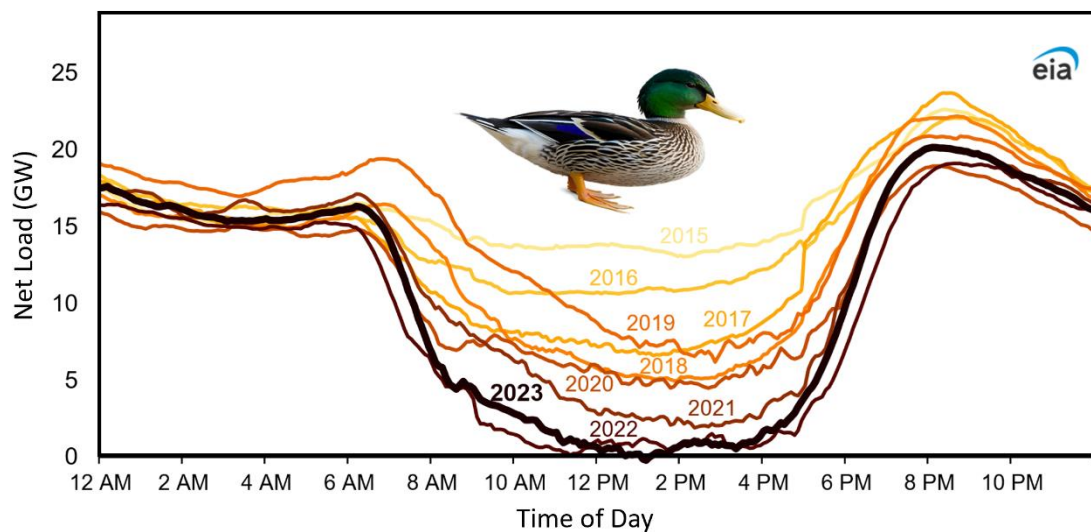


Figure 2. The “duck” curve of net-load vs. time of day for the lowest net-load day of each spring in California from 2015-2023. Reproduced from [2].

Periods of high net-load on the grid are presently compensated by burning non-renewable coal and natural gas. Instead, batteries could be used to provide energy during the high net-load times by harvesting additional energy during peak generation hours - in other words, “load-leveling” by combining intermittent renewable energy sources with batteries. Unfortunately, batteries are presently not an attractive solution for load-leveling, especially over long periods of storage time on the order of months to years due to high upkeep costs.^{3,4} For batteries to emerge as an economically feasible alternative to non-renewable resources for load-leveling, next-generation materials with higher energy densities and lower costs will be required. While many researchers turn to beyond-lithium chemistries to meet these challenges, we focus herein on relevant materials for cost-effective LIBs, as described in **Chapters 5 and 6**.

High Power Applications for Data Centers

An emerging application of electrochemical energy storage is power delivery for artificial intelligence (AI) datacenters, which face unique grid intermittency issues. In particular, AI datacenters face the distinct challenge of “power quality”⁵, the ability to deliver high power as demanded by the specific application. For AI datacenters, that demand is a rapidly alternating “swing power” pattern for overclocking graphics processing units (GPUs) as part of the AI model training process. The power profile of a representative collection of such GPUs is shown in **Figure 3**, where the normalized power requirement can be seen to oscillate several times per minute for second-long durations.⁵

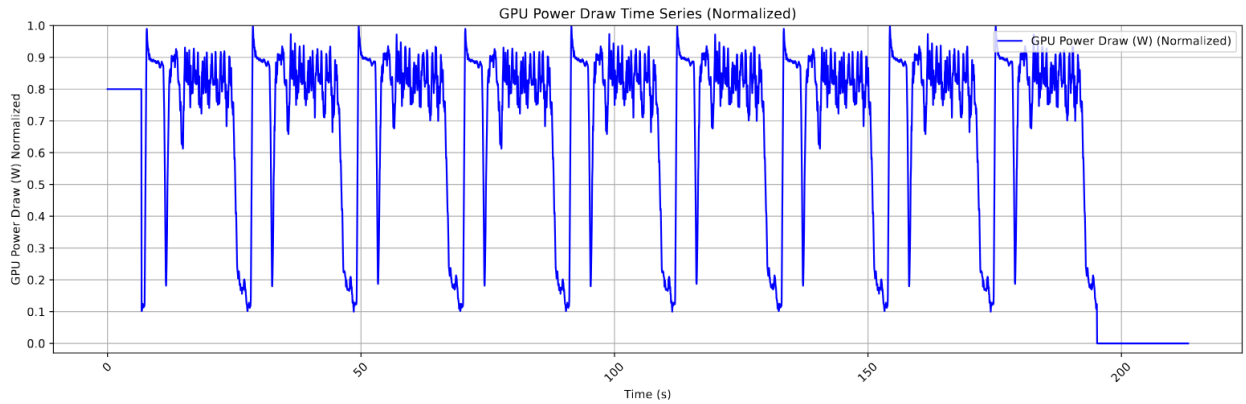


Figure 3. Temporal normalized power profile of a rack of DGX-H100 GPUs during AI model training. Reproduced from [5].

If the large swings in power demand shown in **Figure 3** are to be met by electrochemical energy storage infrastructure instead of other means, batteries that can deliver energy at high power outputs are needed. Presently, there are two commercial solutions to deliver the power quality needed for datacenters via electrochemical energy storage: LIBs with LiFePO_4 (LFP) cathodes and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anodes, and “supercapacitor” systems that store ions at the surface of symmetrical porous carbon electrodes.⁶ The low voltage of the LFP||LTO system (~ 2 V) and the sloping voltage profile of supercapacitors both come with large energy density drawbacks compared to traditional LIB systems. This motivates the search for new high-power lithium-ion storage materials that exhibit a similar capacity to graphite at a similarly low electrode potential. A novel class of such materials is described and explored in **Chapter 4**.

Battery Development for Electric Vehicles

Electric vehicles (EVs), particularly automobiles, represent a crucial research application for batteries. In 2025, EV sales increased by 22% globally, up to 21.6 million units (**Figure 4**), and accounted for $>50\%$ of all new vehicle sales in China.⁷

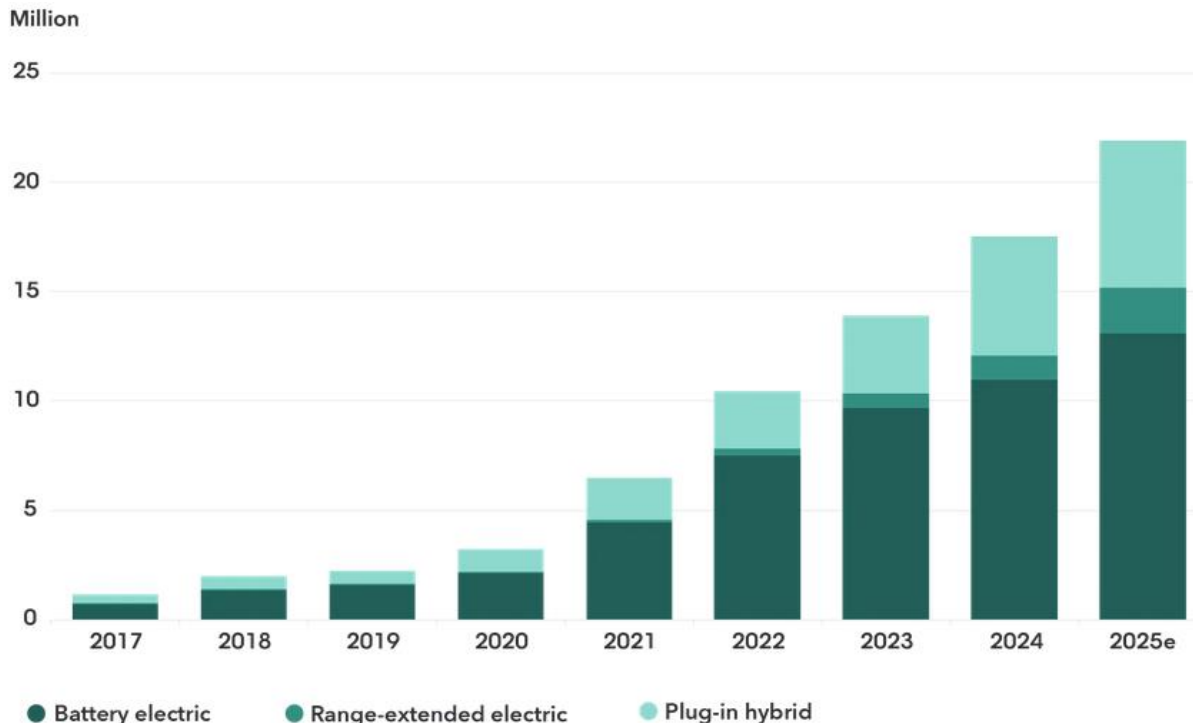


Figure 4. Millions of global passenger EV sales by drivetrain per year. Reproduced from [7].

However, adoption of EVs into the global economy is presently hindered by the cost, charging rate, and distance capabilities of the batteries in these vehicles. LFP and $\text{LiMn}_x\text{Ni}_y\text{Co}_z\text{O}_2$ (NCM, where $x + y + z = 1$) (**Figure 5**) are the two prominent cathode materials deployed in the EV market, while the only primary anode material currently used for EV applications is graphite. All three of these materials are characterized by low to modest specific capacities (theoretical capacities of 160, 275, and 372 mAh g^{-1} for LFP,⁸ NCM111,⁹ and graphite,¹⁰ respectively), limiting the number of miles that an EV can travel on a single charge. Next-generation electrodes like sulfur cathodes ($\sim 1700 \text{ mAh g}^{-1}$)¹¹ and silicon anodes ($\sim 3600 \text{ mAh g}^{-1}$)¹² hold promise for increasing the energy density of next-generation electric vehicles, increasing EV adoption due to the lower cost and longer range capabilities associated with these chemistries.¹³

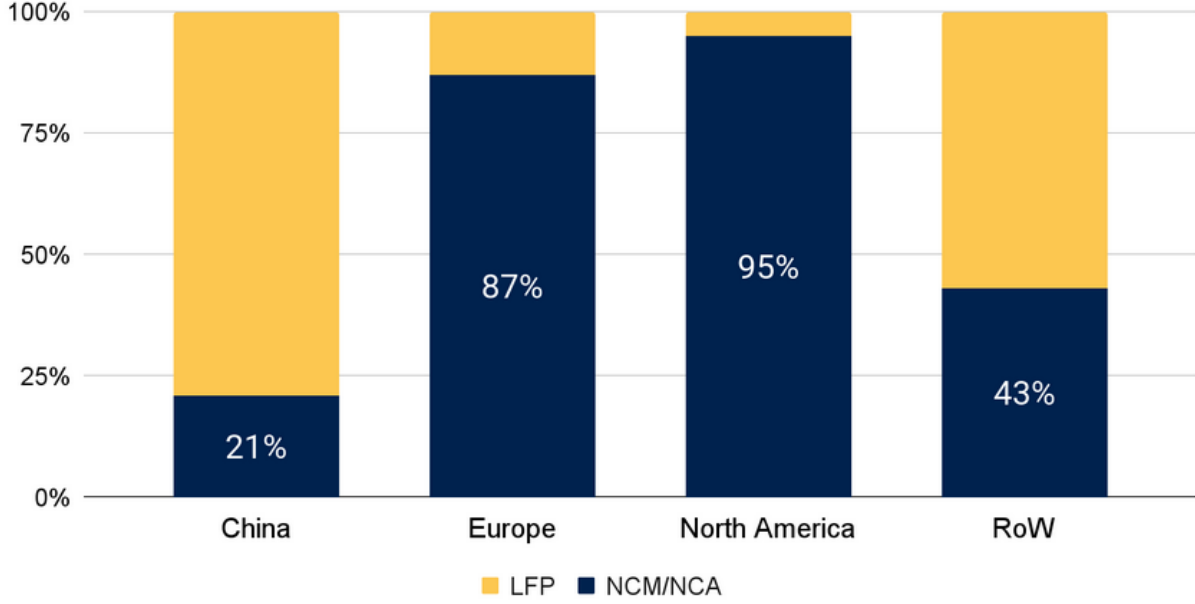


Figure 5. Percent of passenger car and light duty EV sales share by cathode chemistry from Jan-Nov 2025. RoW refers to the rest of the world. Reproduced from [7]. Note that NCA refers to $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ cathodes, which are structural analogs to NCM.

Operating Principles of Batteries

The chief function of a battery is to act as a reservoir of chemical potential, which can be spontaneously discharged to deliver electrical power. As depicted in **Figure 6a**, Li^+ ions migrate between the cathode and the anode of an LIB cell over the course of charging and discharging. The voltage of the cell is dictated by the relative electrochemical potentials of the cathode- and anode-specific lithiation events as shown in **Figure 6b** and **Equation 1**:

$$E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}} \quad (1)$$

where E_{Cell} , E_{Cathode} , and E_{Anode} are the cell voltage, the cathode potential, and the anode potential, respectively. For example, the voltage of an $\text{Li}||\text{TiS}_2$ cell would be lower than an $\text{Li}||\text{LiCoO}_2$ cell since cobalt oxide provides a more stable lithiation environment (i.e., characterized

by a higher electrochemical potential and lower energy) than sulfur. The relationship between the Gibbs free energy and electrochemical potential of a reaction is given by **Equation 2**:

$$\Delta G_{Cell} = -nFE_{Cell} \quad (2)$$

where ΔG_{Cell} is the Gibbs free energy of the reaction, n is the number of electrons transferred in the redox reaction, F is Faraday's constant, and E_{Cell} is the voltage of the cell.

The energy density of a given electrode can then be calculated for a given full cell system by multiplying the average voltage by the limiting electrode capacity, yielding a total energy as shown in **Equation 3**:

$$E_g = E_{Cell} \cdot q \quad (3)$$

where E_g is the gravimetric energy density of the cell, E_{Cell} is the average voltage of the cell, and q is the specific capacity transferred between electrodes during charging and discharging.

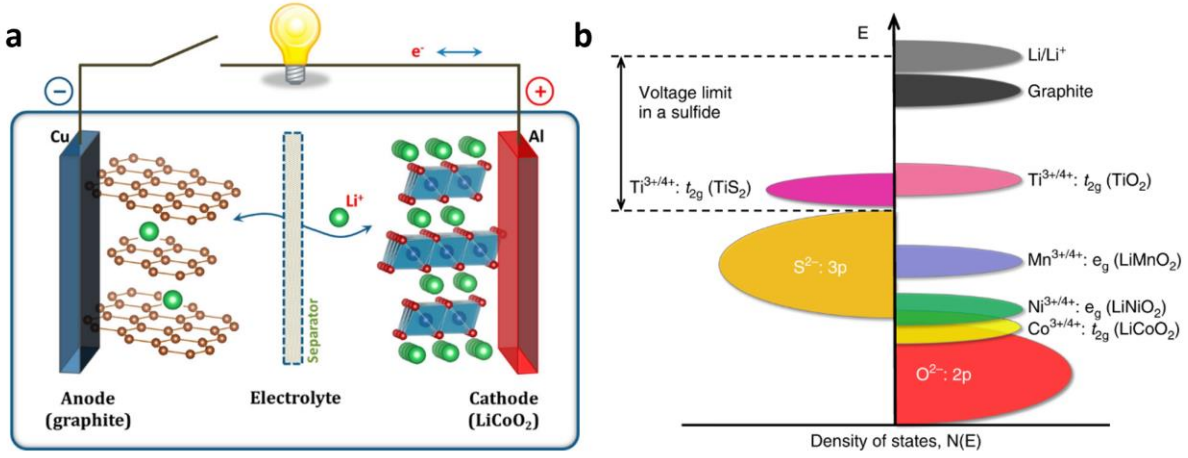


Figure 6. (a) Schematic of an LIB¹⁴ and (b) reduction potential energy landscape of redox events within common LIB materials.¹⁵

The energy density of a cell is a key performance indicator for real-world use. However, other metrics, such as power density are also crucial for certain applications (e.g., AI datacenters, **Figure 3**). Let the power of a cell be defined as in **Equation 4**:

$$P_g[t] = \frac{E_g[t]}{t} \quad (4)$$

where $E_g[t]$ is the energy density at a particular charge/discharge rate, $P_g[t]$ is the power density at that charge/discharge rate, and t is the total charging time at that charge/discharge rate. Frequently, $E_g[t]$ is expressed in units of Wh kg⁻¹, $P_g[t]$ in W kg⁻¹, and t in h. Note that the power density as expressed above is calculated for a series of discrete charging time values, not as a continuous function of t . The dependence of P_g on t arises from the time dependence of $E_g[t]$, which in turn is affected by the change in average potential and capacity from impedance effects at faster charging timescales.

This relationship considers the shifting energy density of a cell due to rate limitations, as well as the time of charge/discharge, to describe the amount of power that can be delivered at that rate. The relationship between power density and energy density can be visualized in a Ragone plot, as shown in the following section.

Types of Electrochemical Energy Storage

The tradeoff between energy and power density for a given energy storage system are commonly visualized in a Ragone plot, as shown in **Figure 7**.¹⁶ Technologies such as Li^+ ion batteries, sodium-ion batteries, solid-state batteries, and supercapacitors all possess different characteristics for energy and power density. In general, the battery technologies offer high energy densities but low power densities. Supercapacitors occupy the opposite extreme, capable of delivering energy extremely rapidly, but only in small quantities. The starred region in **Figure 7** (described below) is the target for next-generation high-power energy storage materials.

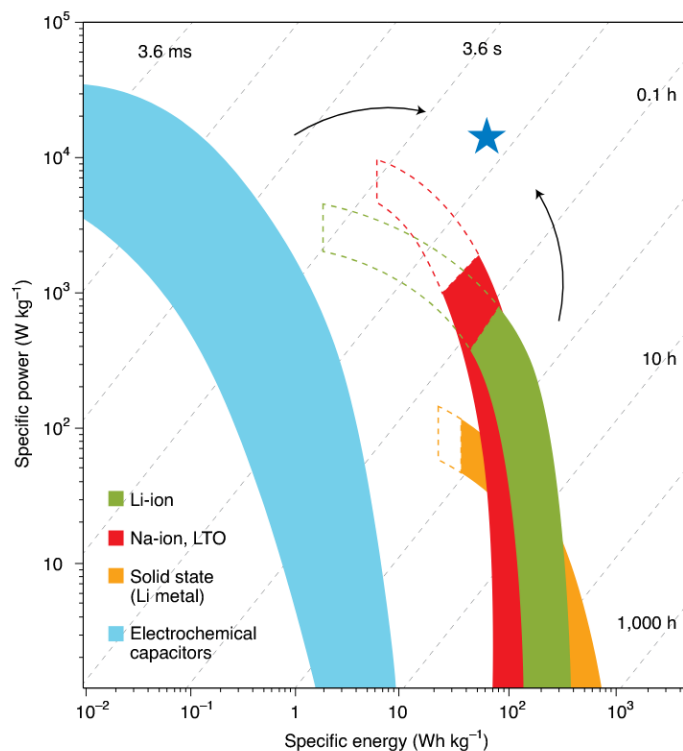


Figure 7. Ragone plot showing the relationship between energy density and power density for relevant energy storage devices. The star represents the target of new, high-power energy storage devices. Dashed line regions indicate changes in performance from the use of advanced cycling protocols. Figure reproduced from [16].

Battery materials store charge faradaically, in that they undergo full charge transfer reduction-oxidation (redox) reactions upon ion insertion. In many battery materials, faradaic charge transfer is coupled with solid-state mass-transfer kinetic of ions within the host lattice (see **Chapter 3**), limiting their kinetics and resulting power density capabilities. Supercapacitors, by contrast, operate only through coulombic forces at the surface of the host material and therefore do not have mass transfer limitations on their kinetics due to a lack of Li⁺ ion diffusion through the bulk. The tradeoff in energy and power between batteries and supercapacitors appears inherently limiting given the fundamental differences in their lithiation mechanisms. However, novel materials have recently been discovered that are capable of ultrafast storage at industrially

relevant energy densities, termed pseudocapacitors.^{17–19} Pseudocapacitors are defined as faradaic charge storage materials that do not exhibit the same mass transfer diffusion kinetic limitations as batteries, making them excellent candidates for ultrafast battery materials that could occupy the high-energy/high-power phase space denoted by the star in **Figure 7**.^{16,20,21} Notably, the discovery of pseudocapacitors is not new, and dates back to the 1960s with the work of Conway and Gileadi.^{22–25} However, their definitions of pseudocapacitance were preliminary and the materials were only discussed in the context of aqueous charge storage systems. By contrast, this discussion focuses on novel materials for high energy-density lithium-ion storage systems.

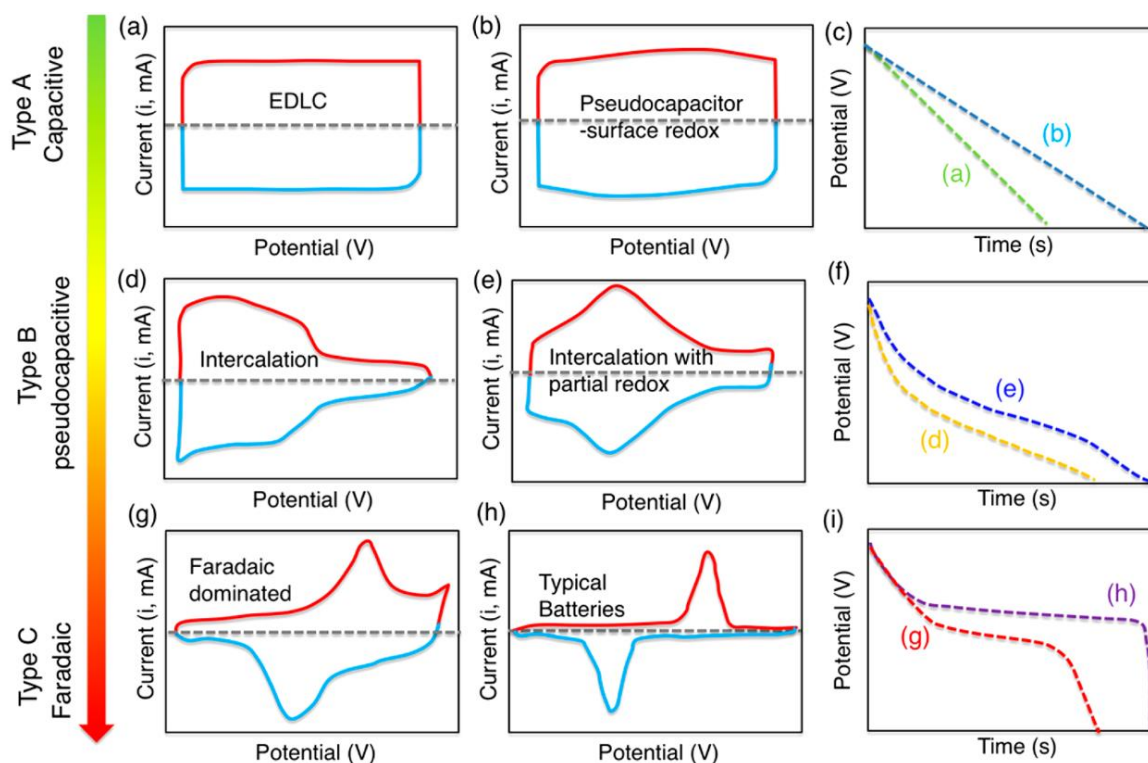


Figure 8. Characteristic voltage profiles and voltammograms for (a-c) capacitive, (d-f) pseudocapacitive, and (g-i) faradaic charge storage materials.

Different types of pseudocapacitance are characterized by distinct electrochemical signatures as shown in **Figure 8**.²⁶ Intercalative pseudocapacitors are of particular note, as they demonstrate very fast charge transfer kinetics and semi-resolved plateau regions as shown in **Figure 8f**. The combination of these two characteristics is ideal for maximizing energy and power density simultaneously for a given cell, as the Li^+ ion insertion energy can be tuned via structural and electronic design of the host.

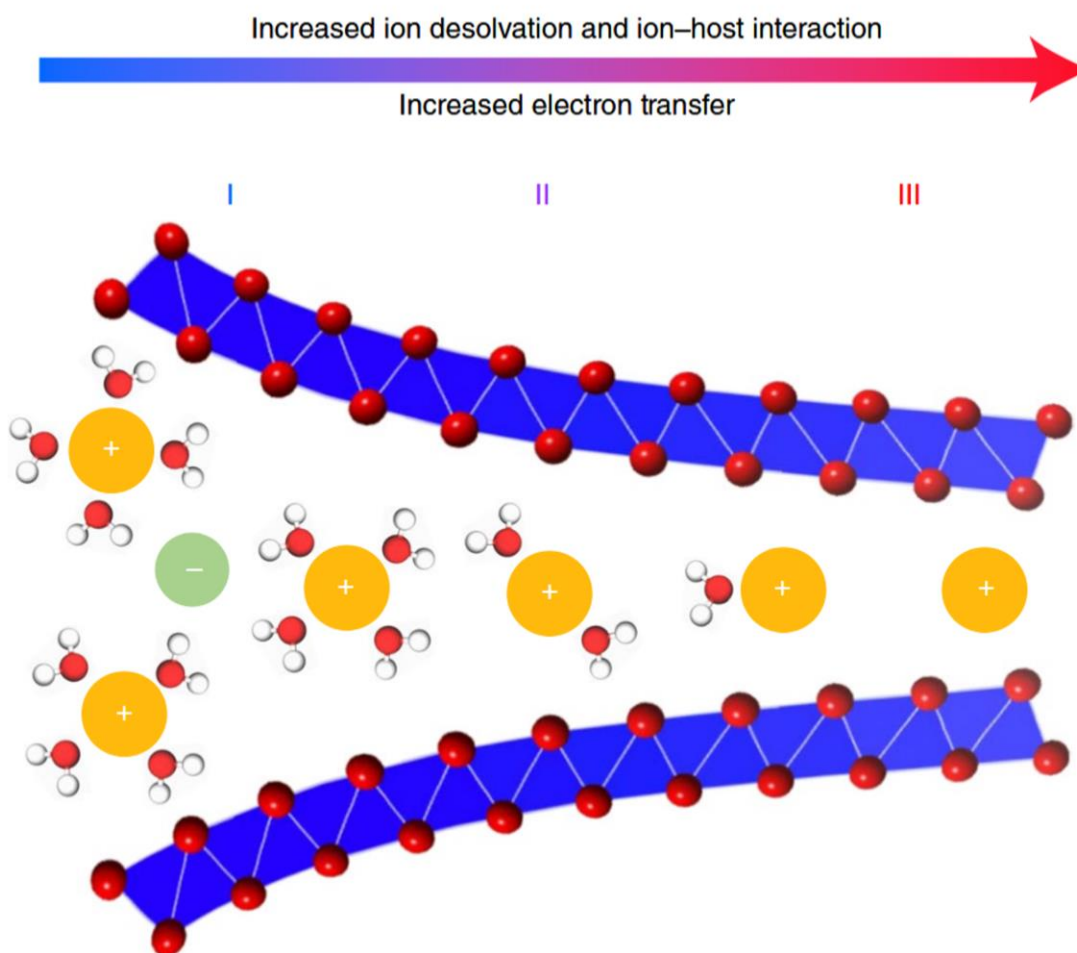


Figure 9. Steric model of intercalative pseudocapacitance depicting greater degrees of ion desolvation for tighter interlayer spacings. Reproduced from [20].

A general model for intercalative pseudocapacitance is shown in **Figure 9**. Recent literature has postulated that Li^+ ion desolvation is the rate-limiting step that causes mass transfer diffusion limitations in battery materials, corresponding to a Type III structure (e.g., graphite).^{20,27–29} In this model, a pseudocapacitive material (Type I or II) would still undergo discrete electron transfer between the ion and the host, but have a gallery spacing wide enough to accommodate co-intercalation of solvent molecules with the ion. The question of whether pseudocapacitance constitutes a single discrete mechanism or a convolution of simultaneous faradaic and non-faradaic processes remains debated. This ambiguity is not purely semantic, and is further compounded by the techniques classically used to measure it.^{30,31}

The standard method for evaluating whether a material exhibits faradaic charge storage, capacitive charge storage, or something in between (i.e., pseudocapacitance) is Randles-Ševčík analysis. In this method, the CV current response of a material is tested as a function of increasing sweep rate. A diffusion-limited battery material presents a current response dependence on sweep rate according to **Equation 5**, while a non-diffusion limited material will present a current response dependence on sweep rate according to **Equation 6**.^{32,33}

$$i \propto \nu^{0.5} \quad (5)$$

$$i \propto \nu^1 \quad (6)$$

where i is the current generated by the voltage sweep and ν is the voltage sweep rate.

Unfortunately, CV cannot be used alone to assess if a mechanism is pseudocapacitive, as “true” pseudocapacitance cannot be distinguished from the linear combination of diffusion limited and capacitive processes.^{30,31} Additionally, such methods can be inappropriate for use in materials with

fast ion-conductivity, but poor electronic conductivity, like the materials explored in **Chapter 4**. In such cases, more advanced methods for assessment of pseudocapacitance must be employed (see **Chapter 3**).

Next-Generation Anode Candidates for Lithium-Ion Batteries

The Graphite Standard

To improve upon graphite, we must first discuss the fundamental working principles of graphite as a lithium-ion anode itself. Graphite has served as the gold standard anode material for LIBs since their commercialization in the 1990s.³⁴ It exhibits a respectable specific capacity of 372 mAh g⁻¹ (as LiC₆), an average voltage of only ~100 mV vs. Li⁺/Li, and extremely high electrochemical stability due to the topotactic nature of LiC₆ formation and native thermodynamic stability.

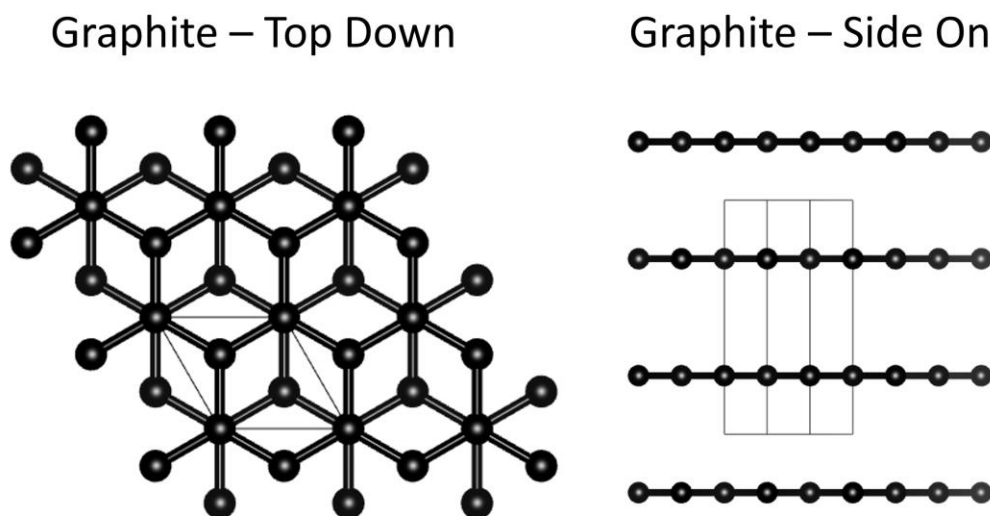


Figure 10. Top-down and side-on views of the graphitic crystal structure.

Carbon materials can generally be delineated into sp^3 -hybridized and sp^2 -hybridized structures. sp^2 -hybridized carbon structures, such as graphite, have rapid electrical conductivity properties arising from their delocalized π -network of electrons in the partially filled unhybridized $2p_z$ orbital. The graphitic structure consists of 6-membered carbon rings, resulting in a hexagonal unit cell (**Figure 10**). Other non-graphite carbon structures such as carbon nanotubes, carbon fibers, graphene, and turbostratic disordered carbons are also primarily sp^2 -hybridized, lending them strong conductivity properties and the capability to store lithium-ions through the reduction of the un-hybridized $2p_z$ orbital.

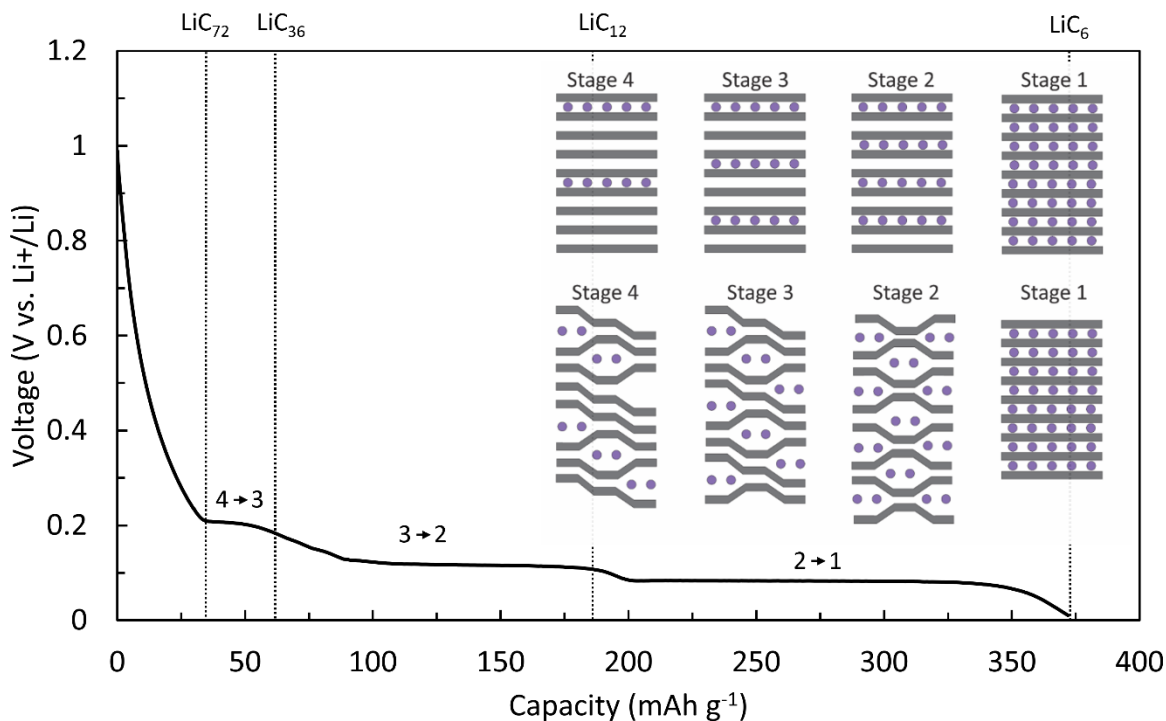


Figure 11. Lithiation voltage profile of graphite at a slow rate ($C/100$, a 100 h charging time). The inset figures depict (top) Rüdorff and Hofmann³⁵ and (bottom) Daumas-Hérold³⁶ models of Li^+ ion intercalation in graphite. Note that the capacity of the graphite electrode was normalized to 372 mAh g^{-1} for clarity. Annotations and dotted lines are presented to guide the eye. The inset was reproduced from reference [37].

Li^+ ion intercalation between graphitic sheets is the main mode of ion storage for sp^2 -hybridized carbon structures. Two models of staged Li^+ ion intercalation in graphite are shown alongside an experimental voltage profile for lithium insertion into graphite in **Figure 11**. The Rüdorff and Hofmann model (top) assumes that symmetry coupling effects dominate, resulting in continued filling of single galleries until they are full, going from every 4th gallery (stage 4) to every gallery (stage 1) in concerted steps, as each stage must complete its formation before the next staging can begin. The Daumas-Hérol model takes a slightly different approach, in which certain galleries partially fill in an alternating pattern to minimize steric strain during intercalation, while maintaining periodicity (as measured by in situ diffraction). The dotted lines on the voltage profile correspond to filling stoichiometries for these models: Stage 4 (LiC_{72}), Stage 3 (LiC_{36}), Stage 2 (LiC_{12}), and Stage 1 (LiC_6). These symmetrically relevant stoichiometries correspond to the experimentally observed plateau transitions in the voltage profile when it is normalized to the theoretical capacity of LiC_6 . Notably, the actual staging mechanism of lithium in graphite is still contested within the literature, with different opinions on the structure and even stoichiometry of the electrochemically synthesized staged compounds.^{38–40}

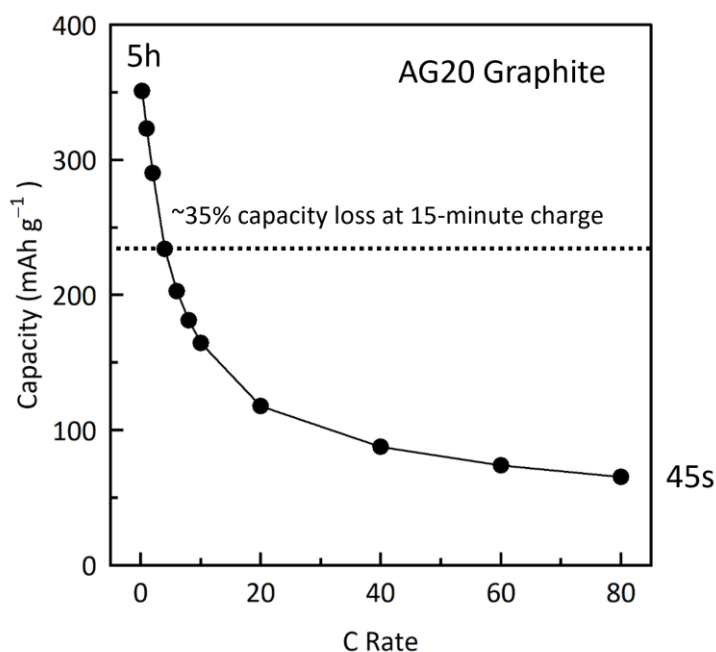


Figure 12. Rate capability of a synthetic graphite (AG20,⁴¹ 20 μm particle size) in a cell with a lithium metal counter electrode.

While there are very few materials that can improve upon its average potential and electrochemical stability, there are many materials with a higher specific capacity and/or higher rate capability than graphite. Rate capability is generally reported as the capacity retention from cycling at faster “C-rate”, which is a unit describing how many times a cell can be charged within an hour. For example, a 10C rate would correspond to the rate at which a cell could be charged ten times (i.e., six minutes), whereas C/10 would be the rate at which a cell could be charged by 1/10th of its capacity in an hour, corresponding to a ten-hour charging time. Despite its excellent electronic conductivity, graphite demonstrates poor rate capability due to the large degree of phase change and desolvation required to store lithium-ions within the graphitic lattice (**Figure 9**), causing it to lose 35% of its capacity when cycling rate increases from a 5-hour cycle (C/5) to a

15-minute cycle (4C) as shown in **Figure 12**.^{20,21} The rate limitation of graphite is attributable to the slow process of lithium intercalation into tight graphitic galleries ($d_{(002)} = 3.34 \text{ \AA}$ for pristine graphite). Formation of staged graphitic intercalated compounds requires a first-order phase transition and near full desolvation of intercalated Li^+ ions, resulting in the flat voltage profile shown in **Figure 11**.^{29,42,43} Together, these factors result in sub-par rate capability as shown in **Figure 12**, motivating the search for other carbon materials that are capable of faster charge storage.

(i) Advanced Carbon Materials for LIB Anodes

The high natural abundance of carbon incentivizes the development of alternative carbon-based materials for high-power applications.^{44,45} Turbostratic disordered graphitic materials, often categorized as soft (“graphitizable”) or hard (“non-graphitizable”), have been previously investigated as LIB anodes – in fact, a variant of soft carbon was the first commercialized anode for LIBs by Sony in 1991, though it was quickly replaced with graphite once suitable electrolyte systems were developed.³⁴ We note that “soft” and “hard” carbon designations were coined by the prominent X-ray crystallographer Rosalind Franklin in the 1940s and 50s,^{46–49} and hence these terms will be used throughout this discussion. While both soft and hard carbons undergo disordered intercalation and surface storage lithiation reactions, hard carbons also undergo closed-pore filling processes, leading to their ascent as the premier sodium-ion battery (SIB) anode material at the time of writing.^{50–55}

The disordered nature of turbostratic carbons result in larger d-spacings due to steric repulsion from curvature and disorientation of adjacent graphene layers, resulting in more facile ion storage.^{46–49,56–58} Some disordered carbon materials with high hydrogen content have also

shown a remarkable increase in capacity compared to graphite, however that capacity has been shown to be extremely rate limited and is associated with a prohibitive degree of voltage hysteresis.^{59,60}

Although the enlarged interlayer spacings in disordered carbons can enhance rate capability, the structural disorder simultaneously lowers reversible capacity and raises the average lithiation potential. This is due to the heterogeneity inherent to an amorphous crystal structure. The Li^+ ion density of intercalated disordered carbons cannot approach that of a closest-packing graphitic crystal structure, and the varied lithiation environments from the turbostratic nature of disordered carbon creates a variety of lithium insertion site energies, linearizing the voltage profile and decreasing the energy density of the anode.

As described in **Chapter 1**, a primary objective of this dissertation is to study Li^+ ion storage in an ordered hexa-peri-hexabenzocoronene (HBC) herringbone structure to establish a new class of crystalline carbon structures for higher rate lithium-ion insertion. Other PAHs have been studied as Li^+ ion anode materials, but exhibit similar charge storage characteristics to disordered carbon, with what appears to be graphitic-type intercalation being the only notable charge storage mechanism.⁶¹ The phase space of PAH structures is shown in **Figure 13**. The four major PAH crystal structures are described by Desiraju and Gavezzotti as herringbone, sandwich, γ , and β . The four structures are formed due to varying “gliding” and “stacking” forces, the ratio of which describes how the size of a given molecule’s π -cloud stabilizes a stacked structure through π - π interactions. Notably, intercalative pseudocapacitance has only been demonstrated for γ -structure PAHs insofar, with only HBC presenting reversible charge storage in the crystalline form.

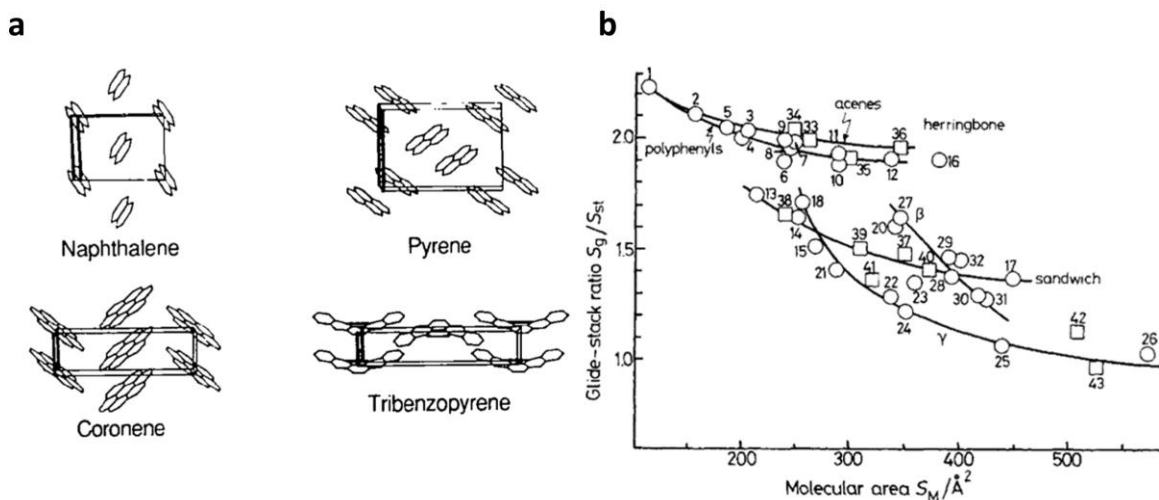
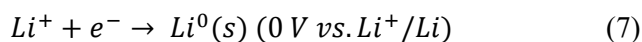


Figure 13. (a) The four basic aromatic crystal packings as exemplified by naphthalene (herringbone), coronene (γ), pyrene (sandwich) and tribenzopyrene (β). (b) Glide-stack ratio vs. molecular area for 43 different PAHs. Each line describes a subcategory of PAH crystal structure: herringbone, sandwich, β , and γ . Reproduced from [62].

(ii) Non-Carbon Materials for LIB Anodes

Alloying and conversion storage mechanisms are also extremely important to consider for next-generation LIB materials. The topotactic nature of intercalation causes it to be an extremely reversible mode of ion storage, given that the crystalline framework is largely retained upon ion (de)intercalation. However, that same topotactic characteristic limits the density of ions that can be stored within a given material.

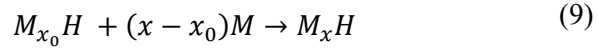
The energetic boundary conditions of a modern LIB system are defined by lithium metal plating/stripping and electrolyte oxidation at the low and high potential limits, respectively. The plating reaction of a lithium-ion to solid lithium is shown in **Equation 7**:



where Li^+ is a lithium ion and $Li^0(s)$ is lithium metal. For lithium to be thermodynamically inserted within an anode material, a given lithiation reaction must have a reduction potential above that of lithium plating (i.e., it must have a more favorable Gibbs free energy of formation than lithium metal). Simplistically, this means that the more the attractive forces (e.g., orbital overlap coupling) outweigh the repulsive forces (e.g., coulombic repulsion) of a formed phase, the more stable the energy of formation and the higher the reduction potential at the anode. This is described by Joshi et al. in **Equation 8**.^{63,64}

$$V = - \frac{E(M_xH) - E(M_{x_0}H) - (x - x_0)E(M)}{x - x_0} \quad (8)$$

corresponding to a hypothetical lithiation reaction:



where V is the average insertion voltage, E is the energy of a given phase, M_xH is the lithiated host, $M_{x_0}H$ is the delithiated host, M is the alkali metal reactant, and $x - x_0$ is the stoichiometric quantity of alkali metal being stored. **Equation 8** encodes the stabilization effect of host-guest coupling, the energy requirement for structural deformation of the host lattice, and the electrostatic repulsion of neighboring intercalated ions by the calculated difference in energy between the products and reactants. The maximum capacity of a material can be defined within this framework as the number of lithium ions that can be inserted into a host before V becomes negative due to changes in energy in any of the above factors. It follows that a higher anode potential is not necessarily beneficial for energy density (in fact it decreases energy density according to **Equation 1**, but it can enable an increase in capacity depending on what types and magnitudes of forces are limiting the insertion of more lithium ions into the host structure.

Equation 8 describes a theoretical framework for selecting appropriate Li^+ ion host materials by the stability of a lithiated state in comparison to the delithiated state. The potential of a particular lithiation event can be predicted by stabilizing host-ion interactions, decreasing the energy required for host phase change, or screening coulombic repulsion between neighboring Li^+ ions. This effect is exemplified in the theoretical study of a borylated analog of graphite, BC_3 . The electron-deficient boron atoms within the graphitic lattice of BC_3 cause an increase in coupling between the Li^+ ion and the host lattice, increasing the lithiation potential. Thus, BC_3 is postulated to be capable of intercalating nearly double the number of Li^+ ions compared to graphite (858 and 372 mAh g^{-1} for BC_3 and graphite, respectively) before the Li-Li coulombic repulsion and structural deformation cause the intercalation potential to become less favorable than lithium plating.

An obvious design approach for next-generation anode materials would then be to investigate host materials for Li^+ ion storage that have stronger interaction energies with Li^+ ions, screen coulombic repulsion between ions, and have a lower energetic penalty for structural reorganization. This logic has led to the investigation of elemental silicon as a next-generation Li^+ ion anode. Due to its large negative enthalpy of lithiation, combined with the ability for full structural rearrangement under relevant thermodynamic conditions, Si can store up to 3.75 Li per 1 Si atom before plating lithium, compared to 1 Li per 6 C atoms in graphite, resulting in a $\sim 10\times$ increase in gravimetric capacity (3579 mAh g^{-1} for $\text{Li}_{15}\text{Si}_4$, compared to 372 mAh g^{-1} for LiC_6).^{12,65,66}

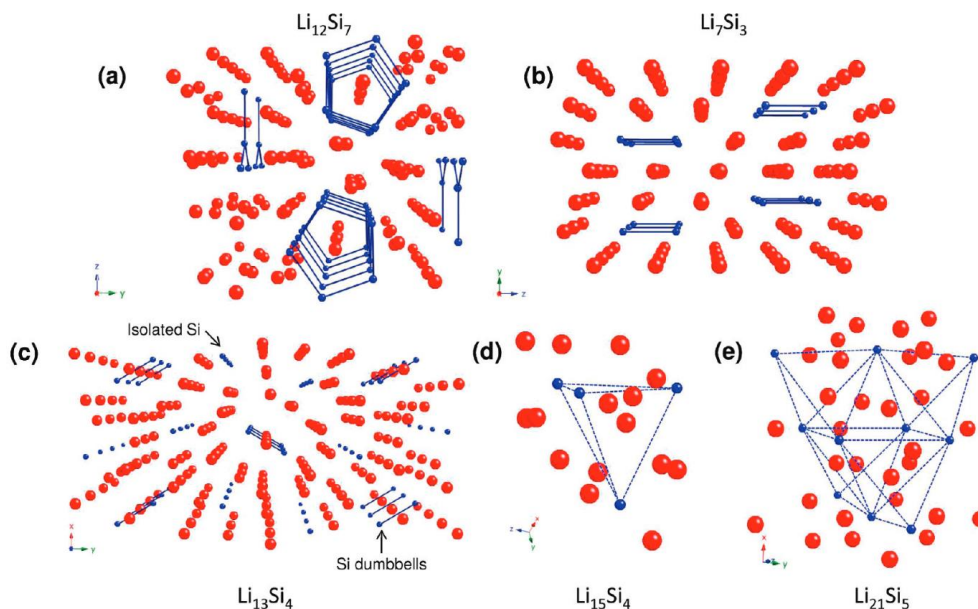


Figure 14. Structural representations of (a) $\text{Li}_{12}\text{Si}_7$, (b) Li_7Si_3 , (c) $\text{Li}_{13}\text{Si}_4$, (d) $\text{Li}_{15}\text{Si}_4$, and (e) $\text{Li}_{21}\text{Si}_5$. Li and Si atoms are shown in red and blue, respectively; blue lines: Si-Si bonds; blue dashed lines: closest Si-Si contacts > than 3.0 Å. Reproduced from [67].

The lithiation mechanism of silicon includes formation of several amorphous intermediates simultaneously, such as $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , and $\text{Li}_{13}\text{Si}_4$, before formation of crystalline $\text{Li}_{15}\text{Si}_4$ when fully lithiated to <10mV vs. Li^+/Li , as revealed by operando NMR spectroscopy (**Figure 14**).⁶⁷ Notably, there are literature reports that use the stoichiometry and corresponding capacity of $\text{Li}_{21}\text{Si}_5$ when introducing silicon. However, the $\text{Li}_{21}\text{Si}_5$ phase does not form under standard temperature and pressure conditions, and thus should not be used for energy density benchmarks in silicon anodes, unless in the context of specialty applications.⁶⁸

While the theoretical performance of silicon is promising, with great capacity comes great expansion. Conversion of Si to $\text{Li}_{15}\text{Si}_4$ causes a >300% volumetric expansion over the course of lithiation, as every Si-Si bond is broken and replaced with an Li-Si bond.⁶⁹ This expansion is the root of several silicon degradation mechanisms when cycled in an LIB; including delamination,

particle fracture, and continuous solid electrolyte interphase (SEI) formation as depicted in **Figure 15**.^{70–77}

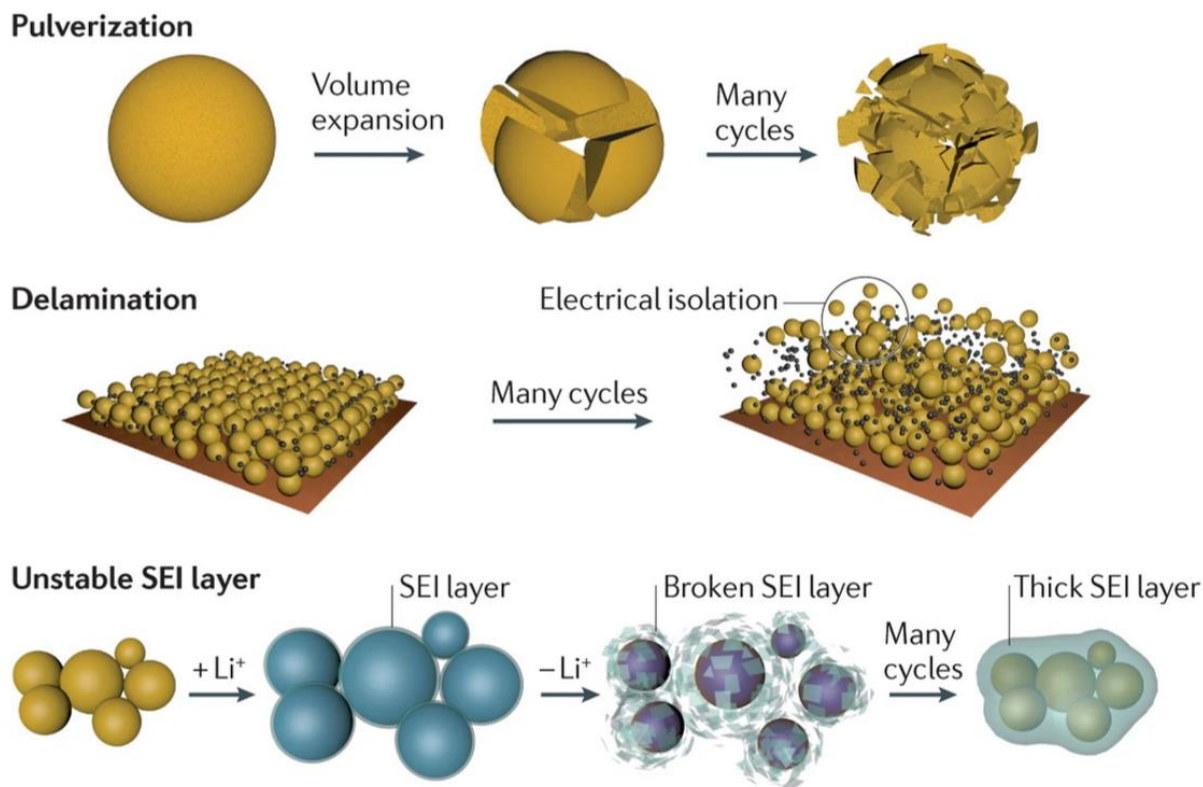


Figure 15. Schematic depiction of the three primary degradation mechanisms of silicon: pulverization, delamination, and continuous SEI formation. Reproduced from [69].

Two classes of silicon-based materials are currently under investigation with the goal to mitigate these expansion-induced degradation mechanisms: (i) partially oxidized silicon (SiO_x) comprised of nanodomains of Si and SiO_2 , and (ii) silicon-carbon (Si/C) composites where the silicon is intimately combined with a carbon substrate.^{78–80}

The lithiation mechanism of SiO_x is like that of silicon, but with several key distinctions. SiO_x is comprised of nanodomains of Si and SiO_2 as stated above. However, a primary chemical environment within the material is the interface between the Si and SiO_2 domains, representing

nearly a quarter of local diffraction environments.⁸¹ While bulk SiO_2 is electrochemically inert, these interfacial domains are thought to promote the irreversible formation of so-called expansion “buffering phases”, such as Li_2O and Li_xSiO_y , that could account for the promising electrochemical stability of the material.^{82,83} However, such buffering phases are also irreversibly formed, incurring a huge penalty in first-cycle coulombic efficiency, necessitating mitigation techniques such as prelithiation.^{83,84} Another strength of SiO_x is that the nano-sized Si environments in fully disproportionated SiO_x do not form crystalline $\text{Li}_{15}\text{Si}_4$ upon deep lithiation, the generation of which is deleterious for electrochemical stability.^{85,86} SiO_x anodes are covered in more detail in **Chapter 5**.

On the other hand, Si/C uses a carbon scaffold as its “buffering” phase, facilitating the expansion of the silicon phase into porous void space.⁸⁰ While SiO_x must have a particular disproportionated structure to function properly as an LIB anode,⁸⁷ Si/C is an umbrella term encompassing a host of silicon and carbon morphologies. The most common types of Si/C composites are synthesized mechanochemically^{88,89} or by chemical vapor deposition (CVD) of silane gas onto a carbon scaffold. In this work, we focus on the latter CVD method, as it is of particular fundamental and industrial interest.^{78,79,90–93} Si/C composites are covered more thoroughly in **Chapter 6**.

Both carbon and silicon materials discussed throughout this chapter have unique roles and challenges in the LIB anode landscape. Carbon possesses impressive stability and modest energy density characteristics arising from its topotactic lithium insertion mechanism, whereas silicon exhibits a much higher energy density at the cost of electrochemical stability due to large volumetric expansion when lithiated. The contrast in structural properties and applications for

carbon and silicon anodes for LIBs result in differing approaches to their study, which will be explored in the following chapter.

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CHAPTER THREE

METHODS

The research in this dissertation required the use of many non-traditional techniques designed to deconvolute complex systems into their constituent parts. We carry out this work with the goal of isolating variables which have an outsized impact on materials properties, which may otherwise not be observable. **Chapter 3** has been written to shed additional light on techniques which may benefit from being expounded upon, in ways that are not possible within their respective chapters.

Pseudocapacitance After Randles–ŠevčíkDeconvolving Ionic and Electronic Conductivity

Chapter 4 focuses on a class of molecular crystal hydrocarbons which were not previously known to have rapid lithiation kinetics, likely due to polarization effects which can dominate traditional battery testing protocols.¹ Two of the most prevalent battery testing techniques, cyclic voltammetry (CV) and galvanostatic charge and discharge (GCD), simultaneously probe the ionic and electronic conductivity properties for a given system. Therefore, both measurements are affected by mass transfer limitations and polarization effects simultaneously. This convolution poses difficulties when trying to isolate the impact of either the ionic or electronic conductivity on the performance of battery materials. This work uses modern techniques to address this problem for both CV and GCD cases. As the GCD case has been previously addressed by work in our group,² this section will focus on solutions to the polarization problem in Randles–Ševčík CV analysis.

Effects of Polarization on Randles–Ševčík Analysis

In **Chapter 4**, Randles–Ševčík analysis will be used as an initial survey to quantify the pseudocapacitance of several hexa-peri-hexabenzocoronene (HBC) materials. The base principle of the technique is simple, as described in **Chapter 2**. In a CV experiment, ion-storage materials present an $i \propto \nu^b$ relationship, where i is the current passed, ν is the sweep rate of the voltage in a CV experiment, and b is the relational exponent between the two.³ The b -value of this proportionality denotes the diffusion limitation of the system; diffusion-limited battery materials present a b -value of 0.5, while capacitive (surface storage, diffusion *unlimited*) mechanisms present a b -value of 1.⁴ Therefore, the diffusion limitation of a given material can be calculated by taking the slope of the $\log(i)/\log(\nu)$ plot as shown in **Figure 1**.

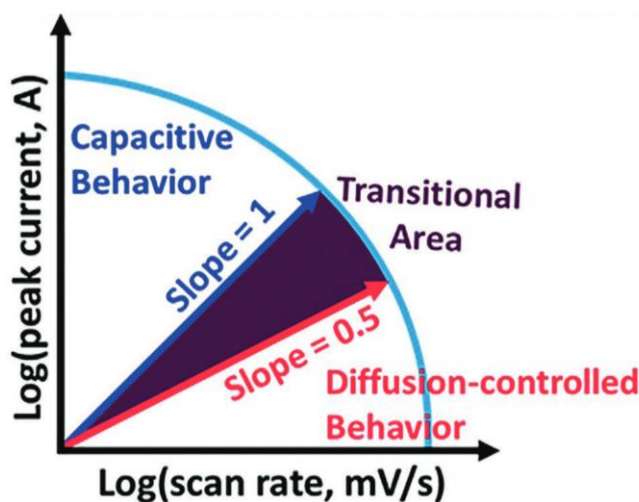


Figure 1. Schematic representation of a Randles–Ševčík $\log(i)/\log(\nu)$ plot, with capacitive (blue) and diffusion-controlled (red) slopes. Reproduced from [4].

A material that shows *some* diffusion limitation is depicted as the “transition area” in **Figure 1**, and is also referred to as “pseudocapacitive”. However, what happens when the slope of

the $\log(i)/\log(v)$ plot deviates from a linear line shape? Many materials show a “curling” phenomenon in their Randles–Ševčík plot when scanning at higher rates, which obfuscates the linear regression analysis, as shown for three HBC-derived materials in **Figure 2**. In all cases, the curling is attributable to polarization effects, which cause peaks of interest to shift out of the voltage window being scanned and artificially depresses the peak current. This is best demonstrated in the most resistive case, h-HBC, in **Figure 2a**. The resulting curl in the Randles–Ševčík plot of h-HBC in **Figure 2d** is much more pronounced and occurs at lower scan rates than for the more conductive p-HBC and c-HBC materials (**Figure 2e** and **f**) that exhibit less polarization. Curling effects are crucial to consider for low-potential LIB anode materials because the lithium plating reaction dominates at <0 V vs. Li^+/Li , effectively restricting the voltage window of the experiment. Thus, a small shift in CV peak position arising from polarization can result in a non-meaningful result from Randles–Ševčík analysis of low potential LIB materials.

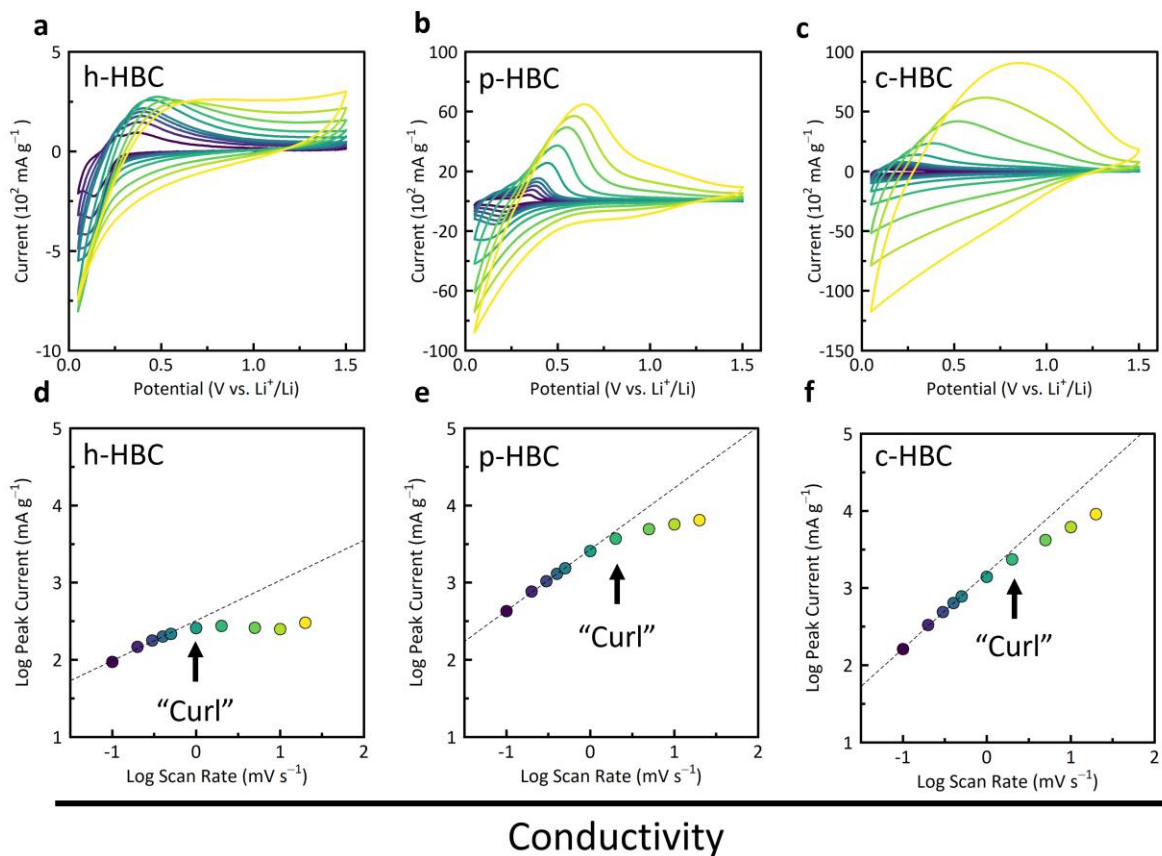


Figure 2. Variable sweep rate CV (top) and Randles–Ševčík plots (bottom) of (a, d) h-HBC, (b, e) p-HBC and (c, f) c-HBC from 0.01–1.5 V vs. Li^+/Li at scan rates of 0.1–20 mV s^{-1} .

Complications in Potential-Dependent Analyses

The effect of CV polarization on Randles–Ševčík analysis becomes particularly deleterious when plotting the slope of the $\log(i)/\log(v)$ plot (i.e., “b”) as a function of electrode potential as shown in **Figure 3**. Note that several values of b are below the physically relevant limit of 0.5, especially in the electrode potential regions in which there are peaks. The polarization effect is particularly exacerbated for samples with low electronic conductivity, such as h-HBC in the blue trace. Thus, alternative methods of analysis must be employed to accurately measure the potential-

dependent pseudocapacitance of low electrical conductivity materials, as discussed in the following section.

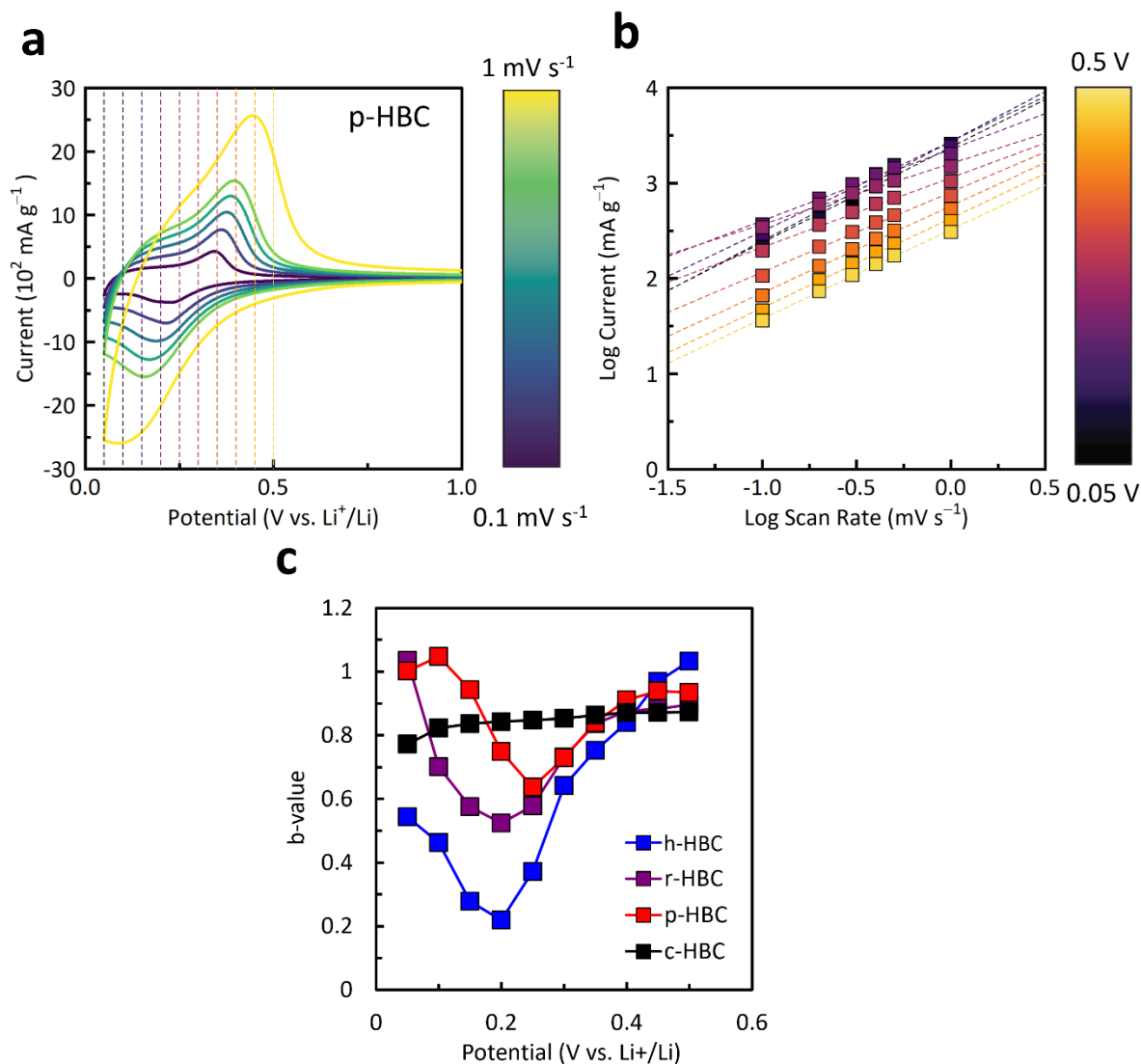


Figure 3. (a) p-HBC 4th cycle CVs from 0.01-1.5 V vs. Li^+/Li and scan rates of 0.1-1 mV s^{-1} , and (b) corresponding single-potential cathodic (lithiation) Randles-Ševčík plots taken at 50 mV intervals from 0.05-0.5 V vs. Li^+/Li ; (c) potential-dependent b-value plots for four HBC derivatives in 50 mV intervals from 0.05-0.5 V vs. Li^+/Li . Reproduced from **Chapter 4**.

Potential Dependent Bode Analysis for Resistive Electrodes

Randles–Ševčík analysis has been shown above to be limited in the case of samples with low electronic conductivity and redox events circa the plating and stripping potential of lithium. Thus, a more robust methodology for assessing the pseudocapacitance of these materials is needed. In recent years, a method for measuring pseudocapacitance called stepped-potential electrochemical impedance spectroscopy (SPEIS) has re-emerged.^{5–9} SPEIS is performed by measuring electrochemical impedance spectra (EIS) at different equilibrium potentials across the electrode potential profile to observe the impedance of an ion-storage system at various states of charge. The voltage step profile and current response of h-HBC during SPEIS is shown in **Figure 4**. The Bode plot for each potential step can be plotted by converting AC impedance values into real capacitance with **Equation 1**:

$$C' = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (1)$$

where C' is the real capacitance, $Z''(\omega)$ is the imaginary impedance as a function of angular frequency, ω is the angular frequency, and $|Z(\omega)|^2$ is the magnitude of the total impedance. The Bode plot for each potential can be plotted as a surface, as shown in **Figure 5**. The surface Bode representation demonstrates similar information to a cyclic voltammogram, such as charge storage response at a certain potential, but in the near-complete absence of polarization effects due to the long potential equilibration and small potential perturbation of the AC sine wave (5 mV).

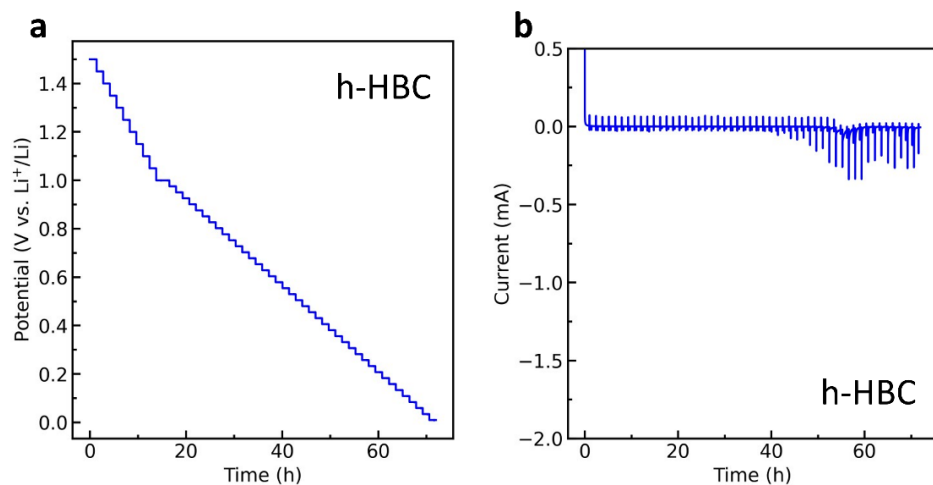


Figure 4. (a) Potential stepping profile and (b) current response of an h-HBC||lithium metal cell during SPEIS. Cells were stepped from 1.5-1.0 V and 1.0-0 V vs. Li^+/Li in 50 and 25 mV increments, respectively with a 1 h rest in between steps. Reproduced from **Chapter 4**.

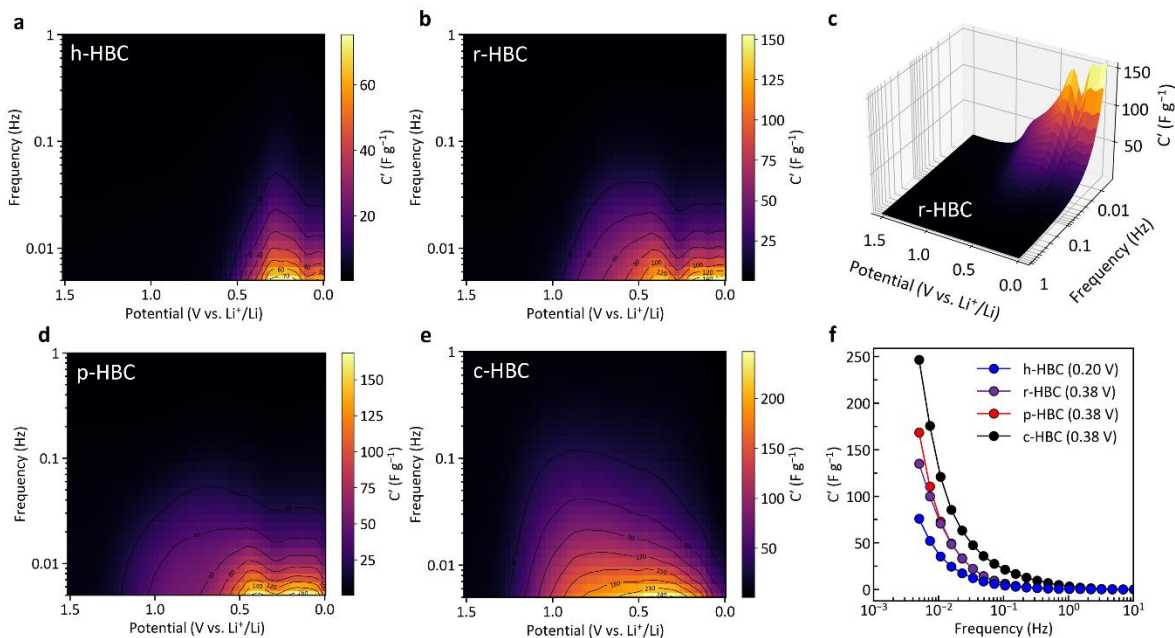


Figure 5. Real capacitance (C') as a function of EIS frequency (i.e., Bode plots) and potential (i.e., 3D Bode plots) of (a) h-HBC, (b-c) r-HBC, (d) p-HBC, and (e) c-HBC. (f) Standard Bode plots at selected potentials for all four HBC materials. Reproduced from **Chapter 4**.

Operando Synchrotron Energy Dispersive X-Ray Diffraction
(EDXRD)

Spatial Resolution of EDXRD

X-ray diffraction (XRD) is a crucial technique for elucidating the periodic structure of solids. The governing equation of XRD, Bragg's law is shown in **Equation 2**:¹⁰

$$n\lambda = 2d\sin(\theta) \quad (2)$$

where n is the order of the diffraction, λ is the wavelength of incident light, d is the distance between two planes in the real space crystal lattice for which the constructive interference condition of Bragg's law is satisfied, and θ is the angle of the incident light with respect to the parallel plane.

Generally, XRD is carried out in an angle-dispersive manner, where the λ of a benchtop light source (usually a copper filament) is held constant. Then, different values of d are measured as the angle θ is varied by a goniometer. However, angle-dispersive experimental designs have an inherent spatial resolution limitation. As the X-ray source and detector are moved in an angle-dispersive measurement, the volume of material being probed, termed the “gauge volume”, is constantly changing as shown in **Figure 6**, causing the gauge volume to decrease as the angle goes from θ_1 to θ_2 . Because the gauge volume is constantly changing in such an experiment, spatial resolution is extremely difficult, particularly in the reflection detection geometries that are most common for benchtop XRD instruments.

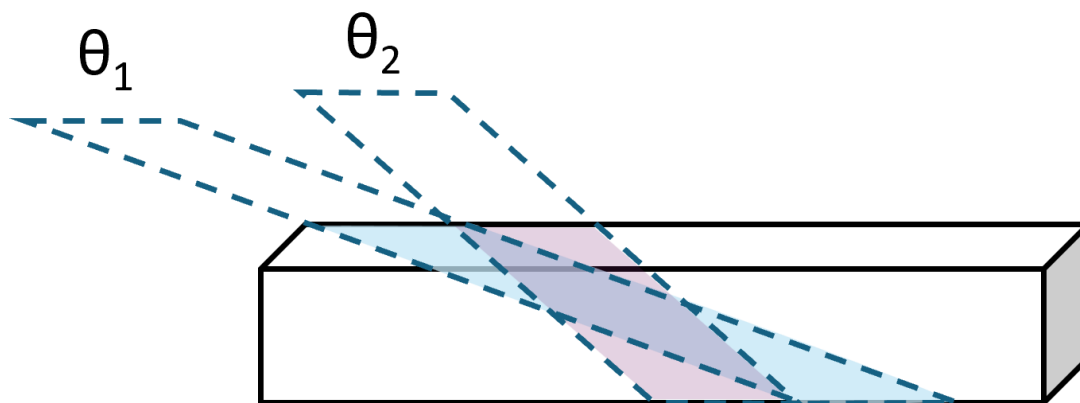


Figure 6. Schematic of gauge volume in a solid at two different incident angles. The increase in incident angle from θ_1 to θ_2 results in a decrease in corresponding gauge volume ($V_1 > V_2$).

In energy-dispersive XRD (EDXRD), θ is held constant and λ is varied due to the polychromatic nature of the incident light. An energy-resolved detector is then used to find the values of λ which satisfy Bragg's law. However, due to the requirement of a high flux of polychromatic white light, the use of EDXRD is restricted to synchrotron applications. The modulation of λ , rather than θ allows for the measurement of a precise gauge volume down to the μm^3 scale by modulating beam slit widths, which are depicted in the experimental setup in **Figure 7**.¹¹ The spatial resolution capabilities of EDXRD can be used to perform so-called “x-ray dilatometry”, which measures the expansion of a electrode within an intact coin cell by tracking the spatially resolved edge of certain diffraction peaks during operation.¹² Such experiments are the focus of future work, particularly in measuring the operando expansion of the Si/C composites from **Chapter 6**.

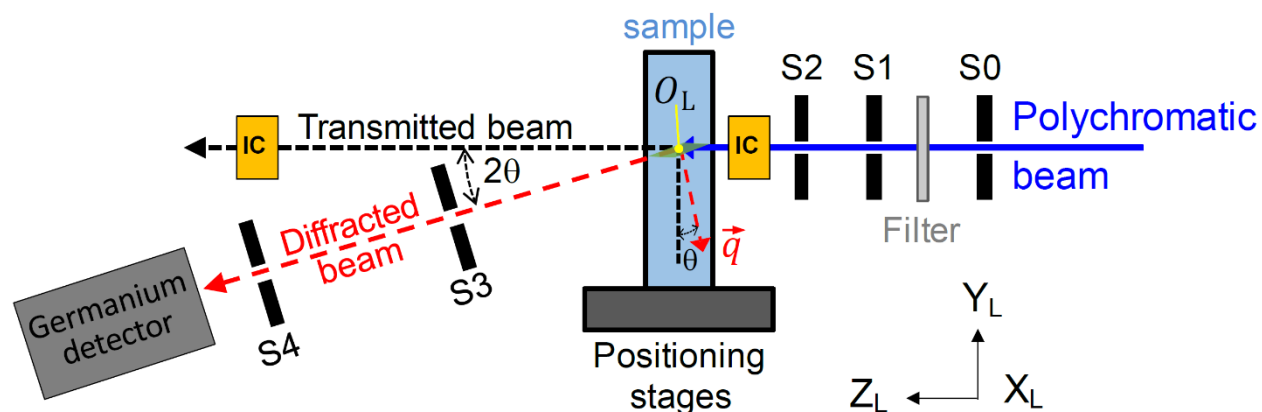


Figure 7. An experimental setup schematic of the EDXRD setup at 6-BM-A at the APS. Reproduced from [13].

Experimental Benefits for Resistive Carbon Materials

Beamline 6-BM-A at the Advanced Photon Source (APS), where the work in **Chapter 4** was carried out, uses high-energy X-rays (~ 50 -100 keV). These X-rays are substantially greater in energy than the absorbing edge of most atoms and can be transmitted through the casing of stainless-steel coin cells. EDXRD at 6-BM-A can therefore be used to find an electrochemically active region inside of an intact coin cell and measure its diffraction pattern, *operando*. The use of an intact coin cell is crucial for studying materials with low electronic conductivity such as those presented in **Chapter 4**. The high resistivity of such materials makes them extremely difficult to cycle in a high-impedance benchtop optical test cell. Furthermore, the small X-ray scattering cross section of carbon results in an extremely diffuse diffraction signal. EDXRD can solve both problems, as an intact coin cell is used. The use of a standard electrode with a Cu current collector, the stack pressure of a 2032-coin cell, and the high flux of synchrotron light allow for optimal electrochemical performance and simultaneous visualization of traditionally weak carbon diffraction features. An example is shown in **Figure 8**, where an r-HBC coin cell was successfully

cycled to a standard capacity, and the diffraction of the semi-crystalline (001)* reflection was measured simultaneously.

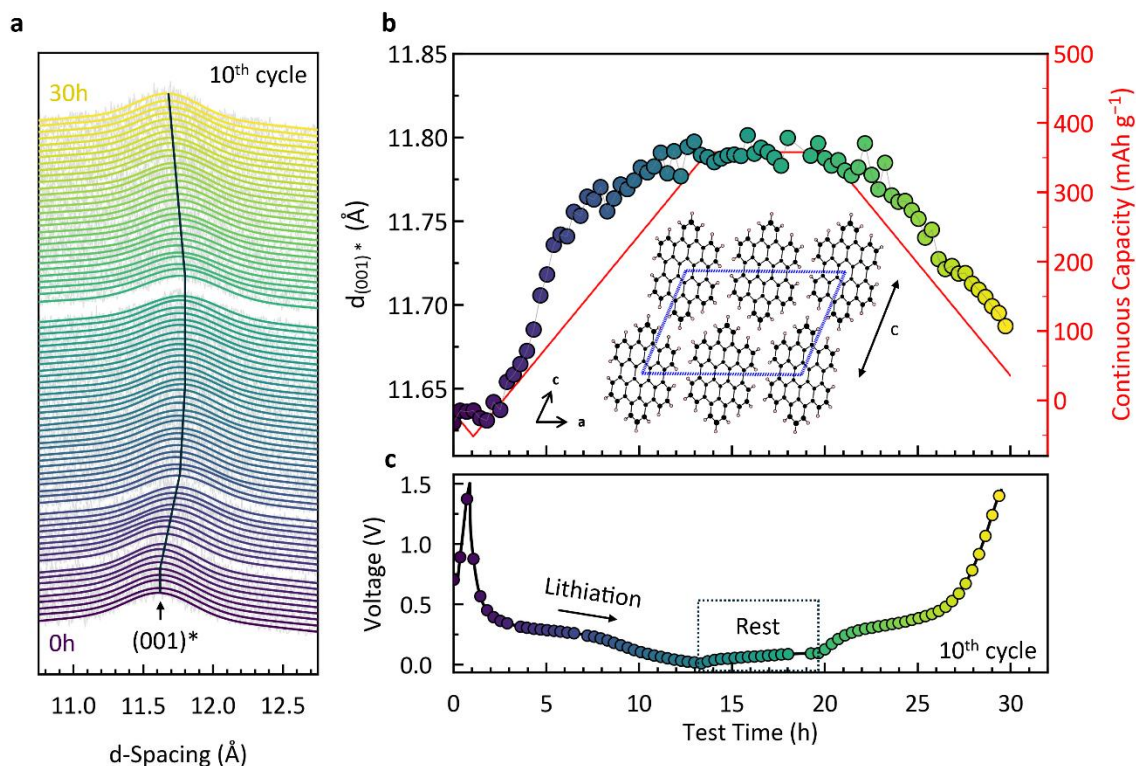


Figure 8. (a) EDXRD patterns of the (001)* region of r-HBC over the course of the 10th cycle lithiation and delithiation between 0.01-1.5 V vs. Li⁺/Li at 40 mA g⁻¹ and the corresponding (b) d_{001}^* and (c) voltage as a function of time. The inset figure shows the crystal structure of r-HBC (CCDC no. 1173297) along the b-axis. Reproduced from **Chapter 4**.

As an important note for this technique, the method of coin cell fabrication has been shown to have a significant impact on the local chemistry measured *operando* within the cell. For example, if the cell is not fabricated in a symmetric fashion (with centered electrodes, spring, and spacers), a stack pressure gradient is formed across the surface of the electrode. This can result in spatial heterogeneity in the diffraction measurement, as higher pressure regions of the cell interface

will have different lithiation kinetics than regions of less compression. The high-energy nature of the light at 6-BM-A enables radiography measurements for visualization of the as-fabricated cell as shown in **Figure 9**, which depicts a coin cell full cell which was crimped with an off-center spring, resulting in a pressure gradient across the surface of the electrode stack.

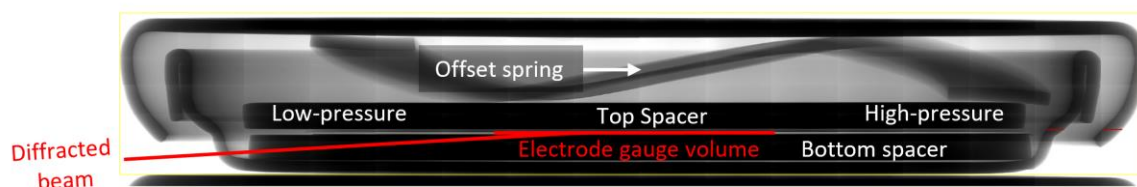


Figure 9. Radiograph of a coin cell full cell with an off-center spring. Image credit: Dr. John Okasinski.

Three-Electrode Studies

Working Principles

Resolving the behavior of a single electrode in a two-electrode system is non-trivial due to the convolution of the two electrode potential profiles within the overall cell voltage profile. As a result, researchers generally choose between measuring (i) a single electrode against a pseudo-reference lithium chip, sacrificing the ability to measure relevant electrode systems; or (ii) a two-electrode system, and using differential analysis techniques to try to deconvolve the constituent potential profiles through modeling.¹⁴ This problem can be solved by the addition of a third electrode to the cell, which can measure the potential of the two constituent electrodes simultaneously while they interact with each other. However, the placement and chemistry of that third electrode can severely impact the quality of results for a given measurement.¹⁵ Nonetheless,

a properly designed 3-electrode cell with a small and centrally located reference can be used for studying industry-relevant battery systems containing cathode and anode materials with dynamic profiles. An example of this configuration is shown in **Figure 10**.

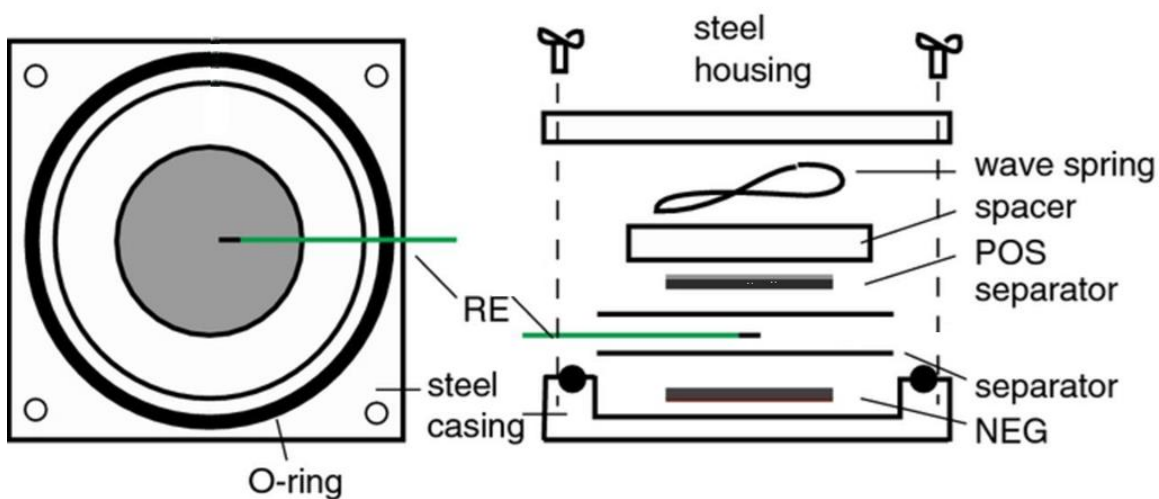


Figure 10. 3-electrode fixture cell schematic. Adapted from [15]

The addition of a reference electrode allows for the deconvolution of the constituent electrode profiles, as shown in **Figure 11** for an $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ (LMFP64)|| $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) battery system.

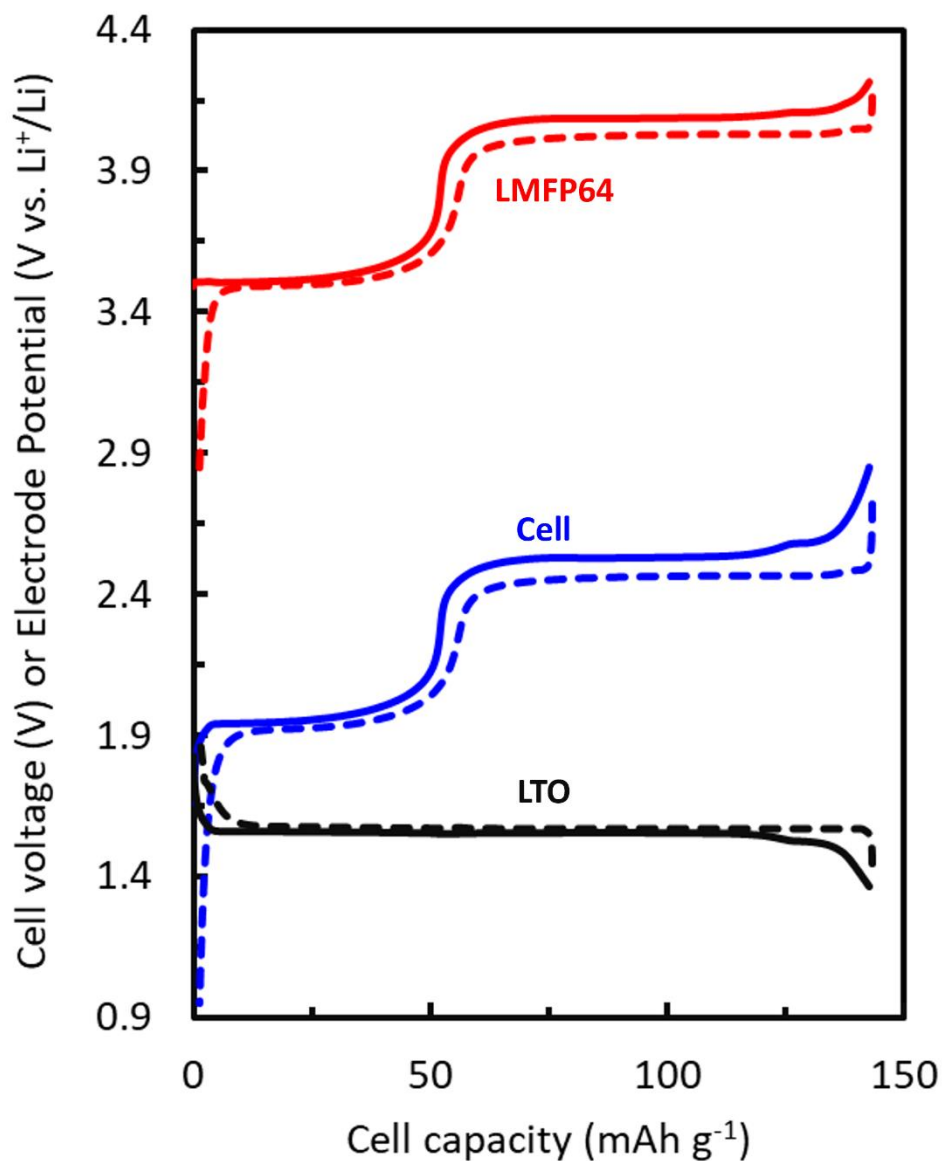


Figure 11. Capacity-voltage profiles for the LMFP64/LTO cell (blue), LMFP64 electrode (red) and LTO electrode (black) collected from a 3-electrode cell with a Li reference electrode. Reproduced from **Appendix**.

Three-Electrode Impedance Measurements

Probing the *operando* electrode profile dynamics within a cell enables unintuitive and powerful analyses. One example of such an analysis is the decoupling of cathode and anode area

specific impedance (ASI) effects in a full cell (**Figure 12**) by measuring how much of the cell voltage change during hybrid pulse power characterization (HPPC) testing is attributable to potential changes of the cathode versus the anode. For the cell shown in **Figure 12**, the impedance features of the cell voltage profile can be clearly attributed to redox reactions occurring in the cathode. Such an assignment would not be possible in a traditional 2-electrode cell, given that even the most “benign” counter electrodes such as LiFePO_4 , LTO, or lithium metal present a non-zero, but undeterminable, impedance.^{16,17}

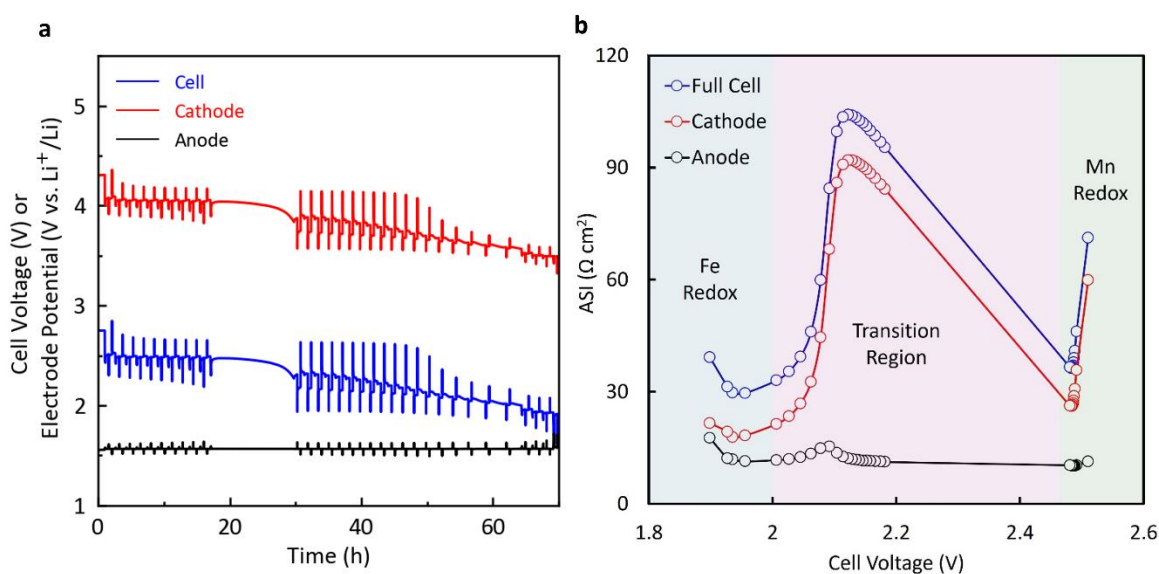


Figure 12. (a) Temporal voltage profile and (b) corresponding ASI plot of the cell (blue), cathode (red), and anode (black) in an LMFP||LTO three-electrode cell during cell discharge. Reproduced from **Appendix**.

Electrochemical *In-Situ* Dilatometry (ECD) of Silicon Anodes

Cell Construction and Experimental Considerations

Because expansion is the root cause of degradation in silicon anodes, methods for measuring that expansion, such as electrochemical *in-situ* dilatometry (ECD), are crucial for diagnosing modes of electrode failure. A schematic diagram of the ECD cell used in **Chapter 5** (EL-Cell, ECD-3-nano, Germany) is shown below in **Figure 13**. The ECD cell uses a lithium metal chip and a porous glass frit to isolate the dilation of an electrode of interest, as the bottom half of the cell is held stationary.

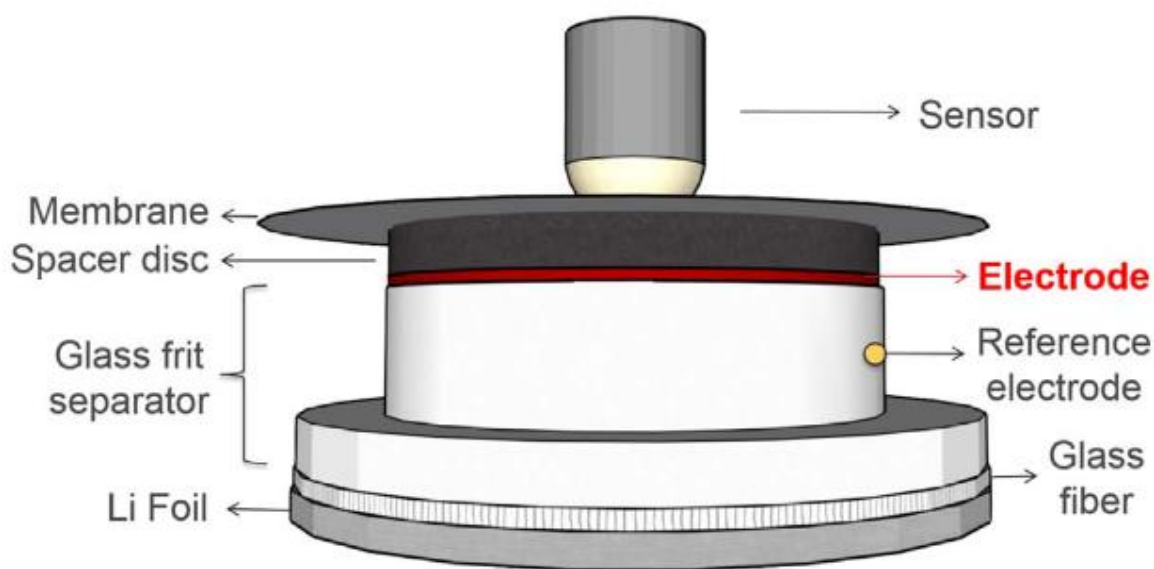


Figure 13. Schematic illustration of the electrochemical dilatometer cell. The vertical displacement of the working electrode (red) is transmitted through the thin metal membrane to the sensor. The separator is a stiff porous glass frit which is fixed in position, hence, only dimensional changes from the working electrode are detected. Reproduced from [18].

A representative experiment using a standard protocol derived from previous work is shown in **Figure 14**, in which the ECD cell was subjected to two formation/diagnostic cycles (15 h of C/30 lithiation, followed by delithiation to 1.5 V) and then one slow and deep cycle at a C/30 rate to 10 mV vs. Li^+/Li , followed by a 10 hour hold at that potential. The cell was subsequently delithiated at the same C/30 rate to a potential of 1.5 V vs. Li^+/Li and held for another 10 hours to explore the entire range of electrode expansion during operation.¹⁸

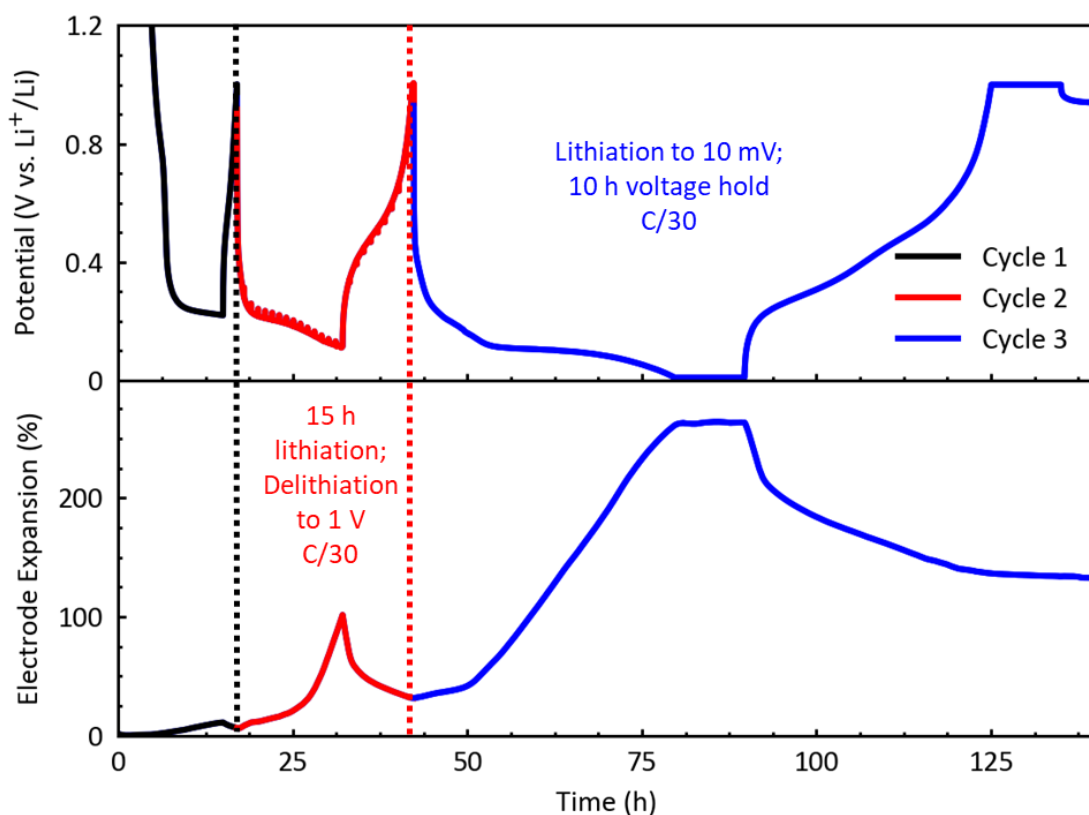


Figure 14. (top) Electrode potential and (bottom) expansion ECD profiles of a silicon electrode.

While dilation measurements are extremely useful, the custom design of the ECD-3-Nano cell requires certain experimental considerations for optimal usage. Most notably, the seals in the

ECD-3-Nano do not provide a sufficiently hermetic seal for long-term usage outside of a glovebox (this issue has been fixed in modern iterations of the cell).^{19,20} Therefore, benchtop experiments with the ECD-3-Nano must take place over an appropriate time scale and with relatively air-stable electrolyte systems (e.g., those without LiPF_6 salts) to ensure accurate results.¹⁸

Additionally, the stack pressure of the ECD-3-Nano (1 N)¹⁹ is sufficiently low that modes of mechanical deformation, such as electrode wrinkling, can inhibit measurements that may be possible in coin cells. Such a case is shown in **Figure 15a** and **b**, where an electrode from a disassembled coin cell is shown. The corresponding ECD data from a sister cell (**Figure 15c**) shows that the wrinkling (indicated by irreversible expansion) causes both significant buildup of impedance as shown by the magnitude of potential change during current interrupts in the second cycle (red), and a corresponding capacity fade as indicated by the rapid deterioration of the voltage profile in the third cycle (blue). Analogous coin cells did not show significant capacity fade due to their higher stack pressure (**Figure 16**).

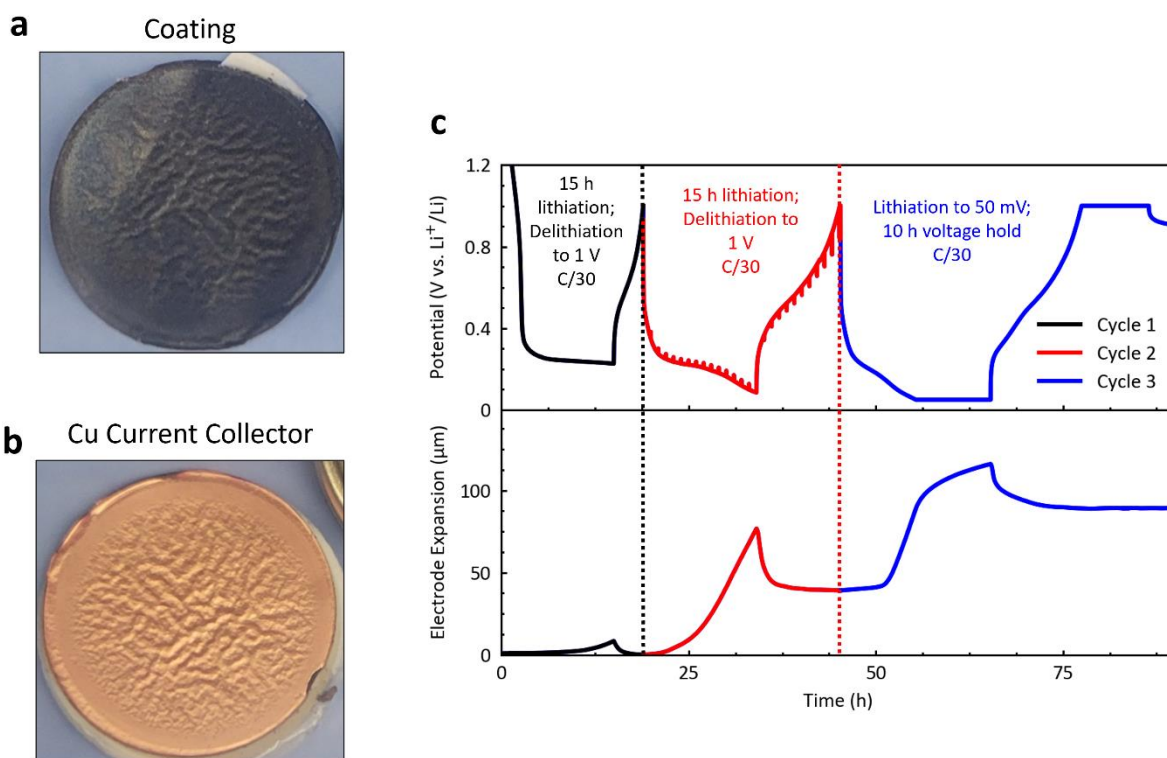


Figure 15. (a) coating and (b) copper current collector of a cycled silicon anode from a coin cell. (c) ECD voltage and expansion profiles for a sister electrode. Note the lower cutoff potential of 50 mV for this cell. Photo and coin cell fabrication credit: Avi Gargye.

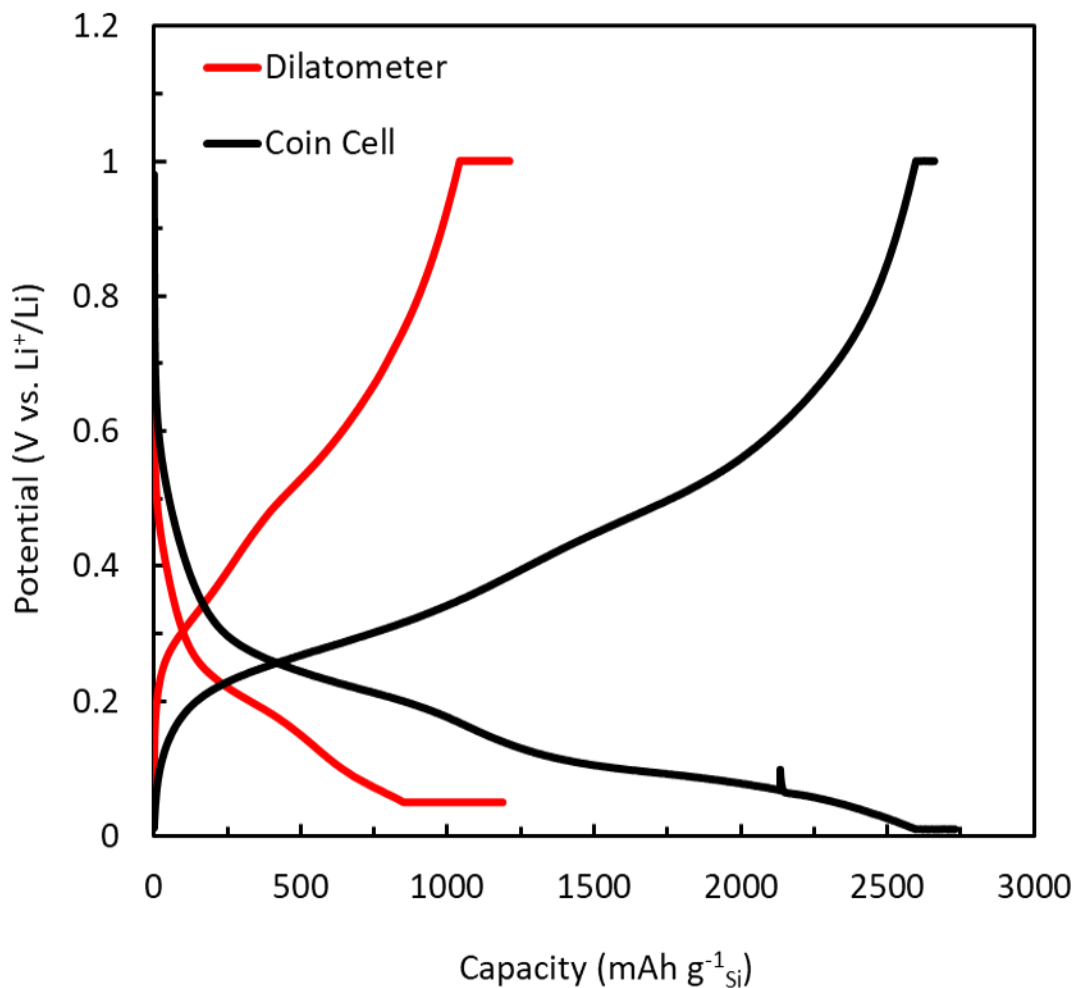


Figure 16. C/30 3rd cycle lithiation and delithiation profiles of the same silicon electrode in the ECD cell (red) and coin cell (black).

Additional consideration should be given to thick and high-loading electrodes. For example, in the case of thick electrodes, wetting and gas bubbles can pose a significant problem as shown for an industrially-relevant thick SiO_x/Graphite (Gr) electrode (42 μm coating thickness, contrasted with a ~ 15 μm thickness for previously explored electrodes) in **Figure 17**. The SiO_x/Gr voltage profile shows significant polarization and voltage fluctuations from electrical contact issues, ultimately polarizing down to plating potentials. Partway through the 10-hour voltage hold

of the third cycle (blue), the ECD cell shows a spontaneous electrical connection, allowing for the extremely rapid lithiation of the SiO_x electrode, causing a corresponding expansion in the cell of $\sim 140\%$. The rapid expansion, however, was interrupted by a precipitous drop in apparent electrode thickness. This is very likely due to the popping of a bubble that formed on the electrode itself during charging, which served to artificially increase the expansion values and disrupt electrical connection in the cell. This explanation is further supported by the proper operation of the cell after the reconnection event. This effect was only observed for thick electrodes.

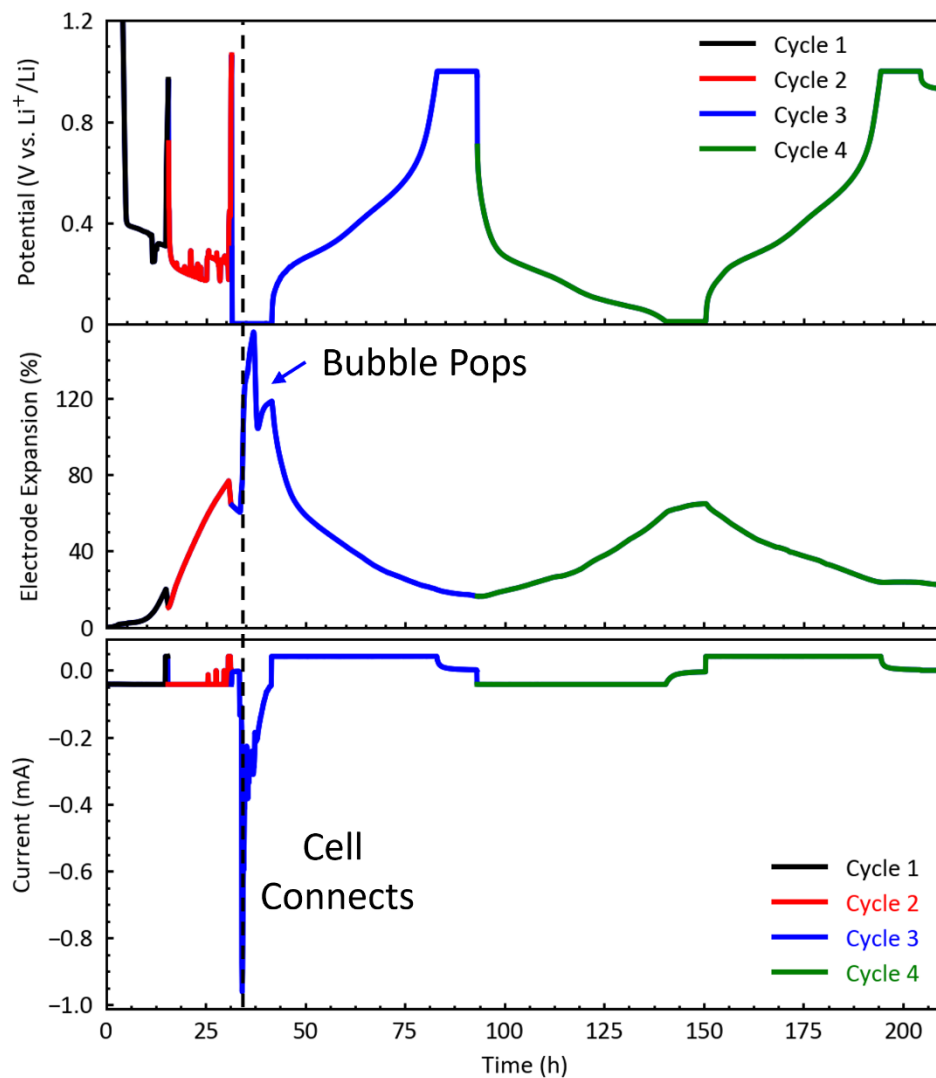


Figure 17. Potential (top), expansion (middle), and current (bottom) profiles of an SiO_x electrode in the ECD cell.

DTGA Deconvolution by Gaussian Integration

TGA of Si/C Composites

Thermogravimetric analysis (TGA) is a common method for determining thermal stability properties of novel materials, as well as quantifying phase fractions in heterogeneous materials.

The primary objective of TGA is to measure the change in weight of a sample as it is heated in a chosen atmospheric condition. By determining the change in weight, and the temperature at which that change in weight occurs, it is possible to ascertain how much of a certain component is in your sample, as well as its relative thermal stability. In this work, two chemical oxidation reactions were observed to establish relative phase fractions of silicon, carbon, and SiO₂ in Si/C composites (**Chapter 6**):



Note that **Equation 3** results in the formation of a solid, whereas **Equation 4** results in the formation of a gas. Therefore, the TGA signatures of silicon and carbon oxidation are weight gain and loss events, respectively. The SiO₂ remains static in weight over the course of TGA, as it is already fully oxidized before the experiment begins. Schematic TGA curves for pure C, Si, SiO₂, and a 1:1:1 mixture of C, Si, and SiO₂ are shown in **Figure 18** alongside a depiction of the oxidation of an Si/C composite particle with a native oxide layer.

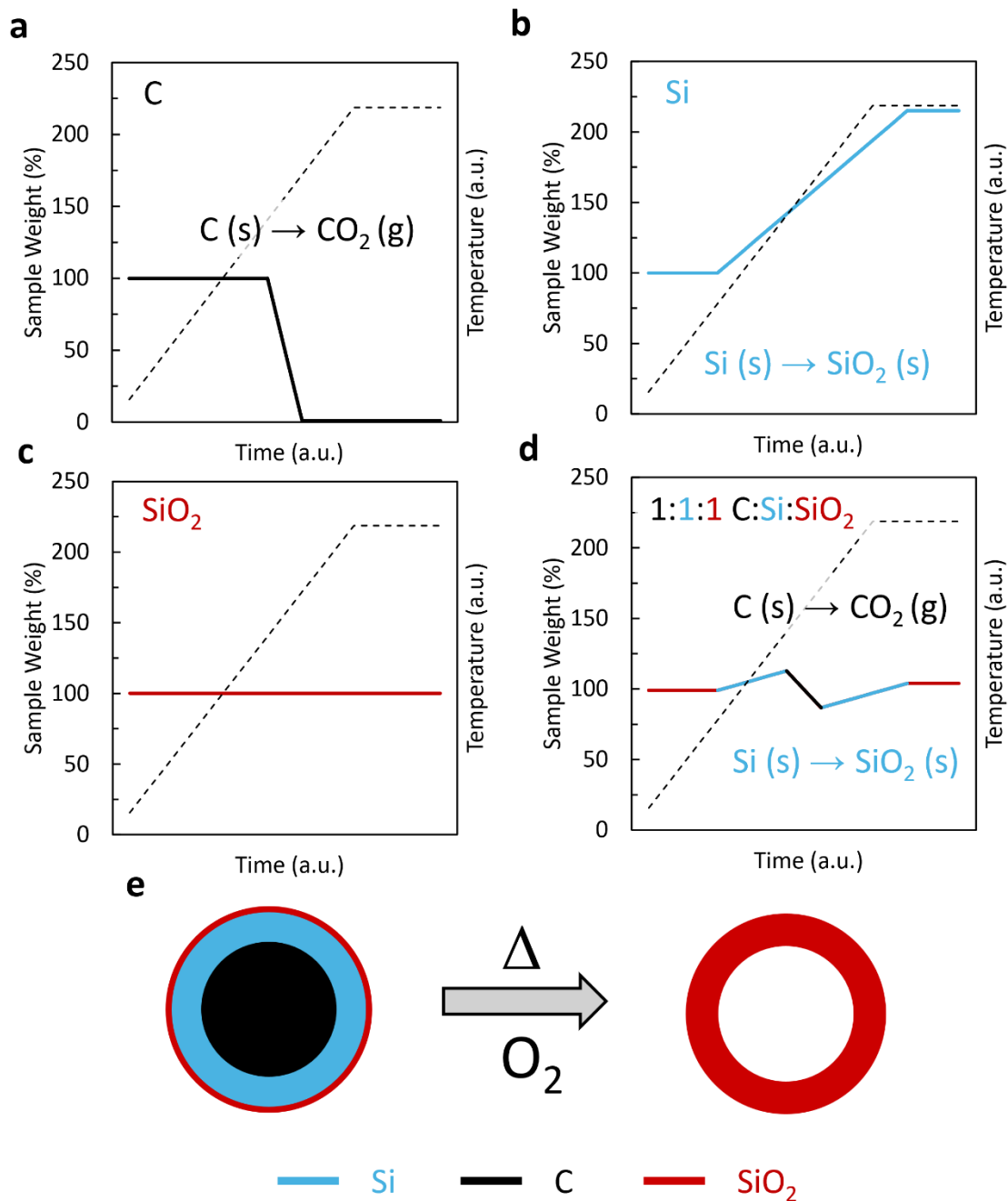


Figure 18. Example TGA curves for (a) pure carbon, (b) pure silicon, (c) pure SiO_2 , and (d) a 1:1:1 mixture of carbon, silicon, and SiO_2 ; (e) schematic representation of silicon oxidation and carbon combustion in Si/C composite. Reproduced from **Chapter 6**.

The use of TGA for quantification of silicon in Si/C composites is already well established in the literature.^{21,22} However, current methods do not account for any silicon oxidation that occurs simultaneously during carbon combustion; nor can they account for any amount of SiO₂ present within the sample before the TGA experiment. Additionally, TGA in the literature is most frequently conducted at temperatures too low to carry out full oxidation of silicon, particularly if there is bulk silicon present in the sample.

DTGA of Si/C Composites

In **Chapter 6**, a gaussian deconvolution method of silicon content determination is presented, which can determine silicon content in a composite, even for events which are partially overlapped with carbon regions in the TGA profile. An example for a Si/C composite made from silane and acetylene deposition onto a Super P scaffold which had previously been heat treated to 1200 °C (SPL) is shown in **Figure 19**.

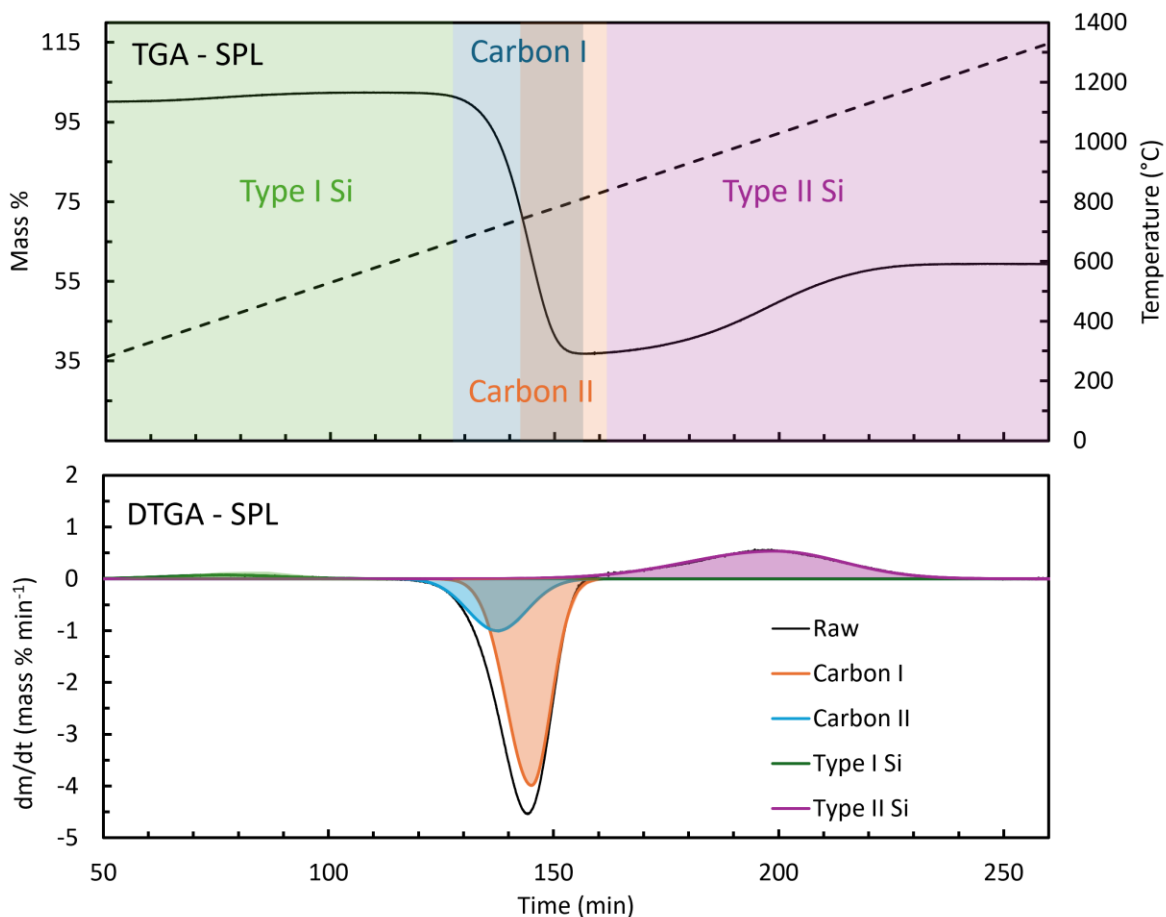


Figure 19. (top) TGA and (bottom) DTGA profiles of an SPL-derived Si/C composite. Profiles are fit to four gaussian-type features for SP-derived composites: Type I Si, Type II Si, Carbon I, and Carbon II.

The archetypal Si/C composite can be broken down into four features in order of combustion temperature from low to high: Type I Si, Carbon I, Carbon II, Type II Si. Currently, Carbon I and Carbon II are assumed to be attributable to passivation carbon from acetylene deposition and the carbon scaffold, respectively. Type I Si and Type II Si are categorized as nanoscale and bulk silicon, respectively.

Because the mass gain event in the DTGA is addition of oxygen from **Equation 3**, the wt% of Si can be derived via a simple mass conversion using the molar masses of O₂ (32 Da) and Si (28 Da). The carbon wt% in the sample can be directly derived from the area under the weight loss curve in the corresponding DTGA features, as the change in sample weight can be directly attributed to loss of carbon mass from **Equation 4**. SiO₂ content can be calculated by back-calculating the amount of silicon present in the sample initially and subtracting it from the final mass of the sample after all oxidation reactions as shown in **Equation 5**:

$$wt\%_{SiO_2} = wt\%_{Final} - wt\%_{Si} \cdot \frac{60}{28} \quad (5)$$

where $wt\%_{SiO_2}$ is the wt% of SiO₂ present in the sample before TGA, $wt\%_{Final}$ is the final wt% of the sample after all oxidation is completed, $wt\%_{Si}$ is the wt% of Si as determined by gaussian integration, and $\frac{60}{28}$ is the molar mass ratio of SiO₂ to Si.

Error Analysis and Quantification

Under the assumption that an Si/C composite is wholly comprised of Si, C, and SiO₂, the error of the analysis can be calculated by taking the difference between the theoretical and experimental sum of their weights according to **Equation 6**:

$$\%_{Error} = 100\% - (wt\%_C + wt\%_{Si} + wt\%_{SiO_2}) \quad (6)$$

The $\%_{Error}$ for 18 Si/C composites synthesized for **Chapter 6** is shown in **Figure 20**, which demonstrates an average error of 1.3 wt% and a standard deviation of 1.2 wt%.

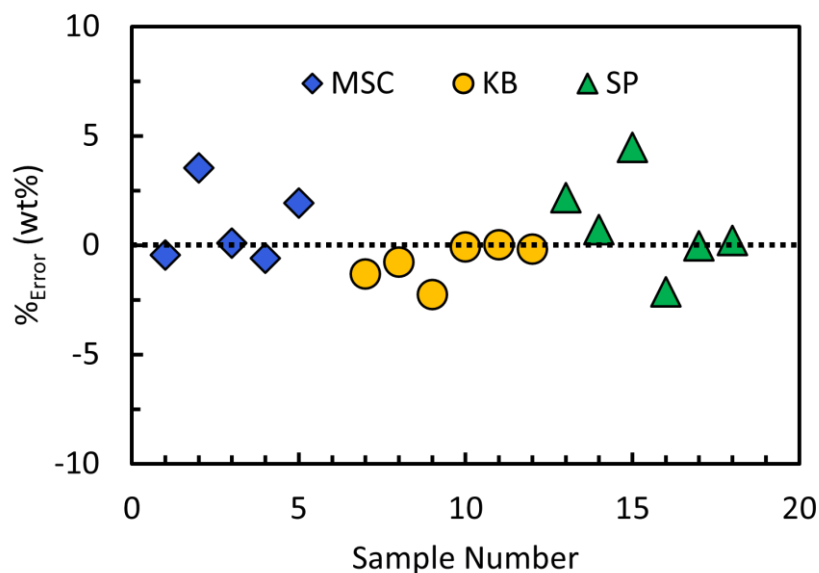


Figure 20. %*Error* of 18 Si/C composites made with distinct carbon scaffolds derived from thermal treatment of MSC-30 (MSC), Ketjen Black (KB), and Super P (SP). Reproduced from **Chapter 6**.

The values obtained by differential TGA can be compared with values measured by other techniques, such as energy dispersive X-ray spectroscopy (EDS) as in **Figure 21a**, which shows a general agreement between silicon, carbon, and oxygen contents for the two techniques. As described in **Chapter 6**, the systematic difference between the two (greater silicon content for EDS, greater carbon content for TGA) can be attributed to errors in carbon quantitation for EDS due to the small size of the carbon nucleus and electron cloud, as shown in **Figure 21b**. Such errors can be propagated due to the normalized nature of the analysis.

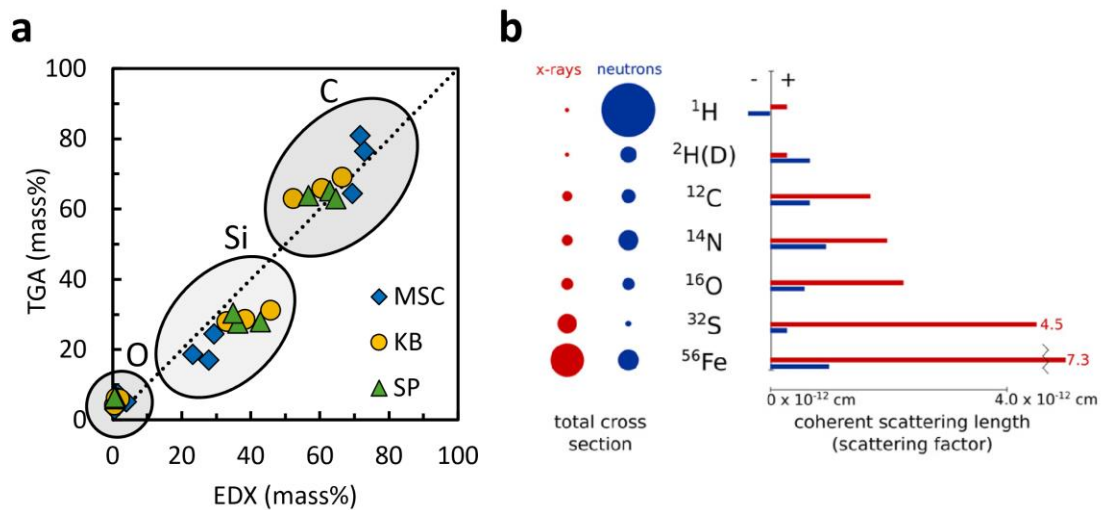


Figure 21. (a) TGA-derived vs. EDS-derived elemental compositions for MSC- (blue), KB- (gold), and SP- (green) Si/C composites. Reproduced from **Chapter 6**. (b) X-ray and neutron scattering cross sections and scattering lengths for several elements. Reproduced from [23]. Shaded circles in panel (a) are grouped by element for clarity.

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CHAPTER FOUR

STRUCTURAL ORIGIN OF PSEUDOCAPACITIVE LITHIUM-
ION STORAGE IN A CRYSTALLINE HYDROCARBON FOR
RAPID CHARGING BATTERIESContribution of Authors and Co-Authors

Manuscript in Chapter 4

Author: Charles McDaniel

Contributions: Fabricated cells, carried out characterization, analyzed data, and wrote the manuscript.

Co-Author: John Okasinski

Contributions: Experimental guidance.

Co-Author: Adele Jordan

Contributions: Assistance with experimental design.

Co-Author: Nicholas P. Stadie

Contributions: Advised with the experimental direction, interpreted results, and assisted in writing and editing the manuscript.

Manuscript Information

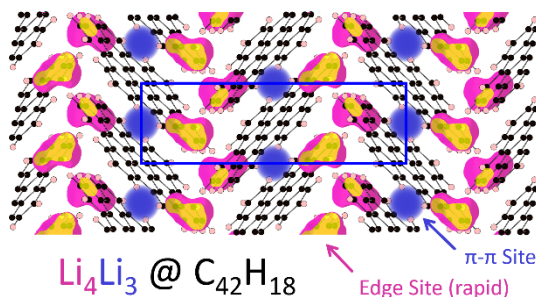
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Abstract

The electrochemical lithiation of a series of structured organic materials based on hexa-peri-hexabenzocoronene (HBC) shows the hallmark characteristics of pseudocapacitance, an intermediate mechanism between capacitive and faradaic charge storage that is of great interest for rapid charging energy storage applications. The rapidly lithiable binding sites correspond to specific lattice environments in the molecular crystal structure of HBC (up to 7 per molecule, or $\text{Li}_7\text{C}_{42}\text{H}_{18}$), as confirmed by structural characterization and electrochemical analysis. The exclusive presence of hydrogen-decorated edges in the crystal structure of HBC, and the independence from any role of oxygen content, establishes its novel mechanism of intercalation. This combined with a large density of sites and a low potential of lithiation permits both high energy density (823 Wh kg^{-1}) and extremely high-power density (16 kW kg^{-1}) not previously observed for a carbon-based anode material in lithium-ion batteries (LIBs).

TOC Image

Introduction

The need for renewable energy resources is rapidly increasing as the world transitions away from the limited resource of fossil fuels, but such renewable resources are intermittent and therefore require appropriate storage.¹ Batteries are at the forefront of technology for next-generation electrochemical energy storage, for both mobility and stationary grid applications. However, state-of-the-art batteries typically only permit a slow charging rate (~ 0.5 h) to achieve completion.² This shortcoming has negative implications for both the ability of a battery to handle power surges in the grid and for acceptable charging times in mobile applications. Graphite has been the anode of choice since the commercialization of the lithium-ion battery (LIB) in the 1990s, but it cannot accommodate rapid charging demands; its capacity is reduced by 50% at a 4C (15 min) charging rate and it suffers from unintentional and dangerous lithium plating at rapid current rates owing to its very low potential of lithiation.³⁻⁵ The US Department of Energy (DOE) has laid out three requirements of next-generation batteries: a 5-15 min charging time (to 80% state of charge), a cost of $< \$100$ per kWh, and a 300 mi (480 km) range per charge.⁶ Thus, discovering materials and systems with extreme fast charging (XFC) capabilities while retaining a high energy density and composition based on highly abundant elements has become a high priority.

Materials with pseudocapacitive charge storage mechanisms are good candidates for next generation LIB anodes due to their rapid charging capabilities.⁷ Such materials have been proposed to store lithium ions through redox reactions that only require partial desolvation of the active ion from the electrolyte, thus not limited by the slow kinetics of complete desolvation.⁸ Intercalative pseudocapacitance, in particular, endows some pseudocapacitive anode materials with a more distinct potential plateau than materials with exclusively surface storage mechanisms, thereby

increasing the energy density of the system.⁹ Unfortunately, most pseudocapacitive anode materials reported to date are ill-suited to lithium storage, have poor energy density due to a high average lithiation potential, or are prohibitively expensive (i.e., based on low-abundance elements).^{7,10–14}

Polycyclic aromatic hydrocarbons (PAHs) are a class of planar molecules comprised of 6-membered carbon rings that represent fragments of graphene, the building block of graphite. PAHs stack in a layered fashion (“ π - π stacking”), just like graphene stacks to form graphite, but the molecular nature of PAHs leads to the important and differing role of edge-on or “CH- π interactions” unique to each molecule. The hexa-peri variant of HBC ($C_{42}H_{18}$, **Figure 1a**), a relatively large and highly symmetrical PAH, exhibits a γ -herringbone crystal structure (**Figure 1b**), a distinct class of PAH structures with significant CH- π character in addition to a slipped π - π stacking motif.^{15,16} The relatively narrow interlayer spacing in crystalline HBC, promoting higher electrical conductivity through the π - π stacking direction, makes HBC a viable candidate for lithium-ion storage. Furthermore, the γ -herringbone structure of HBC could also allow for the rapid diffusion of lithium ions through the molecular crystal, making it an appropriate model for understanding lithium-ion diffusion kinetics in molecular PAHs. Little or no previous research has been performed on large un-substituted PAHs as lithium-ion electrode materials.^{17,18}

Herein, we explore the structure-function relationships between the crystallographic/conductivity properties and related electrochemical properties of HBC, a solid molecular hydrocarbon whose structure can be systematically altered via heat treatment under inert atmosphere. Four forms of HBC were assessed: hexagonal HBC (h-HBC), recrystallized HBC (r-HBC), polymerized HBC (p-HBC), and carbonized HBC (c-HBC). HBC is an ideal model material

for understanding the lithiation mechanism of PAHs due to its ability to be lithiated as a neat precursor with its molecular crystal structure intact.¹⁷ Optimized heat-treated variants were prepared with a C/5 reversible capacity of $\sim 350 \text{ mAh g}^{-1}$ and a low average voltage of $\sim 0.25 \text{ V}$ vs. Li/Li^+ . Of highest interest, the pseudocapacitive sites in p-HBC, which comprise 80% of the total lithiation sites and were found to be reversibly lithiated under XFC conditions ($< 7.5 \text{ min}$), indicating a new type of hydrocarbon pseudocapacitance not related to the presence of heteroatoms. Other variants, especially r-HBC, were also found to exhibit high rate-capability, sufficient capacity, and low average potential as well.

Results

Structural Changes of HBC Upon Heat Treatment

The laboratory synthesis of HBC is a 1-step oxidative cyclodehydrogenation reaction of hexaphenylbenzene as the precursor.^{19–21} The commercially available form of HBC is comprised of poorly crystalline hexagonally packed columnar stacks, as shown in **Figure 1c-1d**, and is referred to herein as h-HBC.^{22–25} Recrystallization of HBC can be achieved upon heat-treatment of h-HBC to $600 \text{ }^{\circ}\text{C}$ under vacuum,²⁶ involving a slight lattice expansion to within 3% of the single-crystal (001) spacing (**Figure 1d**), producing r-HBC.²⁶ The Raman spectrum of r-HBC exhibits three primary peaks: the D_1 ($\text{A}_{1\text{g}}$), D_2 ($\text{A}_{1\text{g}}$), and G_1 ($\text{E}_{2\text{g}}$) peaks, which correspond to two ring breathing modes and the in-plane ring deformation motion of the sp^2 hybridized carbons, respectively.^{27,28} Raman spectroscopy also reveals the presence of two phases in r-HBC: grey and yellow (**Figure S1**). The grey phase of r-HBC is shown in **Figure 1c**. The phase heterogeneity is also evidenced by the presence of broadened amorphous peaks in the X-ray diffraction (XRD) pattern of r-HBC. The surface area decreases from 35 to $5 \text{ m}^2 \text{ g}^{-1}$ when h-HBC is converted to r-

HBC, which is consistent with increased crystallographic ordering. The measured hydrogen content of r-HBC by combustion analysis is 25.0 at%, which is close to the theoretical value ($C_{42}H_{18}$, or 30 at% H) (**Table 1**).

Upon further heat treatment to 700 °C (p-HBC), the molecular structure of HBC partially polymerizes, resulting in the loss of several XRD peaks, leaving only a broad (100) peak at $2\theta = 7.68^\circ$ and a very broad stacking peak at $2\theta = 25.6^\circ$. p-HBC exhibits a higher bulk electrical conductivity (**Table 1**) and a decrease in the intensity of the D_1 (A_{1g}) edge breathing mode compared to r-HBC, likely due to a decrease in the number of internal edge sites upon polymerization.²⁹ Upon further heat treatment to 1000 °C, the transformation of HBC from a molecular solid into a disordered graphitic carbon is observed. The Raman spectra in **Figure 1c** show monotonic trends upon increasing pyrolysis temperature: a broadening of the G_1/G (E_{2g}) peak, a decreasing intensity of the D_1 peak, and an increasing I_D/I_G ratio. These trends coincide with a decreasing hydrogen content and increasing electrical conductivity (**Table 1**). Hence, these changes are attributable to the reorganization of herringbone-ordered molecular regions into extended graphitic networks.^{30,31} Upon the formation of c-HBC, the (100) peak of the monoclinic HBC molecular crystal is almost entirely diminished and an intense graphitic (002) reflection appears ($d = 3.35 \text{ \AA}$).

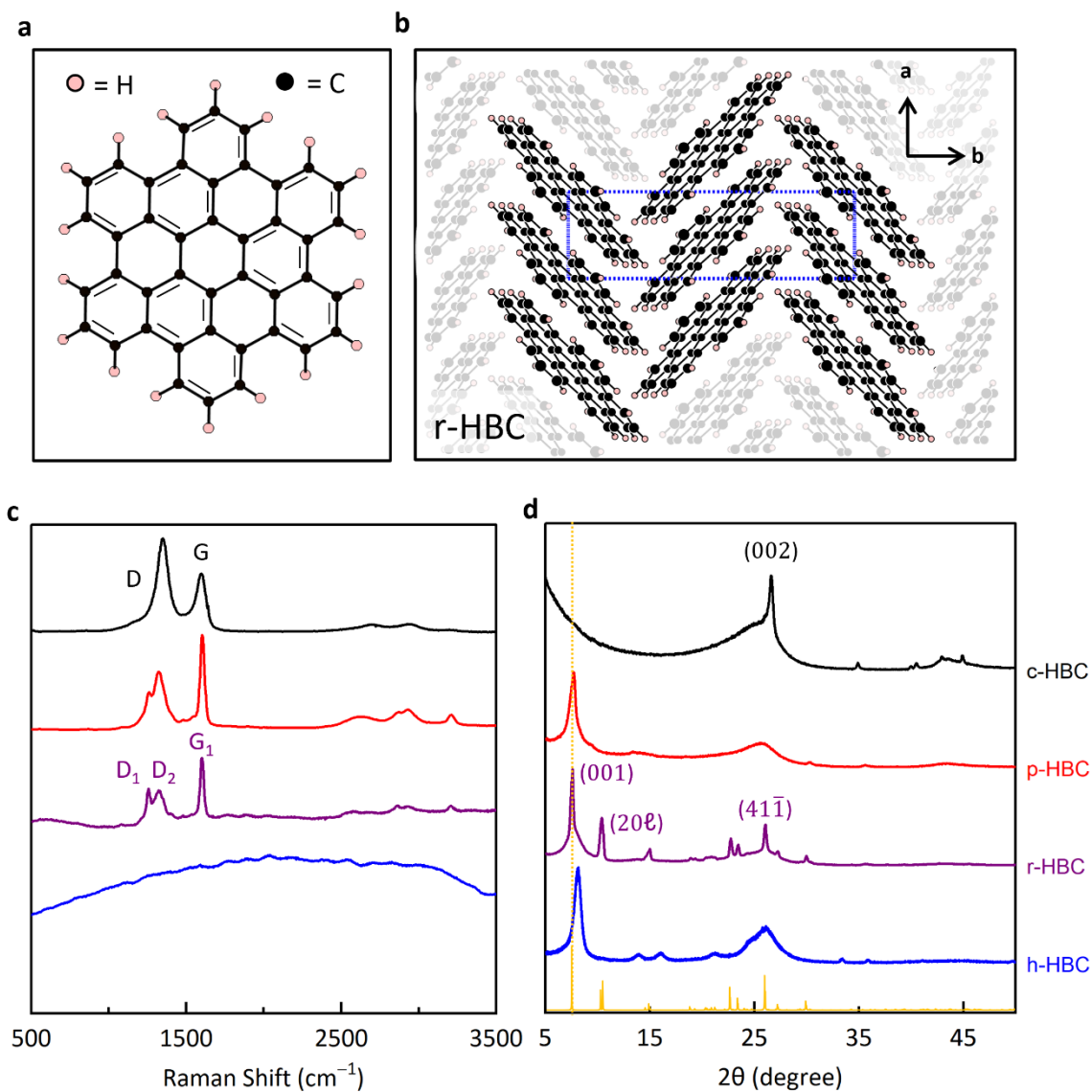


Figure 1. (a) Organic molecular structure of HBC and (b) monoclinic (P21/a, no. 14) herringbone crystal structure of r-HBC (CCDC no. 1173297).²⁶ (c) Raman spectra and (d) XRD patterns of h-HBC (blue), r-HBC (purple), p-HBC (red), and c-HBC (black). The simulated pattern for the monoclinic herringbone structure of HBC (CCDC no. 1173297) is shown in yellow.

Table 1. Physical properties of hexagonal (h-), recrystallized (r-), polymerized (p-), and carbonized (c-) HBC.

Material	I(D)/ I(G)	Pos _{D1} (cm ⁻¹)	Pos _{D2/D} (cm ⁻¹)	Pos _{G1/G} (cm ⁻¹)	Interlayer HBC Spacing (Å)	In-Plane HBC Spacing (Å)	Electrical Conductivity (S cm ⁻¹)	Hydrogen Content (at %)	Surface Area (m ² g ⁻¹)
h-HBC	-	-	-	-	3.41	10.9	1.1×10^{-6}	28.3	35
r-HBC	0.54	1256	1321	1601	3.41	11.6	5.5×10^{-7}	25.0	5
p-HBC	0.61	1262	1321	1603	3.48	11.5	2.2×10^{-4}	20.0	5
c-HBC	1.6	-	1350	1597	3.51 (3.35)	-	6.2	4.4	3

The morphological features of the HBC materials change upon heat-treatment in accordance with the underlying phase transitions from h- to c-HBC (**Figure 2**). h-HBC consists of unstructured nano-spheres, agglomerated into larger particles at the micron-scale structure (**Figure 2a**). Upon conversion to r-HBC, crystalline rods comprised of bundles of smaller needles form (**Figure 2b**). Upon further heat-treatment to p-HBC, flakes with a distinct weave pattern are observed, likely constructed from polymerized crystallites of HBC (**Figure 2c**). Upon carbonization, c-HBC exhibits flake-like morphology with no remaining rod-like character, indicative of graphitic carbon (**Figure 2d**). In short, r-HBC presents as a highly crystalline variant of HBC whose crystal structure represents a significant departure from graphite and other solely π -stacked carbon-based solids commonly explored for lithium storage; instead, its crystal structure includes unique interstitial sites between neighboring HBC molecules at the intersections of edges and faces (**Figure S2**), the target of further electrochemical lithiation experiments.

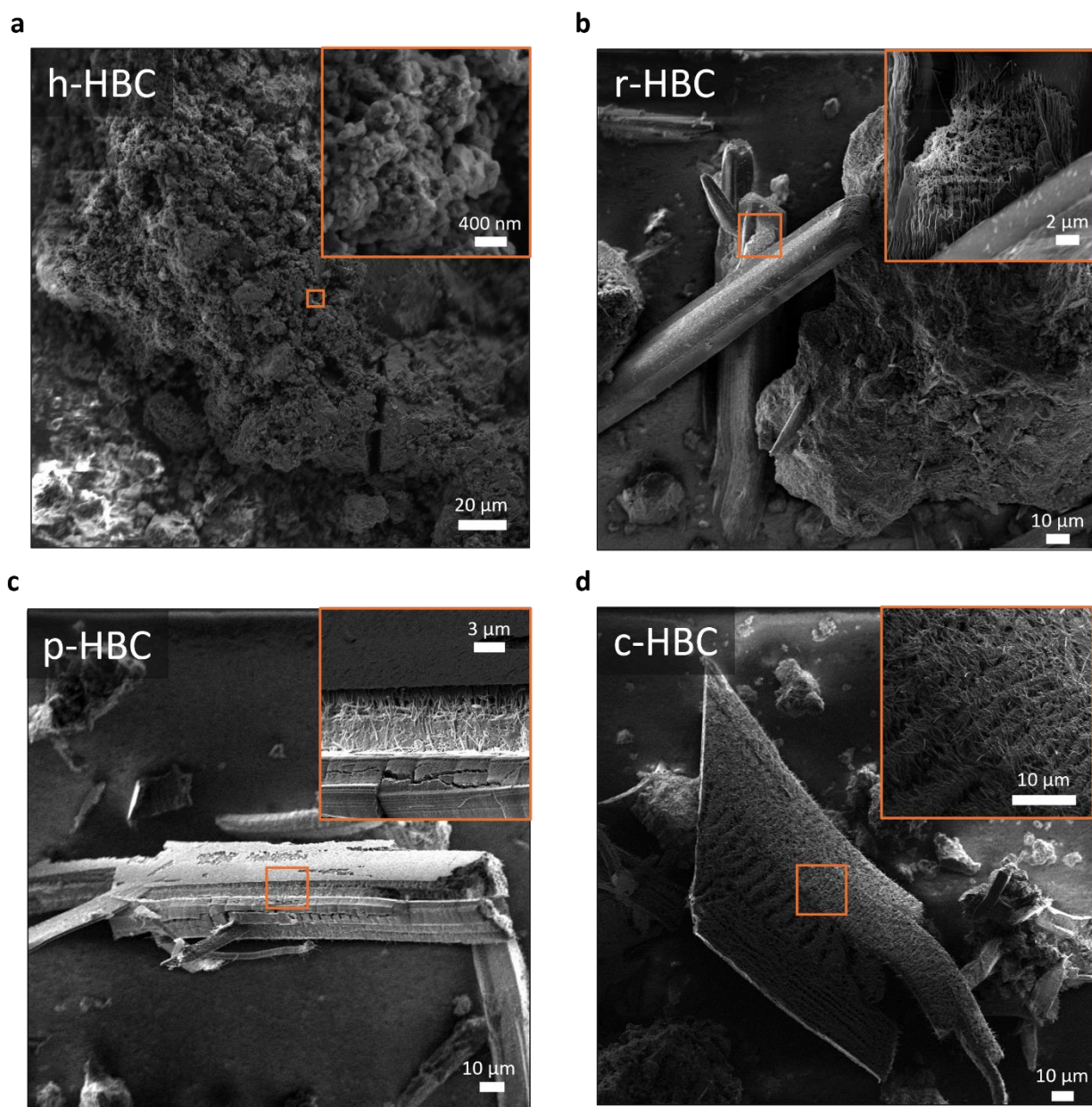


Figure 2. SEM imaging of (a) h-HBC, (b) r-HBC, (c) p-HBC, (d) and c-HBC.

Electrochemical Characterization of HBC Materials

The electrochemical lithiation of all four HBC materials was investigated in coin cell format, against lithium metal as the counter and reference electrode, flooded with 1 M LiPF_6 in a standard carbonate-based organic solvent system as the electrolyte. In its as-received (hexagonal)

state, h-HBC exhibits a primary redox event centered at $E_{1/2} = \sim 0.25$ V vs. Li^+/Li as measured by cyclic voltammetry (CV) (**Figure 3a**). Upon recrystallization into its monoclinic herringbone structure (r-HBC) and subsequent polymerization (p-HBC), the current passed during this lithiation event increases monotonically before disappearing upon carbonization (c-HBC). These gains and eventual loss in current are consistent with changes in capacity measured in galvanostatic charge/discharge (GCD) experiments (**Figure 3b**). The reversible slow-rate (20 mA g^{-1} , $\sim C/20$) delithiation capacity of r-HBC is 361 mAh g^{-1} and increases to 506 mAh g^{-1} for p-HBC, corresponding to final lithiation states of $\sim \text{Li}_7\text{C}_{42}\text{H}_{18}$ and $\sim \text{Li}_{10}\text{C}_{42}\text{H}_{18}$, respectively. Notably, the large capacity at low potentials for p-HBC is found to be extremely rate limited, disappearing when the cycling rate is increased from 20 to 74 mA g^{-1} (**Figure S3**). This capacity could be attributable to Dahn-type “alloying” sites, which are common in carbon materials synthesized at low temperatures that have a high hydrogen content.^{32,33} However, it is also possible that there is a secondary mechanism such as intercalation in the π - π stacking direction between HBC molecules. Ultimately, much of this capacity (especially the broad plateau at ~ 0.25 V vs. Li^+/Li) is lost upon carbonization at 1000°C (c-HBC); this loss is correlated with the diminishing of the primary (001) XRD peak (**Figure 1d**) and diminishing/broadening of the primary (G_1) Raman peak (**Figure 1c**) associated with HBC, clearly indicating that these lithiation sites are native to the HBC molecular crystal structure. In summary, r-HBC exhibits a high lithiation capacity (361 mAh g^{-1} , $\sim \text{Li}_7\text{C}_{42}\text{H}_{18}$) akin to graphite (372 mAh g^{-1} , $\sim \text{LiC}_6$) but with a distinctly higher potential plateau corresponding to its primary lithiation/delithiation event.

A secondary lithiation event at low potentials (near the lower potential limit of lithiation, 0.05 V vs. Li^+/Li) is also observed in r-HBC and c-HBC, and to a lesser extent in p-HBC and h-

HBC (**Figure 3a**). Such a lithiation event is common among all types of disordered graphitic carbon materials,⁷ and we attribute this redox current to the interlayer storage of lithium-ions between stacked molecules of HBC (see **Figure 1b**) like that observed in graphite. Such sites have previously been hypothesized to be lithiable in HBC,^{17,34} but no experimental observation has previously been made. Characterization of this event is notoriously challenging since it occurs near the potential for lithium plating/stripping which is important to avoid in the electrochemical characterization of carbon materials toward lithiation; previous efforts in our group have focused on model materials with known exclusion of any π - π stacking (so-called 3D ZTC) and with identical covalent bonding networks but with π - π stacking (so-called 2D ZTC) to precisely detect and quantify its role in complexly structured materials.³⁵

The rate capability of lithiation of all four HBC materials as well as graphite (a variant referred to as AG-20 that is extensively characterized in past work³) was investigated between 74 mA g⁻¹ (~C/5) and 30 A g⁻¹ (~80C) using a constant current constant voltage (CCCV) protocol, as shown in **Figure 3c**. h-HBC generally exhibits the lowest capacities across all rates (e.g., 247 mAh g⁻¹ at C/5 and 143 mAh g⁻¹ at 1C), likely due to blocked lithiation sites and/or poor ionic conductivity. In recrystallized herringbone form, r-HBC exhibits both a higher C/5 capacity (349 mAh g⁻¹) as well as much higher 1C capacity (277 mAh g⁻¹), despite having a similar or lower electrical conductivity (**Table 1**). This indicates that more lithiation sites are available in the herringbone crystal structure of r-HBC and that lithium conduction pathways are significantly improved, ultimately culminating in a high energy density on par with graphite together with a very high power density (see **Figure S4**). p-HBC has a similar C/5 capacity to r-HBC (352 mAh g⁻¹), but an even faster rate capability, with a 1C capacity of 294 mAh g⁻¹, likely due to its increased

electrical conductivity. c-HBC possesses a lower C/5 capacity than all other explored materials due to its lack of structured binding sites. However, it does possess respectable rate capability, only decreasing from 240 mAh g⁻¹ at C/5 to 205 mAh g⁻¹ at a rate of 1C. Notably, the lack of structured binding sites in the structure of c-HBC linearizes its GCD voltage profile (**Figure 3b**), which significantly decreases its overall energy density, as seen in **Figure S4**.

The increase in electrical conductivity of p-HBC compared to r-HBC is corroborated by electrochemical impedance spectroscopy (EIS), as shown in **Figure 3d**, where the width of the semi-circle in the Nyquist plot (here taken to be the material charge transfer resistance) is directly proportional to the impedance of the lithiation event. As consistent with 2-point probe bulk electrical conductivity measurements (**Table 1**), the material charge transfer resistance of h-HBC is of similar magnitude to r-HBC (**Figure 3d**); both molecular crystals exhibit significantly higher resistance than p-HBC, all of which are higher than c-HBC which contains extended graphitic networks and therefore well-connected electrical conduction pathways.

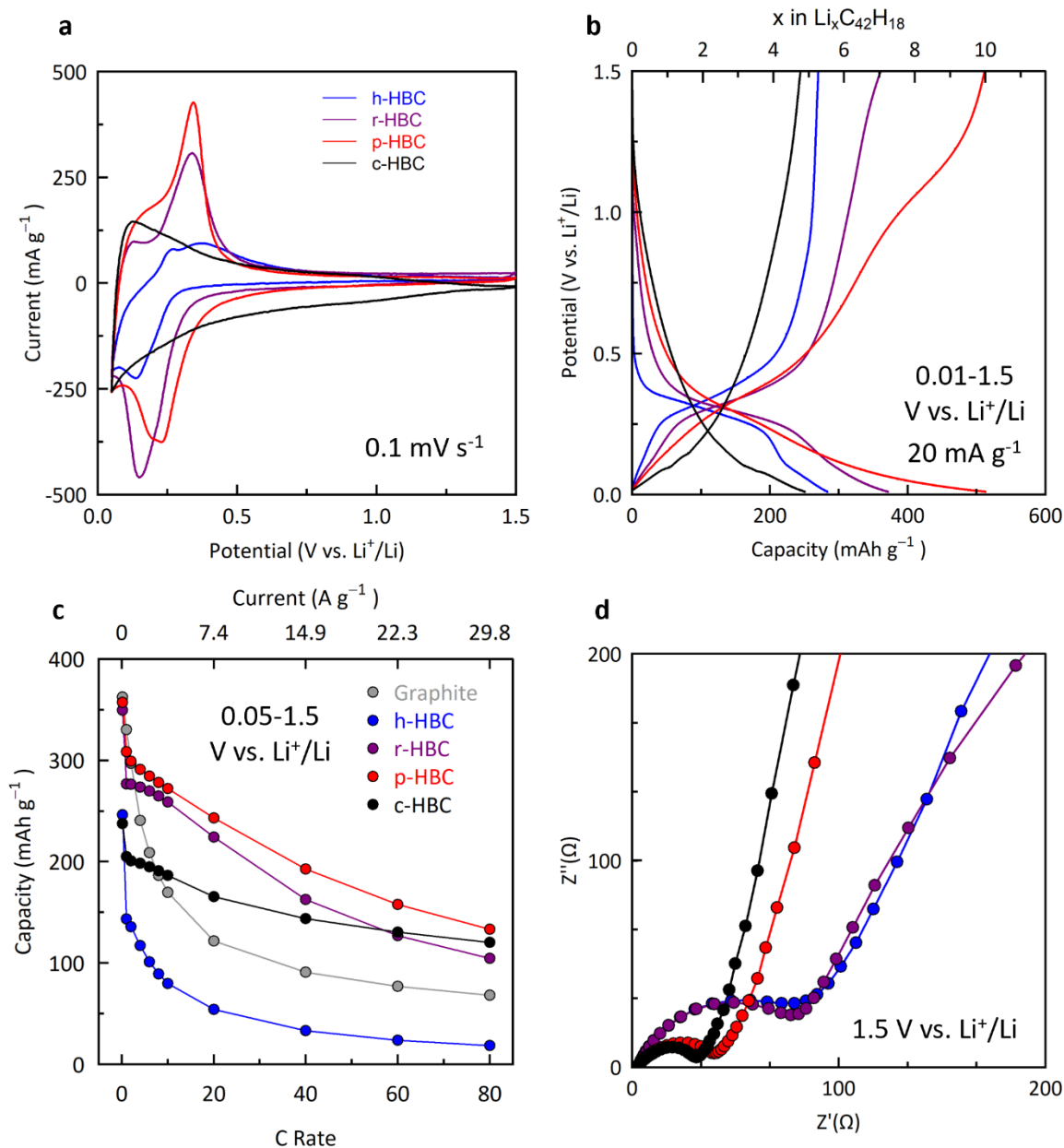


Figure 3. Electrochemical characterization of h-HBC, r-HBC, p-HBC, and c-HBC by (a) CV at 0.1 mV s^{-1} ($\sim 2C$, cycle 4), (b) slow-rate GCD profiles ($\sim C/20$, cycle 10), (c) increasing rate GCD cycling capacity (showing the average across 20 cycles at each rate, from $C/5$ to $80C$), and (d) EIS profiles in the delithiated state (during the 10th cycle). All experiments were carried out in half-cell configuration against excess lithium metal.

The long-cycling stability of all four HBC materials was assessed using a constant current (CC) protocol at a rate of 1 A g^{-1} ($\sim 3\text{C}$ based on a graphite baseline) between 0.01-1.5 V vs. Li^+/Li , as shown in **Figure 4a**. p-HBC exhibited the highest capacity out of all materials at this rate (up to $\sim 260 \text{ mAh g}^{-1}$), as well as the greatest capacity fade: $\sim 3\%$ loss over 600 cycles. The difference in capacities between **Figures 3c** and **4a** is attributable to the different cycling protocol employed; whereas the rate capability tests (**Figure 3c**) were performed using a CCCV protocol, the long-cycling tests (**Figure 4a**) were performed under CC conditions, wherein lithiation is terminated as soon as the voltage limit is achieved.

The overpotential of each HBC material under CC cycling at 1 A g^{-1} , calculated by taking the difference between the average potentials of charge and discharge in each cycle, is shown in **Figure 4b** (see **Figure S5** for the individual average charge and discharge potentials). While h-HBC exhibits a large overpotential of $>0.4 \text{ V}$, representing the combined effects of electrical and ionic resistivity in its tightly packed and poorly organized structure, the overpotential decreases to $\sim 0.2 \text{ V}$ upon recrystallization into the herringbone structure of r-HBC. The overpotential further decreases upon heat-treatment to p-HBC and then c-HBC, mainly due to a corresponding increase in electrical conductivity.

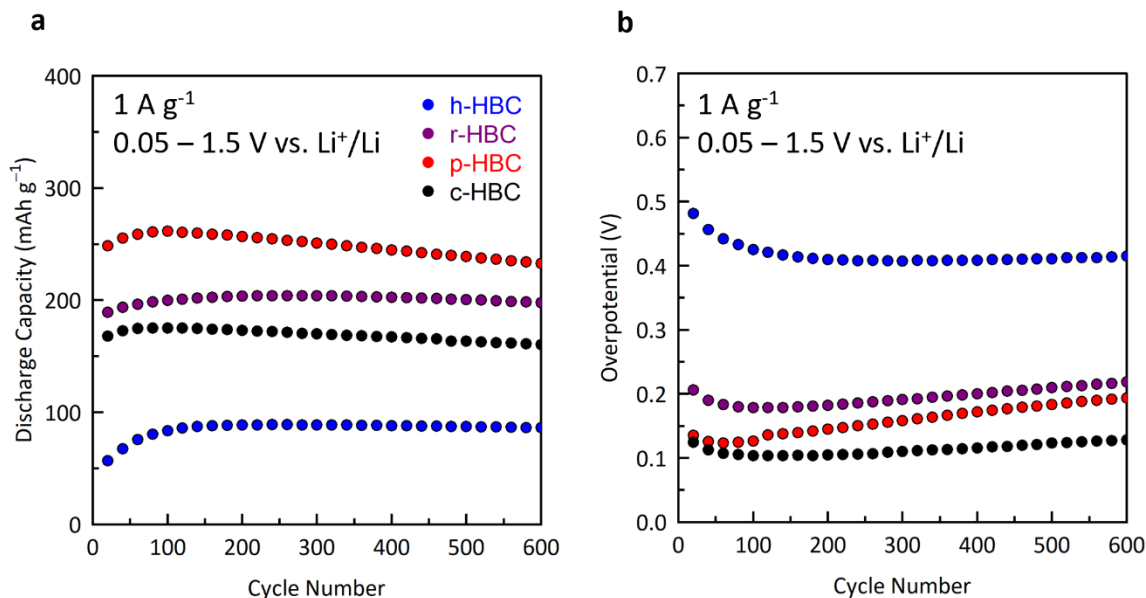


Figure 4. (a) GCD cycling stability and (b) average overpotential for h-HBC (blue), r-HBC (purple), p-HBC (red), and c-HBC (black) at 1 A g⁻¹ between 0.05-1.5 V vs. Li⁺/Li. All experiments were carried out in half-cell configuration against excess lithium metal.

Lithiation sites of HBC

To better understand the electrochemical lithiation of HBC-derived materials, changes in the crystal structure of r-HBC over slow-rate charge/discharge cycling were measured using energy dispersive XRD (EDXRD) under *operando* conditions in fully intact coin-cells against lithium metal. Before lithiation, two major features are evident in the powder pattern of r-HBC at d-spacings of 8.7 and 11.9 Å (**Figure S6** and **Figure 1c**), representative of the (200), (20 $\bar{1}$), and (100) reflections of the monoclinic unit cell. The overlapping (200) and (20 $\bar{1}$) reflections are referred to as the (20 ℓ) peak and were modeled as a single gaussian lineshape. The cells were cycled at a slow rate of 40 mA g⁻¹ down to 0.01 V on lithiation and then returned to 1.50 V vs. Li⁺/Li on delithiation. During the first lithiation, r-HBC loses its characteristic crystallinity at ~0.2 V vs. Li⁺/Li (~600

mAh g⁻¹), becoming semi-amorphous (see **Figure S6**). Upon complete delithiation, a broad peak reappears near the position of the original (001) reflection at a d-spacing of 11.6 Å; this emergent feature is referred to as the (001)* reflection herein.

The position of the broad (001)* reflection could be reproducibly tracked over the course of lithiation and delithiation, providing a convenient handle for changes in the crystal structure of r-HBC during lithium insertion. The primary redox event at ~0.25 V vs. Li⁺/Li causes the (001)* peak center to abruptly shift to higher d-spacing, indicating expansion along the c-axis, as shown in **Figures 5a-5b**. This expansion is significantly reduced during the low-potential redox event, indicating that this secondary event does not cause expansion of r-HBC or that expansion occurred in a different direction (perhaps not observable via diffraction). In total, the (001)* reflection expands from 11.6 to 11.8 Å over the entire course of lithiation, corresponding to a detectable volume expansion of ~2%; expansion along the c-axis indicates the presence of primary lithiation sites located at the intersections of HBC molecular edges (**Figure 5b**, inset). Upon delithiation, the (001)* reflection reverses along a similar path demonstrating the concomitant structural and electrochemical properties of r-HBC. Hence, we refer to the primary lithiation event in r-HBC as “edge site” binding between neighboring HBC molecules in the (001) direction of the original herringbone crystal structure. On the other hand, the low-potential, secondary lithiation event (also observed in electrochemical analysis) is attributable to lithiation between HBC molecules in the π - π stacking direction, as previously discussed; any related expansion along this (41 $\bar{1}$) direction would only have a minor effect on the position of the (001)* peak. Together, the edge sites and π - π sites combine to lend r-HBC its total reversible ~C/20 capacity of 361 mAh g⁻¹.

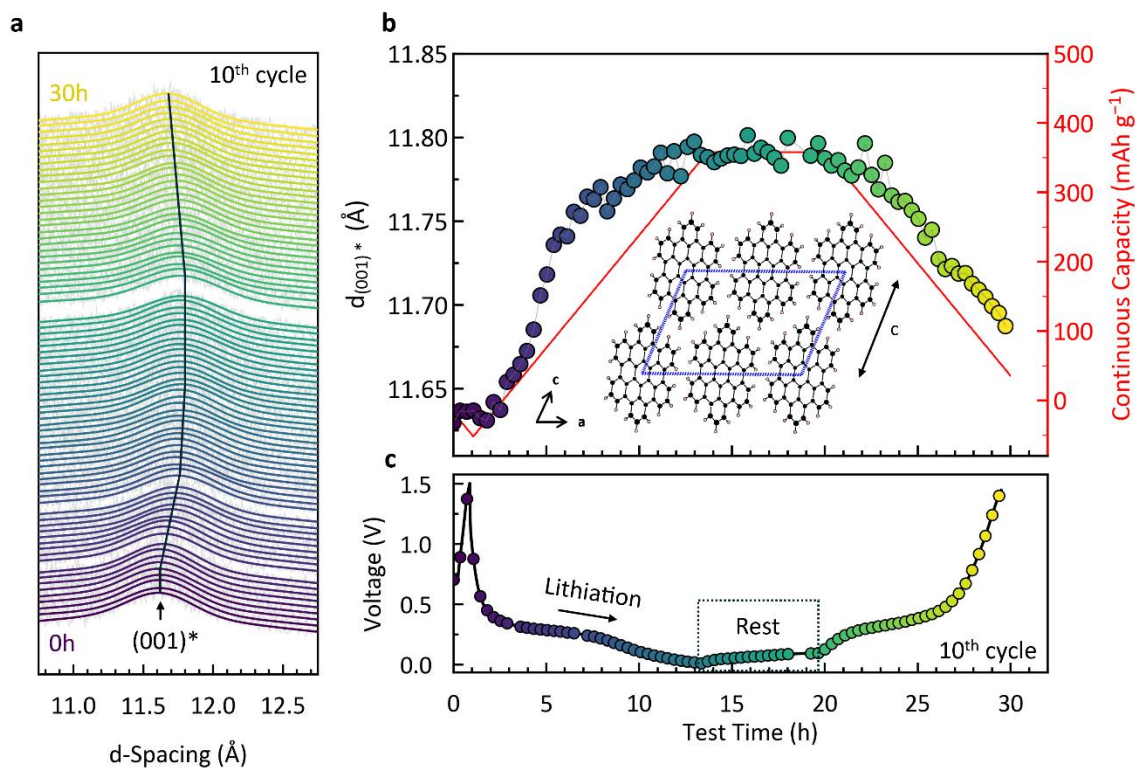


Figure 5. (a) EDXRD patterns of the (001)* region of r-HBC over the course of the 10th cycle lithiation and delithiation between 0.01-1.5 V vs. Li⁺/Li at 40 mA g⁻¹ and the corresponding (b) d_{001}^* and (c) voltage as a function of time. The inset figure shows the crystal structure of r-HBC (CCDC no. 1173297) along the b-axis.

Distinct Features of Edge and π - π Sites

By comparison to r-HBC, h-HBC exhibits a similar GCD profile (**Figure 3**) and hence similar lithiable environments but in lower quantity and with vastly reduced rate capability. The differences in ionic conductivity that directly result from the structural organization of HBC molecules in r-HBC were further explored using galvanostatic intermittent titration technique (GITT), a method combining current pulses with long rest periods to assess kinetics at near-equilibrium potential conditions.

In half-cell configuration, GITT experiments were analyzed using Fick's second law:³⁶

$$D = \frac{4}{\pi\tau} \left(\frac{m_a \bar{v}}{m_m s} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (1)$$

where D is the average ionic diffusivity at a given state of charge, τ is the current pulse duration, m_a is the active mass of the electrode, $\bar{v}$ is the molar volume of HBC, m_m is the molar mass of HBC, s is the surface area of the electrode, ΔE_s is the change in potential between adjacent resting steps, and ΔE_t is the change in potential over the course of a given pulse, excluding the ohmic drop.

Under GITT conditions, h-HBC and r-HBC show a similar lithiation capacity in the high-potential plateau corresponding to the lithiation of edge sites, at ~0.38 V vs. Li^+/Li (**Figure 6**). This lithiation plateau is at a higher potential than observed in slow-rate GCD experiments (**Figure 3b**) owing to the minimal role of cell impedance under such exceedingly slow lithiation conditions as employed in the GITT protocol. r-HBC shows more capacity (405 mAh g^{-1}) than h-HBC (335 mAh g^{-1}) under GITT conditions, due to an enhanced low-potential (π - π site) capacity at $<0.2 \text{ V}$ vs. Li^+/Li . Given the low electrical conductivity of both materials, it is likely that the half-cells simply polarize past the low-potential event during CC charging and discharging, whereas the slow rate and ample relaxation time within the GITT protocol allow for a more thorough characterization of the low-potential region.

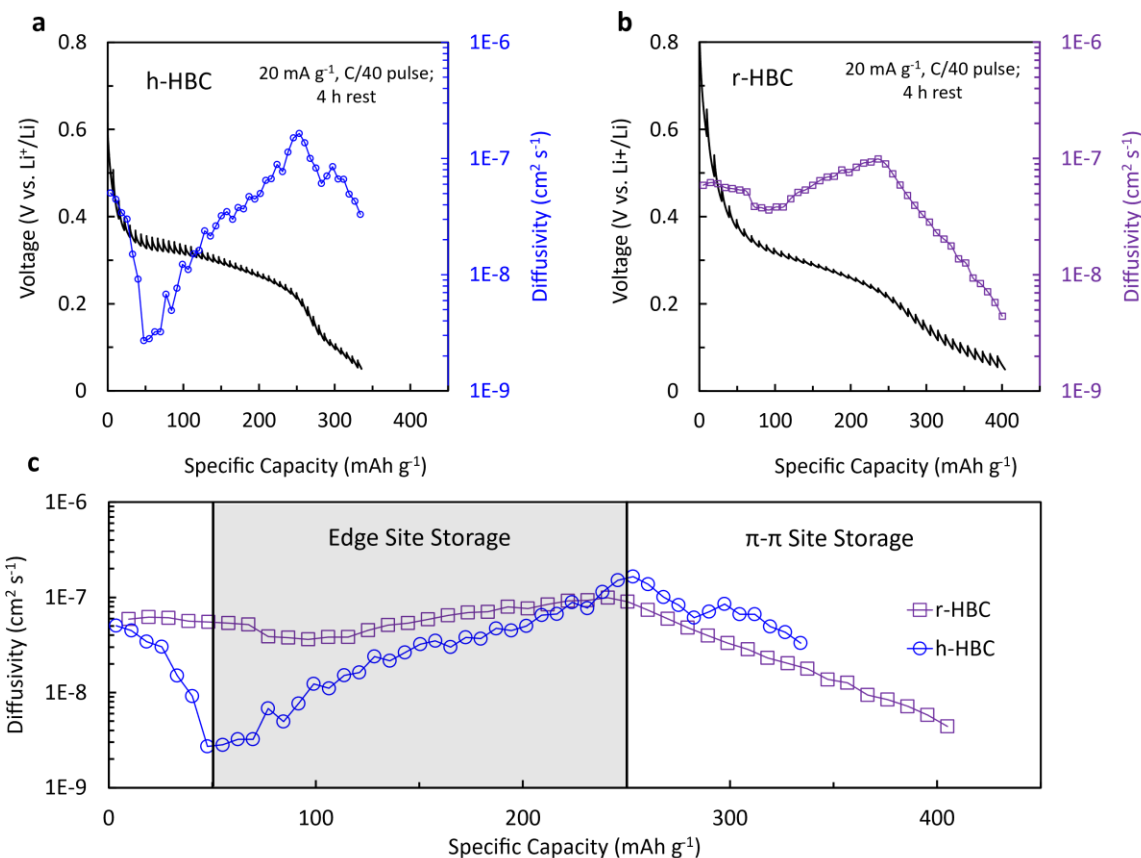


Figure 6. GITT characterization of (a) h-HBC and (b) r-HBC at 20 mA g⁻¹ ($\sim C/20$) between 1.5-0.01 V vs. Li⁺/Li conditions after 10 charge/discharge cycles at 100 mA g⁻¹. (c) Diffusivity of lithium ions in h-HBC (blue) and r-HBC (purple) as a function of capacity, shown on a logarithmic scale, with a vertical line representing the maximum capacity of edge-type lithiation sites.

The diffusivity of lithium ions in h-HBC and r-HBC (calculated via **Equation 1**) as a function of specific capacity is shown in **Figure 6c**. A significant difference is observed between the two polymorphs of HBC in the high-potential, edge-site lithiation region (up to ~ 220 mAh g⁻¹ or $\sim \text{Li}_4\text{C}_{42}\text{H}_{18}$). While the lithium diffusivity in h-HBC decreases along this voltage plateau, that in r-HBC remains relatively constant and typically an order of magnitude higher. This is consistent with the significantly narrower intermolecular (lateral HBC to HBC) distance of only 10.8 Å in h-

HBC instead of 11.6 Å for r-HBC as measured by XRD (**Figure 1d**). At lower potentials corresponding to the lithiation of π - π sites ($>220 \text{ mAh g}^{-1}$), the diffusivity is similar in both polymorphs and steadily decreases until lithiation is complete. This indicates that the kinetics of the secondary (π - π site) lithiation event are relatively unaffected by recrystallization. Similar studies of p-HBC and c-HBC are generally consistent with the above described results, and both exhibit an increased diffusivity in the high-potential region relative to r-HBC (**Figure S7**). In summary, the periodic ion channels in the herringbone structure of r-HBC facilitate significantly faster lithium-ion transport relative to the interstices between columnar stacks of HBC molecules in hexagonal h-HBC.

Structure-Dependent Pseudocapacitance

Finally, several complementary electrochemical analyses employed to assess the type of ion storage mechanism were used to further investigate the lithiation of all four HBC materials.⁹ First, the CV measurements were performed between 0.05-1.50 V vs. Li^+/Li at increasing scan rates from 0.1 to 1.0 mV s^{-1} (**Figures 7a-7d**). The Randles-Ševčík equation describes the relationship between the measured current and applied the scan rate as follows:³⁷

$$I = av^b \quad (2)$$

where I is the peak current passed, v is the scan rate, a is a constant dependent on the experimental conditions, and b is a value between 0.5-1 that depends on the mechanism of charge storage (from faradaic, 0.5, to capacitive, 1).^{37,38} While h-HBC demonstrates a battery-like (faradaic) b -value of 0.44-0.51, r-HBC exhibits a distinctly higher b -value of 0.69-0.70, slightly differing along the anodic and cathodic sweeps, respectively (**Figure 7e**). Hence, r-HBC exhibits a Randles-Ševčík slope that is intermediate between capacitive and faradaic charge storage mechanisms, a regime

commonly referred to as pseudocapacitive.^{39,40} This result is somewhat surprising owing to the similar GCD voltage profiles of these two polymorphs of HBC (**Figure 3b**), but is consistent with their measured rate capability which demonstrates that r-HBC is far less limited in capacity at high rates (**Figure 3c**).

To complement Randles-Ševčík analysis, a further method known as Trasatti analysis^{41,42} was carried out using the same CV data (**Figure S8**). This analysis assesses the normalized rate-independent capacity of active electrode materials, another metric that depends on the mechanism of charge storage (from faradaic, 0%, to capacitive, 100%).^{43,44} By the Trasatti method, h-HBC and r-HBC exhibited ~5% and ~70% rate-independent capacities, respectively, showing the conversion from a highly rate-limited material to a pseudocapacitive material simply upon recrystallization into the herringbone structure. These results corroborate the trends observed by Randles-Ševčík analysis.

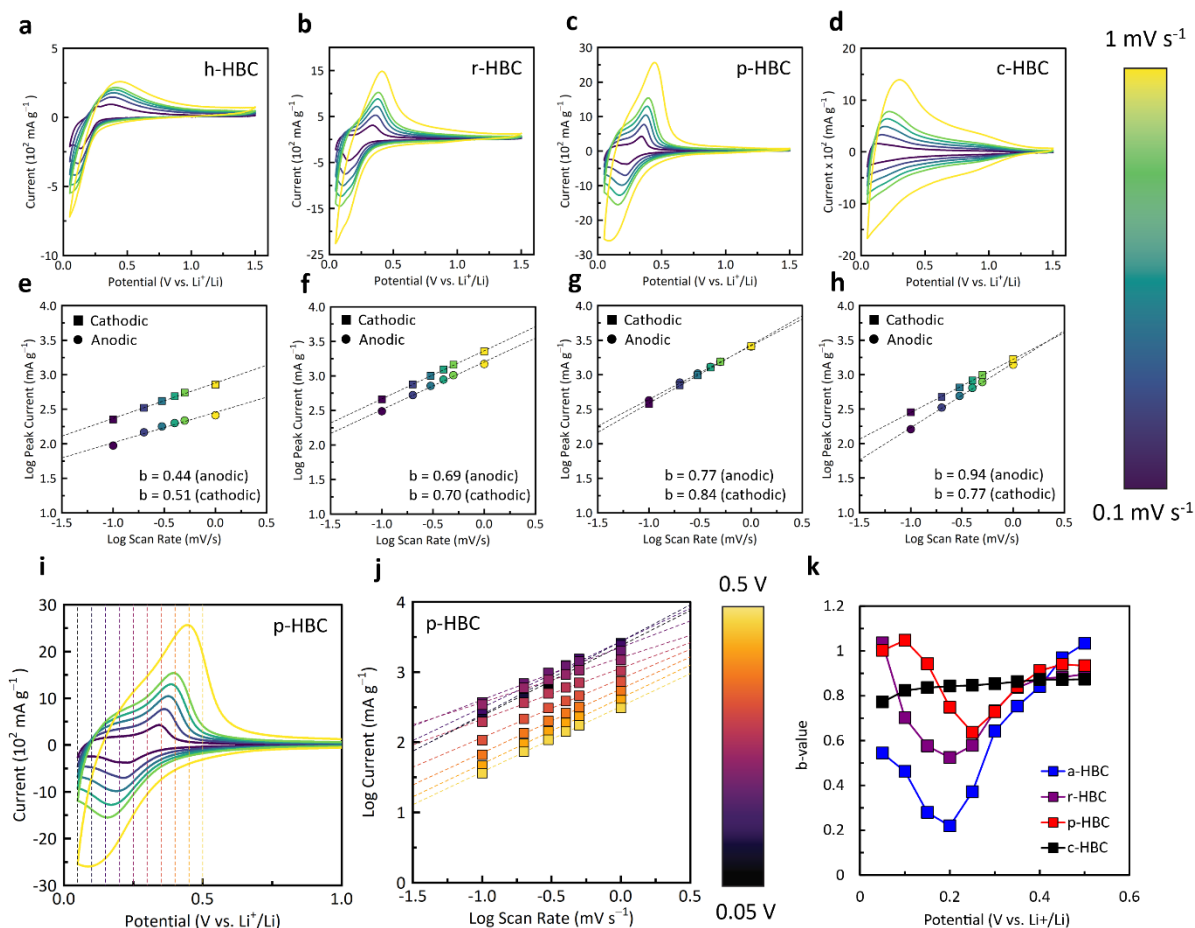


Figure 7. Randles-Ševčík analysis of all four HBC materials. (a-d) CV under increasing scan rates between 0.1 (purple) and 1.0 mV s⁻¹ (yellow) and (e-h) corresponding anodic (circles) and cathodic (squares) Randles-Ševčík plots. (i) CV under increasing scan rates of p-HBC between 0.1 and 1.0 mV s⁻¹ with constant potential sampling lines between 0.05 (black) and 0.5 V vs. Li⁺/Li (yellow), (j) cathodic (lithiation) log current vs. log scan-rate plot for p-HBC at each potential, and (k) cathodic b-value as a function of potential for each HBC material.

By comparison to h-HBC and r-HBC, the Randles-Ševčík analysis of p-HBC revealed a higher b-value of 0.77-0.84, showing that polymerization further increases the capacitive properties of HBC. Finally, c-HBC exhibits the highest b-value of up to 0.94, corroborating that it behaves as a turbostratic disordered carbon and undergoes a capacitive-type mechanism that is extremely different from the bulk, faradaic mechanism of h-HBC. All of these results were also

corroborated by a variant of the standard Randles-Ševčík analysis, where the b -value is calculated as a function of potential rather than simply at the peak current of each CV.¹¹ This analysis was performed in 50 mV intervals from 50-500 mV vs. Li^+/Li (**Figures 7i-7j, Figure S9**). The derived potential-dependent cathodic b -values (**Figure 7k**) show an obvious decrease around the potential of the primary insertion mechanism in h-HBC, r-HBC, and p-HBC (~ 0.25 V vs. Li^+/Li)—consistent with their CV signatures, demonstrating that their primary lithiation event is more kinetically hindered than at other points in the voltage profile.

Finally, potential-dependent Bode analysis of EIS measurements, as recently implemented by Ko and colleagues based on the original method introduced by Bai and Conway, can also be used to distinguish between the faradaic, capacitive, and pseudocapacitive charge storage mechanisms.^{46–51} The real capacitance at each frequency was calculated according to:

$$C' = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (3)$$

where C' is the real capacitance, ω is the angular frequency of the applied wave, $Z''(\omega)$ is the imaginary impedance, and $|Z(\omega)|^2$ is the magnitude of the total impedance. The real capacitance of all HBC materials as a function of frequency and the state of charge (i.e., potential) is shown in **Figure 8**. Corresponding current response and potential dependent Nyquist plots are shown in **Figures S10 and S11**. In addition, standard Bode plots at the potentials of highest interest for each material are shown in **Figure 8c**. The peak capacitance is shown to increase monotonically as HBC is heat treated from h- to r-, r- to p-, and p- to c-HBC. In the potential dependent plots, h-HBC exhibits a narrow distribution of peaks with a predominant feature at 0.2 V (**Figure 8d**), r-HBC and p-HBC exhibit a clear bimodal distribution of capacitance (**Figures 8b and 8e**), and finally c-

HBC exhibits no peak definition and high capacitance. This implies that h-HBC is faradaic, r- and p-HBC are pseudocapacitive, and c-HBC is capacitive.

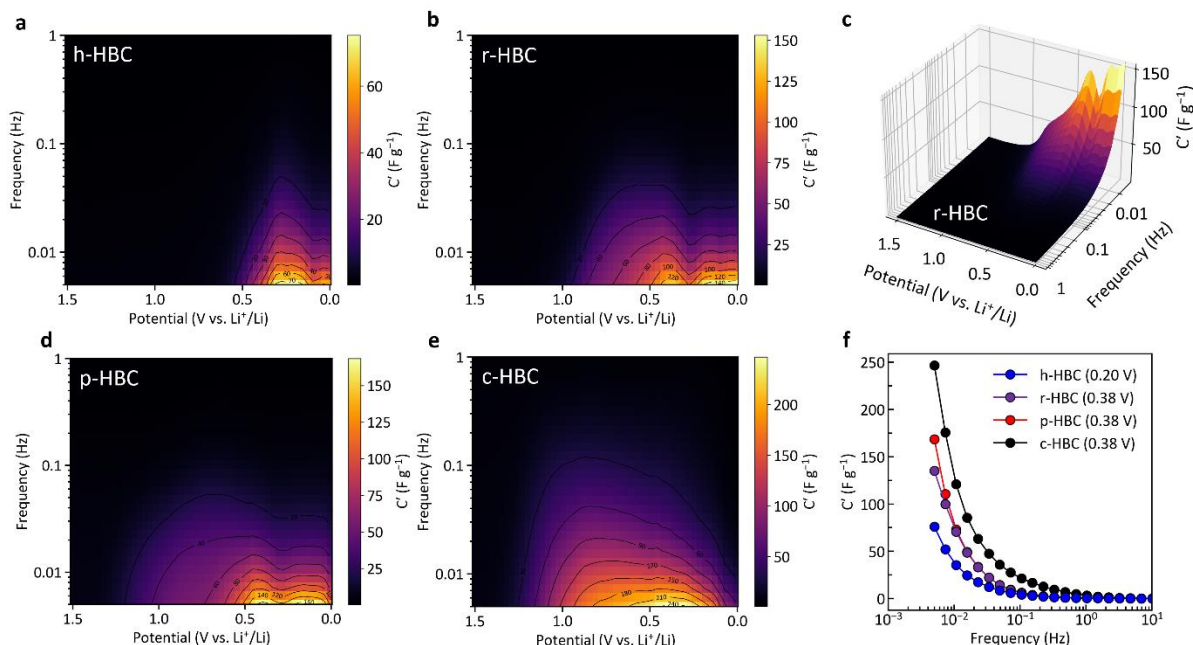


Figure 8. Real capacitance (C') as a function of EIS frequency (i.e., Bode plots) and potential (i.e., 3D Bode plots) of (a) h-HBC, (b-c) r-HBC, (d) p-HBC, and (e) c-HBC. (f) Standard Bode plots at selected potentials for all four HBC materials.

Conclusions

A new model pseudocapacitive material (or series of materials) based on the molecular hydrocarbon HBC has been presented; the pseudocapacitive charge storage mechanism of HBC depends significantly on the structural organization of the HBC molecules. Unlike past pseudocapacitive crystals for lithium storage, HBC-derived materials are predominantly composed of carbon and entirely composed of light elements, with no oxygen present. While the commercially available columnar hexagonal variant, h-HBC, has a relatively low lithiation

capacity and limited rate capability, the recrystallized variant (r-HBC, with a distinct herringbone structure creating edge-type sites between neighboring HBC molecules) exhibits a high capacity, corresponding to $\text{Li}_7[\text{HBC}]$ (or $\text{Li}_7\text{C}_{42}\text{H}_{18}$), in addition to a remarkably high rate capability. Furthermore, the rate capability of r-HBC increases when gently polymerized at 700 °C despite losing some crystallographic reordering, representing a trade-off between crystallinity and electrical conductivity. Upon excessive pyrolysis (e.g., to 1000 °C, referred to as c-HBC), the molecular lithium-ion storage sites in HBC are lost, and only capacitive lithium binding by amorphous carbon remains. The model HBC material for practical applications, p-HBC, retained >97% of its original capacity after 600 cycles, indicating that the desirable kinetic properties of HBC could be accessed reversibly without any major issues such as dissolution of the molecular solid active lithium host. The lithiation mechanism of HBC was analyzed through a combination of *operando* XRD, GITT, variable rate CV, and stepped-potential EIS, all of which reveal a unique event at ~0.38 V vs. Li^+/Li that is unambiguously pseudocapacitive and likely originates from the insertion of lithium ions at edge sites along the (001) direction of crystalline herringbone HBC. This novel pseudocapacitive material for fast and high energy density lithium storage is especially promising for rapid discharge battery applications and opens new avenues for discovering even higher performing PAH crystals for LIB anodes.

Methods

Materials Synthesis

Hexabenzob[bc,ef,hi,kl,no,qr]coronene (referred to herein as h-HBC) was obtained from a commercial supplier (97%, A365850, Ambeed) and used as-received. Heat-treated HBC materials were obtained via the pyrolysis of h-HBC under inert conditions at elevated temperatures. In each

case, ~80 mg of h-HBC was charged into a quartz ampule in an argon-filled glovebox (<0.5 ppm O₂, <0.5 ppm H₂O). The ampules were then sealed with an UltraTorr Swagelok adapter and removed from the glovebox. The ampule was submerged in liquid nitrogen, attached to a stainless-steel Schlenk line, evacuated to 10⁻³ mbar, and then sealed with a hydrogen/oxygen torch. The ampule was heated in a chamber furnace (RWF 12/13, Carbolite Gero Ltd.) up to a set point via a 5 °C min⁻¹ ramp rate and held for 1 h, then naturally cooled to ambient. The products were retrieved by scoring and snapping the ampules in air (caution: polymerization or carbonization result in a high developed pressure inside the ampule). Each sample was washed with acetone and water (3× each) and then dried at 80 °C overnight prior to further investigation.

Materials Characterization

XRD patterns of hand-ground samples were measured using a benchtop powder diffractometer (D2 Phaser, Bruker Corp.) in reflection geometry with Cu K $\alpha_{1,2}$ radiation ($\lambda = 1.54$ Å). Measurements were performed in 0.02° increments for 1 s each from $2\theta = 5$ -60°. Raman spectra were measured using a microscope-equipped spectrometer (LabRAM HR Evolution, Horiba Scientific Ltd.) with a 532 nm Nd:YAG laser source between 500-3500 cm⁻¹. N₂ adsorption measurements were performed using a volumetric Sieverts apparatus (3Flex, Micrometrics Corp.) at ~77 K and surface area was calculated using the Brunauer-Emmett-Teller (BET) model. Elemental (CHO) analysis was determined by flame combustion (Atlantic Microlab Inc.). Two-point electrical conductivity was measured using a sourcemeter (Keithley SMU 2450, Tektronix Inc.) by loading 2-3 mg of material into a glass tube and compressing in a vice between titanium rods until the conductivity reached a maximum.

Operando EDXRD was performed using polychromatic white light at the 6-BM-A beamline of the Advanced Photon Source (APS) at Argonne National Laboratory.⁵² Coin cells with r-HBC-containing working electrodes and lithium metal counter electrodes were affixed to a motorized cell holder, with the r-HBC-containing electrode on top. The detector was fixed at an angle of $2\theta = 0.93^\circ$ and calibrated with a silver behenate standard; the X-ray spectra were measured between 50-120 keV. Pre-formed cells were cycled at 40 mA g^{-1} and pristine cells were cycled at 60 mA g^{-1} , between 0.05-1.5 V vs. Li^+/Li . EDXRD patterns were collected at three different locations through the cross section of the working electrode of each cell over 90 s intervals each; four cells were studied in tandem, resulting in each spot in each cell being scanned every ~ 20 min (a negligible change in lithiation state occurred over the course of any single scan).

Electrode Fabrication

Electrodes were fabricated by mixing the active material (e.g., p-HBC) with conductive additive (Super P, MTI Corp.) and binder (polyvinylidene fluoride (PVDF), MSE Supplies) in an 8:1:1 ratio, in a volatile solvent (N-methyl-pyrrolidone, NMP, Sigma Aldrich). First, the active material and Super P were hand ground together for 15 min in a mortar and pestle to ensure homogeneity of the powder. Then, the solvent and binder were added, and the slurry was mixed for an additional 5 min. The homogenous slurry was then cast via doctor blade with a 165 μm wet gap onto copper foil (12 μm thickness, MTI Corp.). The as-cast slurry was then dried overnight at 80 $^\circ\text{C}$ in air and then transferred to a vacuum oven (VDL 56, Binder GmbH) at 100 $^\circ\text{C}$ and 3 mbar overnight. The active material loading for all electrodes explored herein was between 0.9-1.5 mg cm^{-2} .

Cell Fabrication

Stainless steel coin cells (2032 format, Xiamen AOT Ltd.) were assembled in an argon-filled glovebox (<0.1 ppm O_2 , <0.1 ppm H_2O) by layering a working electrode (described above) on top of a glass fiber separator (Whatman, GF/D) above a lithium chip counter electrode (16 mm diameter, 99.9%, MTI Corp.) , completed with a conical spring and a 1 mm thick spacer. The cell was flooded with electrolyte: 1M $LiPF_6$ in a mixture of ethylene carbonate and dimethyl carbonate (EC/DMC 1:1 by weight) (LP30, Gotion Inc.). The cells were then rested for 3 hours prior to testing to allow for full wetting of the separator.

Electrochemical Characterization

GCD cycling was performed using a battery cycler (CT30001A, Landt Instruments) in an incubator held at 25 °C (KB53, Binder GmbH). Several different protocols were employed depending on the experiment. For the slow-rate voltage profiles (**Figure 3b**), half-cells were cycled 10 times at 20 mA g^{-1} between 0.01-1.5 V vs. Li^+/Li . For cycling stability studies (**Figure 4**), half-cells were cycled 600 times at 1 A g^{-1} between 0.05-1.5 V vs. Li^+/Li . For rate capability tests, half-cells were cycled under the following conditions: CCCV discharge (lithiation) was performed at 74.4, 372, 744, 1488, 2232, 2976, 3720, 7440, 14880, 22320, and 29760 mA g^{-1} , sequentially for 20 cycles each (with the exception of the 74.4 mA g^{-1} rate, which was only for 6 cycles), corresponding to C-rates of C/5, 1C, 2C, 4C, 6C, 8C, 10C, 20C, 40C, 60C, and 80C, respectively, based on the theoretical capacity of graphite (372 mAh g^{-1}). A constant voltage (0.05 V) was held after the galvanostatic step if the cell did not surpass the time allotted based on the theoretical C-rate (e.g., 6 min total at 10C). The cells were then charged (delithiated) at a fixed rate of 5 mA (~ 5

A g^{-1}) unless their discharge rate was below 5 mA, in which case the charge rate was simply the same as the discharge rate. No constant voltage step was applied for the charge. The average CCCV discharge capacity based on 10 cycles across 2 cells (5 cycles per cell) is reported in **Figure 3c**. Ragone analysis of energy and power density (**Figure S4**) was performed on an electrode basis using the same CCCV discharge data. The energy density values were acquired by first calculating the average potential of an HBC-derived electrode by taking the area under the curve of the voltage profile and multiplying by the capacity. The average potential of the electrode was then subtracted from the simulated potential of an LiFePO_4 cathode with an average voltage of 3.45 V vs. Li^+/Li to obtain the cell voltage. The cell voltage for each cycling rate was then multiplied by the gravimetric capacity measured in the half cell to obtain the energy density. The power density was obtained by dividing the energy density by the lithiation time in hours.

GITT experiments were performed on preformed half-cells which had been cycled 10 times between 0.01-1.5 V vs. Li^+/Li at a rate of 20 mA g^{-1} . GITT was then performed under discharge between 1.5-0.05 V vs. Li^+/Li . Each step in the GITT protocol comprised a current pulse of 20 mA g^{-1} for a time corresponding to $1/40^{\text{th}}$ of the reversible 20 mA g^{-1} capacity ($C/40$) for a given electrode followed by a rest for 4 h.

CV was performed starting with fresh half-cells using a high-precision potentiostat (VMP-3e, BioLogic SAS) at increasing scan rates of 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 mV s^{-1} for 4 cycles per scan rate. Randles-Ševčík analysis was performed using two methods: by comparing scan rate and peak current (regardless of potential) or by comparing scan rate and actual current (at fixed potentials), as shown in **Figures 7**. Both analyses used the 4th cycle at each scan rate. Trassati

analysis was carried out for the 4th cycle at each scan rate by integrating the charge under the cathodic (lithiation) trace and plotting versus the inverse root of the scan rate ($v^{-1/2}$).

EIS experiments were performed on cells which had been preformed in a similar protocol to the GITT experiments, by cycling 10 times from 0.01-1.5 V vs. Li^+/Li at a rate of 20 mA g^{-1} on a Landt battery cyclers described above before EIS testing. EIS was carried out on a high-precision potentiostat (VMP-3e, BioLogic SAS) using the stepped-potential electrochemical impedance spectroscopy (SPEIS) technique. Spectra were measured in the discharge direction at specific potentials between 1.5-0.01 V vs. Li^+/Li using an AC amplitude of 10 mV in 50 mV intervals between 1.5-1.0 V vs. Li^+/Li and then 25 mV intervals between 1.0-0.01 V vs. Li^+/Li . At each potential step, the electrode was held for 1 h to equilibrate prior to EIS measurement. Individual EIS spectra were measured between 5 mHz and 100 kHz with 6 points per logarithmic decade, following a previously established protocol⁵¹.

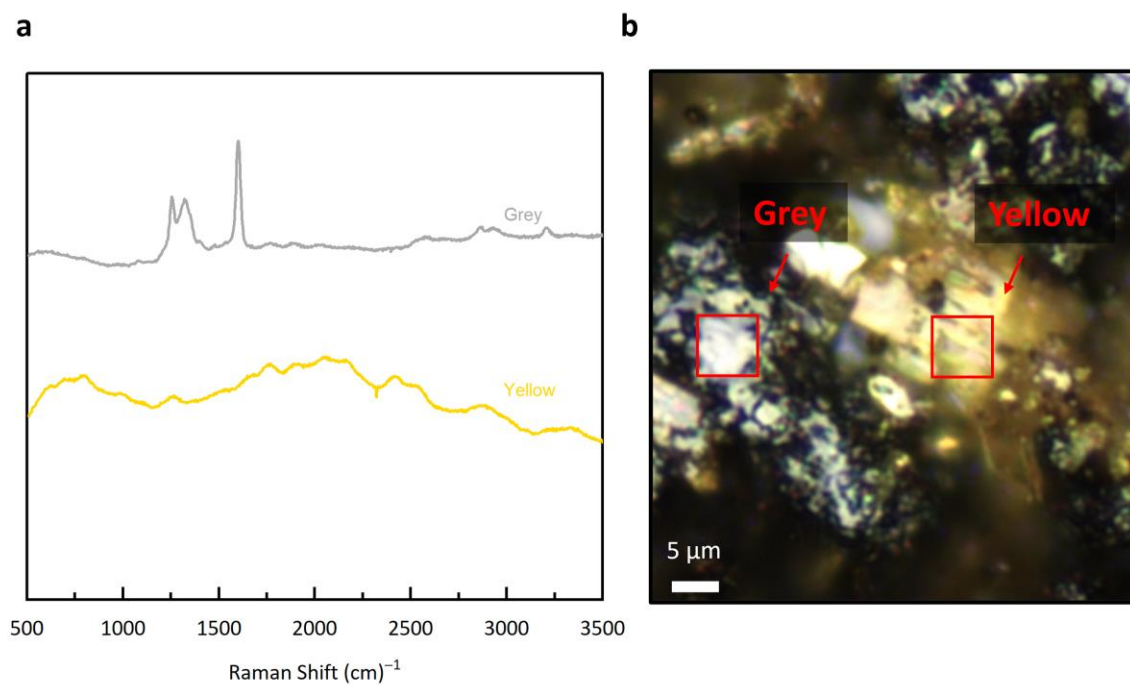
Supporting Information

Figure S1. (a) Raman spectra and (b) microscopy images of two distinct region types observed within r-HBC, referred to herein as grey and yellow.

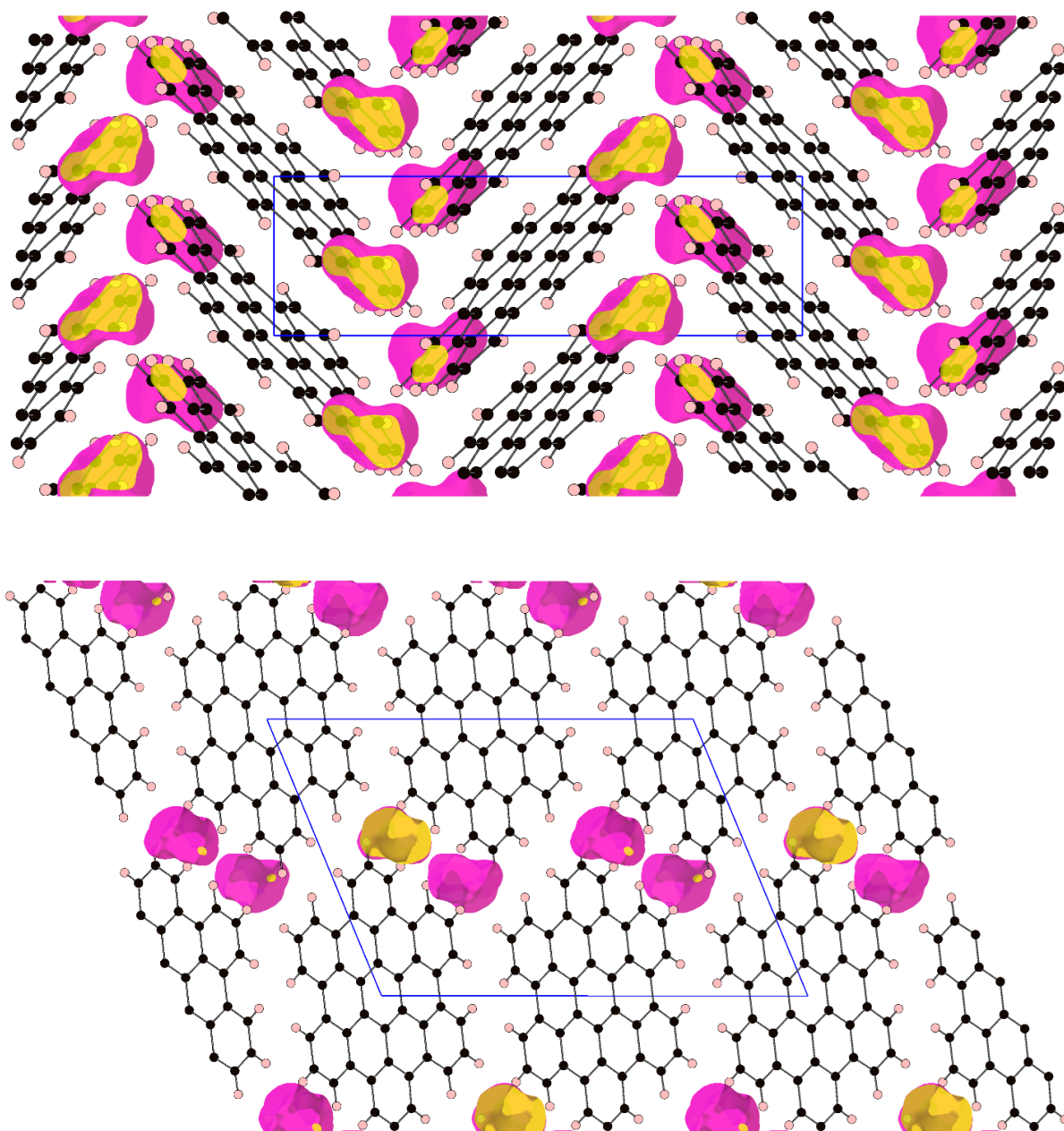


Figure S2. Proposed lithiation sites in the monoclinic herringbone structure of HBC (CCDC no. 1173297) found by searching for voids with a probe of size 0.7 Å, visualized along the (top) [001] and (bottom) [010] directions. Carbon is shown in black and hydrogen is shown in light pink. Each void is pink on the side inaccessible to probes, and yellow on the side accessible to probes. The unit cell is outlined in blue.

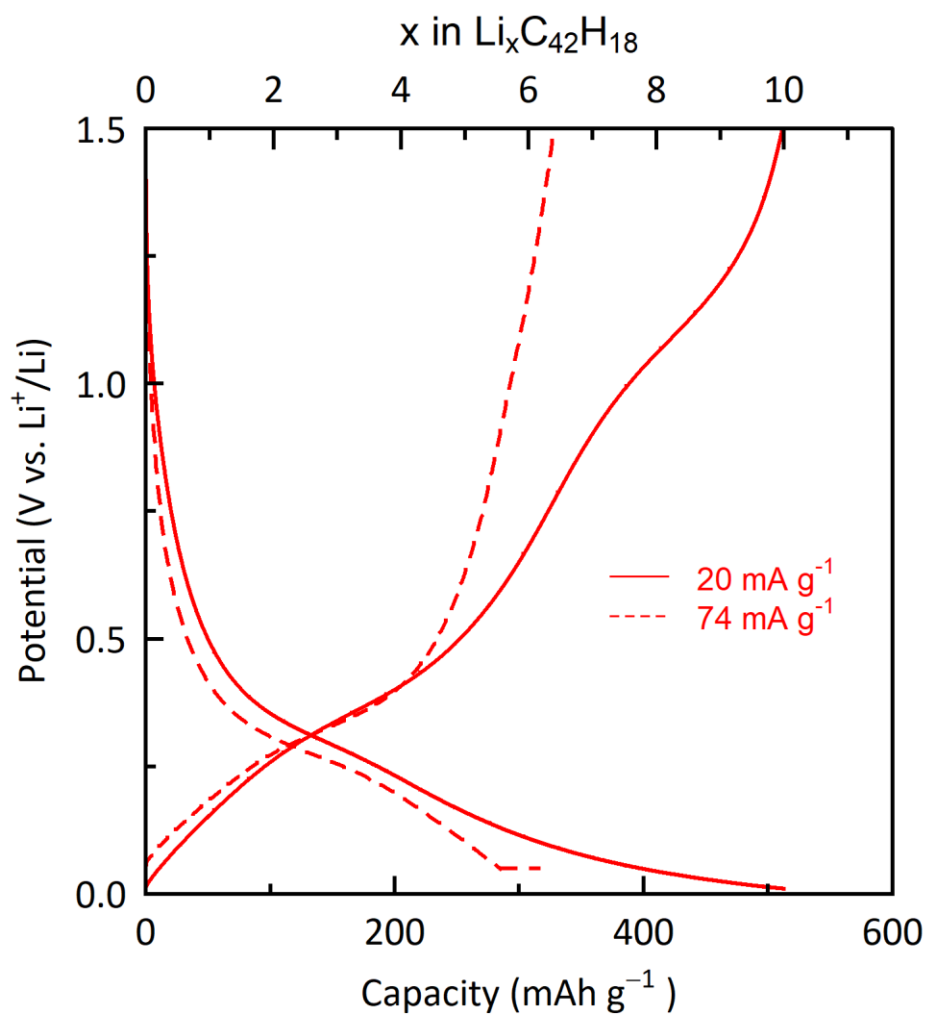


Figure S3. GCD profiles of p-HBC at 20 and 74 mA g^{-1} (5th cycle) between 0.01-1.5 V vs. Li^+/Li , under CC and CCCV protocols, respectively.

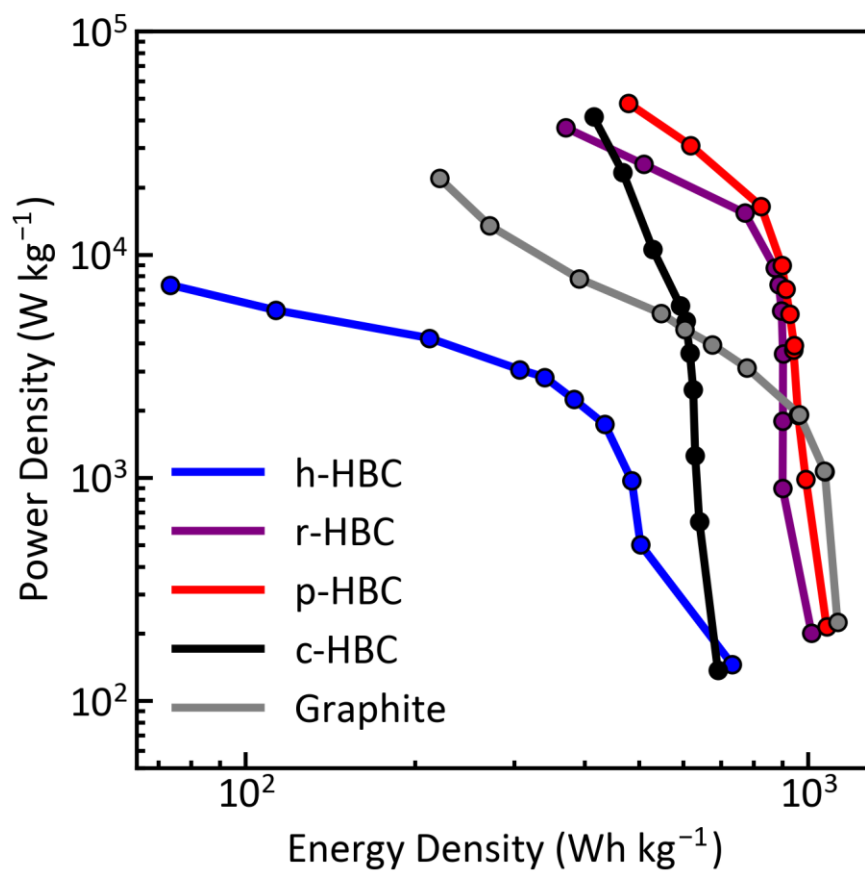


Figure S4. Electrode-specific Ragone plot of h-HBC (blue), r-HBC (purple), p-HBC (red), c-HBC (black), and graphite (grey).

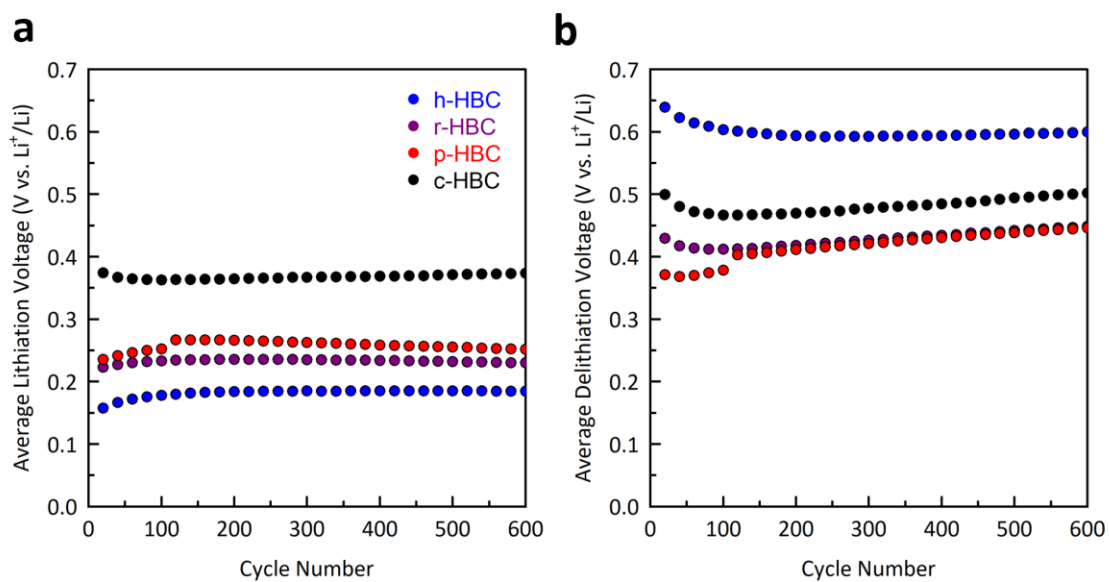


Figure S5. Average (a) lithiation and (b) delithiation potential per cycle for h-HBC (blue), r-HBC (purple), p-HBC (red), and c-HBC (black).

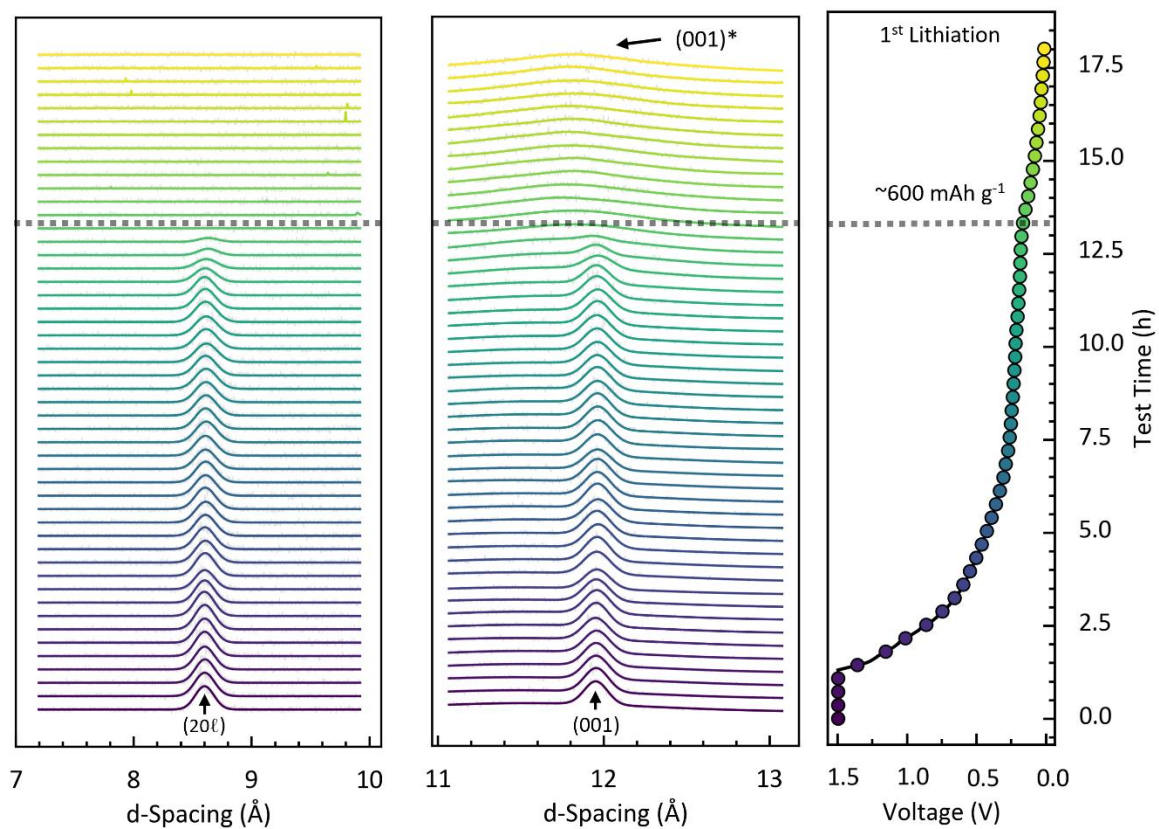


Figure S6. 1st lithiation operando XRD patterns of the (a) (20 ℓ) and (b) (001) reflection regions of r-HBC; (c) accompanying voltage profile with each XRD scan represented as a colored dot.

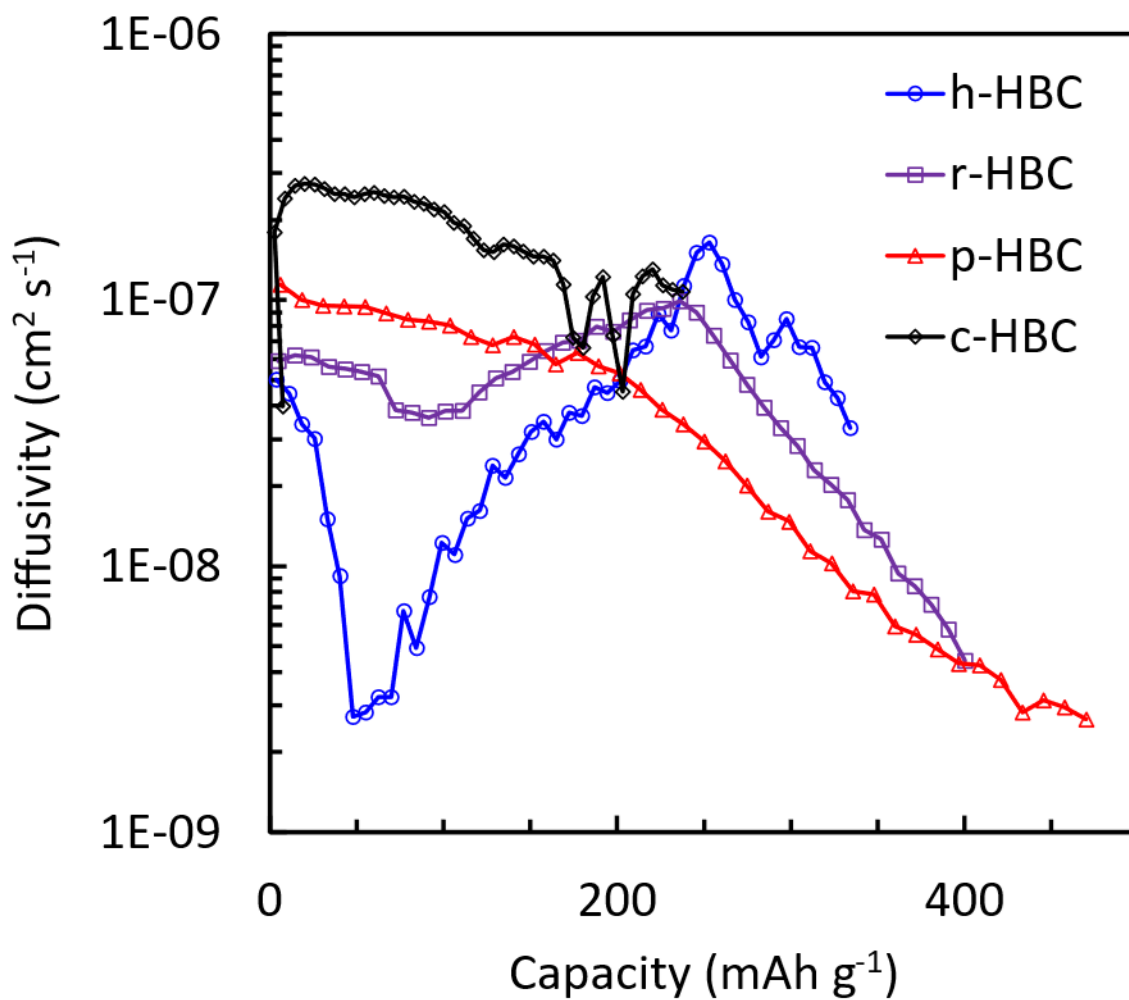


Figure S7. GITT-derived diffusion coefficient for h-HBC (blue circles), r-HBC (purple squares), p-HBC (red triangles), and c-HBC (black diamonds) from 1.5-0.05 V vs. Li⁺/Li. . Data were acquired similarly to those in **Figure 6**.

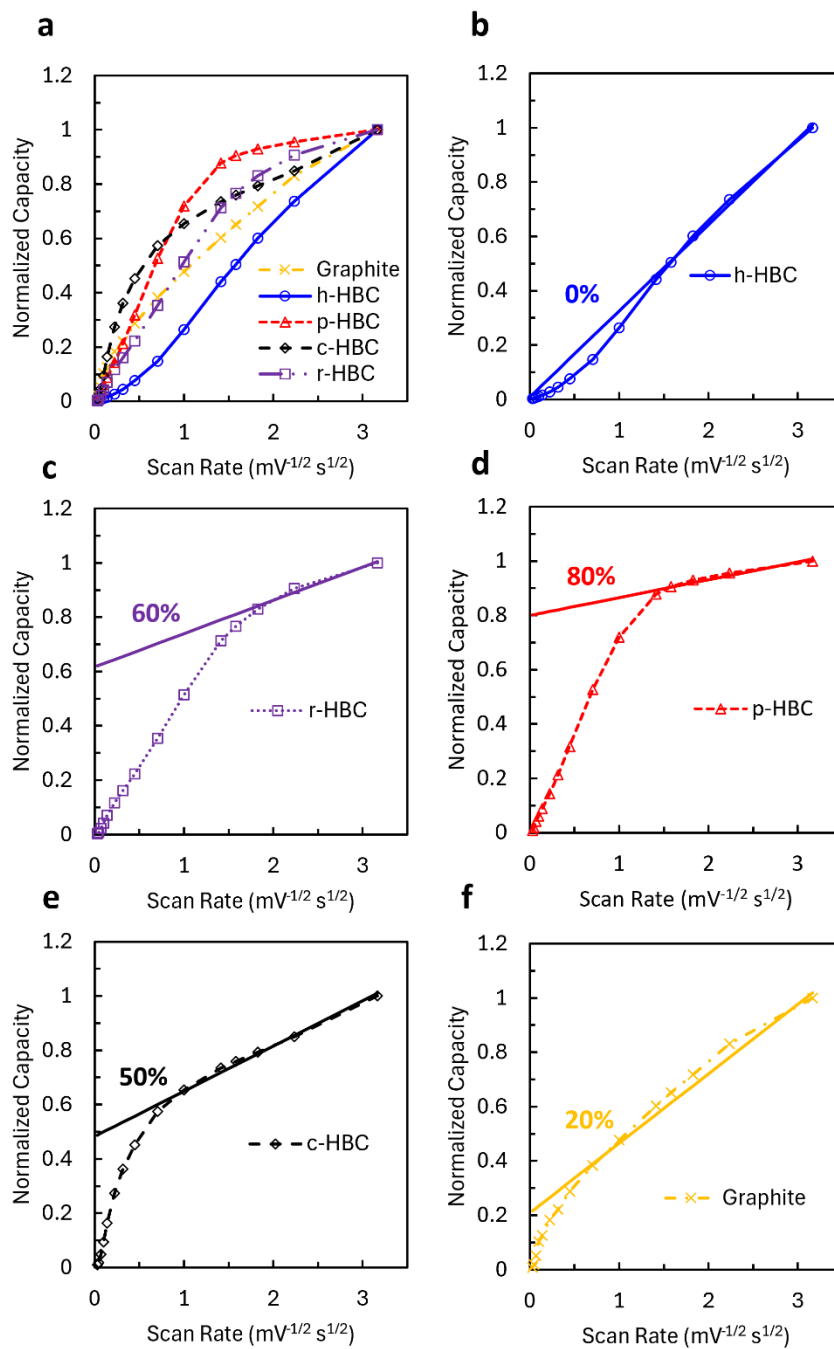


Figure S8. (a) Trassati plot of HBC materials and graphite, showing the integrated cathodic capacity from cyclic voltammetry at various scan rates. Individual Trassati plots for (b) h-HBC (blue circles, solid line), (c) r-HBC (purple squares, dotted line), (d) p-HBC (red triangles, short dashed line), (e) c-HBC (black diamonds, long dashed line), and (f) graphite (yellow crosses, dot-dashed line). Lines are fit to the linear region of each plot to predict the normalized semi-infinite diffusion capacity.

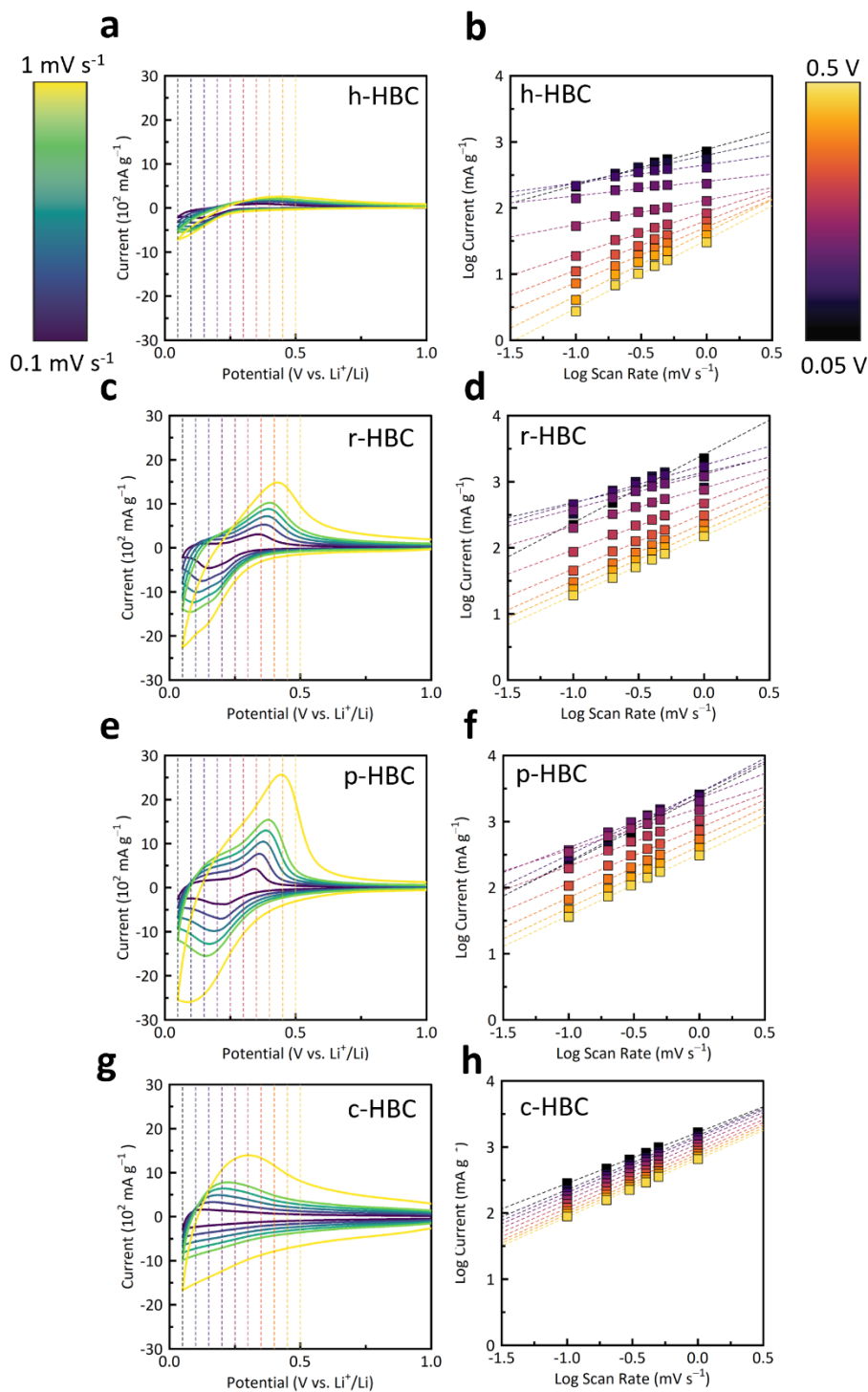


Figure S9. Scan-rate varied CVs (left) and corresponding potential-dependent Randles-Ševčík plots (right) for (a, b) h-HBC, (c, d) r-HBC, (e, f) p-HBC, and (g, h) c-HBC.

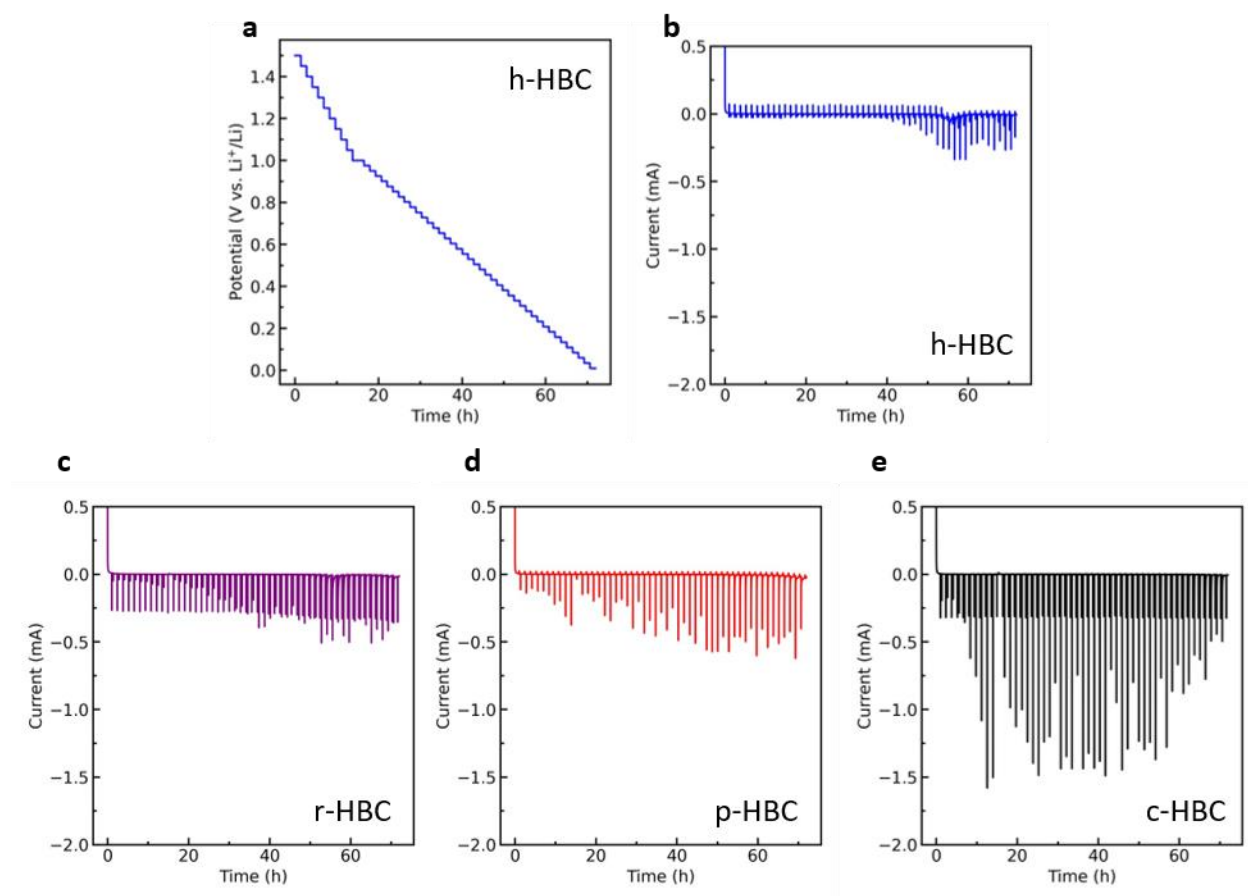


Figure S10. Potential vs. time plot of stepped potential electrochemical impedance spectroscopy (SPEIS) process for all materials investigated.

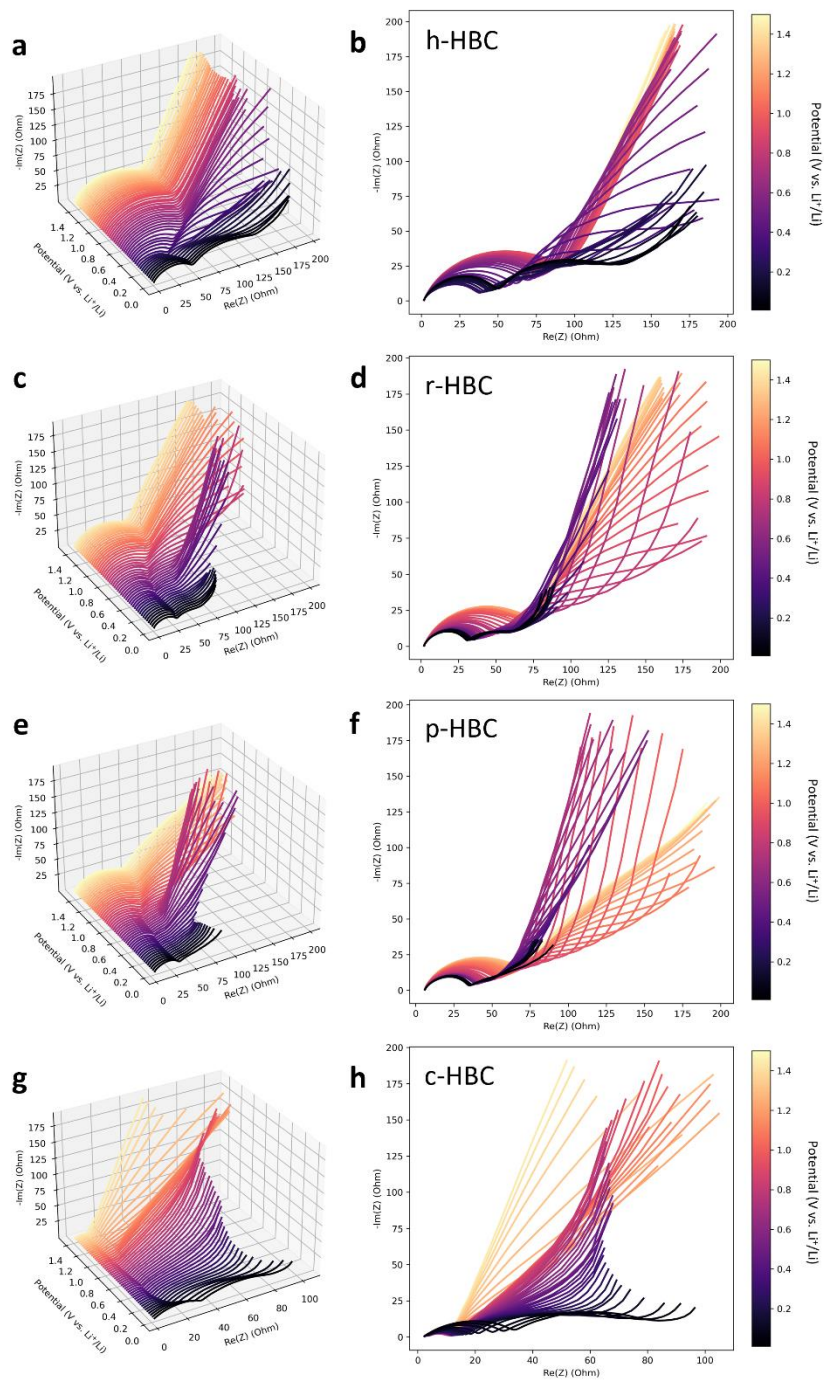


Figure S11. 10th cycle 3D and 2D Nyquist plots of (a, b) h-HBC, (c, d) r-HBC, (e, f) p-HBC, and (g, h) c-HBC.

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CHAPTER FIVE

PRELITHIATED SiO_x /GRAPHITE–NMC811 CELLS:
CAPACITY LOSS, IMPEDANCE RISE AND HIDDEN
DEGRADATION PATHWAYS REVEALED USING THREE-
ELECTRODE DIAGNOSTICS

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Manuscript Information

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Abstract

Electrodes containing SiO_x/graphite(Gr) materials are attractive as anodes for high-energy lithium-ion batteries. However, their mechanical deformation, electrochemical response, and impedance evolution during long-term cycling are strongly coupled, complicating accurate diagnosis of performance fade mechanisms. In this work, the behavior of electrochemically prelithiated SiO_x/Gr anodes paired with NMC811 cathodes is systematically investigated using techniques that include in-situ dilatometry, three-electrode electrochemistry, and multiscale post-cycling microscopy. The SiO_x/Gr electrode exhibits a maximum expansion of 49% upon lithiation to 10 mV vs. Li⁺/Li, with 84% of the expansion and 91% of the capacity being reversible. In full cells, relatively stable cycling with only 12% capacity fade over 500 cycles is observed. Three-electrode experiments reveal cell-level impedance growth, which is dominated by the NMC811 cathode: the SiO_x/Gr anode exhibits minimal net impedance rise and an initial impedance decrease at low potentials. Despite this apparent electrochemical stability, cross-sectional SEM, PFIB tomography, and cryo-STEM reveal irreversible anode thickening caused by the accumulation of an inorganic-rich solid electrolyte interphase (SEI) permeating the anode bulk. Electrode potential-shift analysis further demonstrates that Li⁺ ions released from lithium reservoirs in the prelithiated anode masks true lithium inventory loss during aging. These results demonstrate that low-expansion SiO_x/Gr anodes can simultaneously exhibit favorable cycling and impedance metrics while undergoing substantial, hidden degradation, underscoring the importance of electrode-resolved diagnostics for evaluating prelithiated silicon-based anodes.

Introduction

Graphite anodes have been the standard negative electrode material in lithium-ion batteries (LIBs) since their commercialization in the early 1990s. However, the limited capacity of graphite for lithium (372 mAh g^{-1} for LiC_6) makes it a fundamental bottleneck for energy density in next-generation LIBs. Silicon-based anode materials are at the nexus of near-term energy density enhancement strategies for LIBs due to their high theoretical capacity for lithium (3572 mAh g^{-1} for $\text{Li}_{15}\text{Si}_4$), representing nearly a tenfold increase over graphite. Companies such as LG, Samsung, and Sony have commercially deployed cells with silicon incorporated into their anode formulation.¹⁻⁴ Despite this progress, silicon contents are typically limited to $<5 \text{ wt } \%$, reflecting persistent challenges associated with silicon's large volume change and interfacial instability, which continue to cap achievable energy density gains.

The primary factor limiting greater incorporation of silicon into anode formulations is its large volumetric expansion upon lithiation. Silicon expands by up to $\sim 300\%$ in volume upon lithiation to $\text{Li}_{15}\text{Si}_4$.⁵ This expansion and subsequent contraction during cycling are the root cause of several degradation mechanisms in silicon-containing electrodes including delamination,⁶⁻⁸ particle fracture,^{9,10} and electrolyte consumption.¹¹⁻¹³ To mitigate these issues, two material-level strategies have been widely adopted: embedding silicon nanoparticles within porous carbon matrices (Si/C),¹⁴ and using partially oxidized silicon (SiO_x), which comprises nanometer-scale Si and SiO_2 domains.¹⁵ Both approaches leverage nanoscale silicon environments to suppress particle fracture and incorporate buffering phases or internal voids to accommodate volume changes at the electrode level. However, Si/C materials often rely on capital- and energy-intensive synthesis routes, most commonly chemical vapor deposition (CVD) of silane and hydrocarbons onto porous

carbon substrates, limiting their scalability.^{14,16–18} In contrast, SiO_x can be produced in bulk by co-annealing Si and SiO₂, making it comparatively attractive for large-scale manufacturing.^{19–22}

Despite these advantages, SiO_x is not a drop-in replacement for graphite and has several intrinsic electrochemical limitations. When cycled to full depth of charge, SiO_x exhibits a variable theoretical gravimetric capacity (1300–2400 mAh g⁻¹, depending on x) and a low first-cycle coulombic efficiency (FCE), arising from the irreversible formation of Li₄SiO₄ and Li₂O during the initial lithiation.^{23–27} Additionally, SiO_x undergoes volumetric expansion due to the formation of Li_xSi compounds, which can be detrimental without careful control of electrode composition and operating potential window.²⁷ While strategies such as graphite blending^{22,23} and prelithiation²⁸ have been independently explored to address these challenges, most prior studies consider these mitigation approaches in isolation or focus on half-cell behavior, providing limited insight into the coupled, long-term aging mechanisms of SiO_x-rich (>50%) anodes operating in realistic full-cell configurations.

In this work, we address this knowledge gap by intentionally combining graphite-addition, electrochemical prelithiation, and controlled anode potential windows to investigate the dynamic electrode behavior and aging mechanisms of SiO_x-rich anodes under full-cell operation. Electrochemically prelithiated SiO_x/graphite anodes (70 wt% SiO_x/16 wt% graphite) are paired with NMC811 (LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂) cathodes and evaluated both in 2032-type stainless steel coin cells and in larger three-electrode cells described in prior articles.²⁹ This experimental framework enables direct correlation of full-cell performance with electrode-resolved changes in impedance and potential drift over extended cycling, capabilities that are rarely described simultaneously for SiO_x-based systems.

Using this combined approach, we uncover several non-intuitive aging phenomena. The SiO_x/Gr anode exhibits exceptional mechanical integrity, with no measurable loss of active material and a small capacity gain observed in harvested $\text{SiO}_x/\text{Gr}||\text{Li}$ metal cells. Nonetheless, the full-cells still experience $\sim 12\%$ capacity fade after 500 cycles, indicating that cell-level degradation cannot be inferred from anode stability alone. Impedance analysis and post-cycling characterization reveal that performance decay results from impedance growth and loss of active material (LAM) at the NMC811 cathode, alongside loss of lithium inventory (LLI) driven by continued electrolyte reduction at the anode.

Post-cycling characterization of harvested anodes using scanning electron microscopy (SEM), plasma focused ion beam (PFIB) tomography, and cryogenic scanning transmission electron microscopy (cryo-STEM) reveals that the SiO_x/Gr electrode undergoes an irreversible $\sim 75\text{-}100\%$ thickness increase after aging, arising from the accumulation of a solid-electrolyte-interphase (SEI) both on particle surfaces and within electrode pores. Importantly, the anode contributes to cell aging through an indirect mechanism associated with electrode potential drift: as anode potentials shift to higher values during cycling, the fixed full-cell voltage window forces the cathode to operate at increasingly (undesirable) high potentials, accelerating its impedance growth. Finally, we demonstrate that the lithium reservoir present in the SiO_x anode acts as a capacity-fade “mask”, gradually releasing lithium during cycling and thereby obscuring the true extent of lithium inventory loss. These insights can serve as guidance for future research to enable stable silicon-based anode materials for LIBs.

Experimental

Materials and Electrodes

SiO_x powder was obtained from Osaka Titanium Technologies Co. (D50 = 5.2 μm, specific surface area = 6.3 m² g⁻¹). NMC811 powder for cathode fabrication was sourced from Targray. Single-walled carbon nanotubes (SWCNTs) were obtained from Tuball as an aqueous suspension in carboxymethyl cellulose (CMC). C-45 carbon black was purchased from Timcal. Poly(acrylic acid) (PAA) binder was obtained from Blue Ocean & Black Stone as an aqueous suspension, and poly(vinylidene difluoride) (PVDF, 5130) binder was purchased from Solvay. The anode and cathode current collectors were 10 μm copper foil and 20 μm aluminum foil, respectively. Polypropylene (PP) separators (25 μm thick, Celgard 2500) were used in all cells. The SiO_x/graphite (SiO_x/Gr) and NMC811 electrodes were fabricated at the Cell Analysis, Modeling, and Prototyping (CAMP) Facility at Argonne National Laboratory following previously reported procedures.³⁰ Detailed electrode composition, areal loading, and porosity information are provided in **Table 1**.

Table 1: Electrode specifications for prelithiated NMC811/SiO_x-Gr cells

Electrode Composition	NMC811 Cathode	SiO _x /Gr Anode
Active Material (wt%)	96	70/16
C45/SWCNT (wt%)	1.95/0.05	0/1
Binder (wt%)	2 (PVDF)	1 (CMC)/12 (PAA)
Current Collector	Al	Cu
Current Collector Thickness (μm)	20	10
Coating Thickness (μm)	52	42
Coating Loading (mg cm ⁻²)	14.4	3.18
Active Material Loading (mg cm ⁻²)	13.8	2.8
Porosity (%)	38.0	62.9
Estimated C/10 Areal Capacity (mAh cm ⁻²)	2.92 (2.5 to 4.3 V)	3.04 (0.05-0.7 V)

Cell Assembly and Electrochemical Testing

Test devices consisted of either three-electrode cells incorporating a lithium metal micro-reference electrode, constructed as previously reported²⁹, or 2032-type stainless steel coin cells (Hohsen) assembled with NMC811 cathodes and SiO_x/Gr anodes. The geometric electrode areas were 20.3 cm² for three-electrode cells and 1.54 cm² for coin cells. No electrode overhangs were used in any configuration. Prior to cell assembly, all electrodes were dried under vacuum at 110 °C inside an Ar-atmosphere glovebox. The three-electrode cells and a subset of coin cells were assembled in an Ar glovebox, while additional coin cells were assembled in a dry room at the

CAMP Facility. All cells employed an electrolyte consisting of 1.2 M LiPF_6 in ethylene carbonate/ethyl methyl carbonate (EC/EMC, 3:7 wt/wt; Gen2, Tomiyama) with 3 wt% fluoroethylene carbonate (FEC, Solvay) as an additive.

Electrochemical testing was conducted at 30 °C using a MACCOR Series 4000 battery test system. NMC811|| SiO_x /Gr full cells were initially electrochemically prelithiated in both coin-cell and three-electrode configurations by pairing a thick NMC811 electrode (5.0 mAh cm^{-2}) with the SiO_x /Gr anode (3.04 mAh cm^{-2} , **Table 1**). These cells were subjected to a single cycle in which they were charged to 4.97 mAh cm^{-2} and subsequently discharged at a C/10 rate to a capacity of 3.04 mAh cm^{-2} . The extent of capacity-limited discharge required for prelithiation was determined using three-electrode measurements, targeting an anode delithiation potential of 700 mV vs. Li^+/Li (**Figure A1**). Following prelithiation, the cells were disassembled, and the anodes were rinsed with dimethyl carbonate (DMC) before being transferred to new cells containing fresh NMC811 cathodes (2.92 mAh cm^{-2} , **Table 1**), fresh electrolyte, and new separator.

After prelithiation, formation cycling was carried out in NMC811|| SiO_x /Gr three-electrode cells to establish appropriate cell voltage limits. Charging was terminated when either the cathode or anode potentials reached 4.25 V or 0.05 V vs. Li^+/Li respectively, while discharge was terminated when either the anode potential or cell voltage reached 0.7 V vs. Li^+/Li or 2.8 V, respectively. Formation cycling consisted of five cycles at a C/12 rate. Long-term aging of three-electrode cells was performed by cycling between 2.8 and 4.17 V, using a protocol consisting of one C/20 cycle, followed by 99 cycles at C/3, and a subsequent C/20 reference performance test (RPT) cycle. This sequence was repeated five times, yielding a total of 500 cycles. Hybrid pulse power characterization (HPPC) testing was conducted every 100 cycles. These HPPC tests

consisted of charging the cell to 4.22 V, holding until the current decayed to a C/10-equivalent rate, followed by a series of 10 s, 3C discharge pulses applied at C/20 capacity intervals across the discharge profile.

Formation cycling of NMC811||SiO_x/Gr coin cells was carried out between 2.8 and 4.17 V for the first cycle, followed by two cycles from 2.8 and 4.16 V, all at a C/10 rate. The voltage limits were established based on three-electrode cell measurements, to account for first-cycle irreversibility while delithiating the anode to ~650 mV vs. Li⁺/Li at full discharge. Coin cells were subsequently aged using an analogous protocol to the three-electrode cells, with C/10 RPT cycles instead of C/20 cycles.

Microscopy and Characterization

For cross-sectional SEM analysis, SiO_x/Gr electrodes were prepared using a two-step ion milling procedure, with sectioning at 4.5 kV for 3 h, followed by 3 kV for 3 h to smooth the electrode surface. Imaging was performed using a Jeol IT800HL SEM, and elemental analysis was conducted using an Oxford Ultim Max 40 energy-dispersive X-ray spectroscopy (EDS) detector. The PFIB tomography and cryo-STEM were performed following the methodology described by Quinn et. al.³¹ In brief, the PFIB tomography and EDS were conducted using a Helios Hydra 5 Dual Beam system equipped with an Aztec Ultim Max detector. Multiple sets of SEM images and EDS maps were aligned and segmented with MATLAB, and three-dimensional reconstructions were generated using MATLAB's Image Processing Toolbox. For cryo-STEM analysis, thin cross-sectional lamellae of each electrode were prepared via PFIB lift-out and transferred under cryogenic conditions to a 300 kV monochromated FEI Titan TEM using a Gatan Cryo-Transfer

Station and Gatan Elsa Cryo-Transfer Holder, ensuring air-free transfer. Elemental mapping was performed with an Aztec X-Max EDS Detector.

Results and Discussion

Electrochemistry and Dilatometry of the SiO_x/Gr Electrode

Initial electrochemical characterization of the as-prepared SiO_x/Gr electrodes (**Table 1**) versus a lithium metal counter electrode was conducted in coin cells. The post-formation C/100 voltage and dQ/dV profiles measured between 0.05 and 0.7 V vs. Li⁺/Li are shown in **Figures 1a** and **1b**, respectively. At this rate, the reversible delithiation areal capacity of the SiO_x/Gr electrode was 3.4 mAh cm⁻², which corresponds to a gravimetric capacity of ~1200 mAh g⁻¹_{SiO_x+C}. The dQ/dV profile in **Figure 1b** exhibits two characteristic silicon lithiation features at ~0.23 and ~0.10 V vs. Li⁺/Li, with corresponding delithiation peaks at ~0.25 and ~0.45 V vs. Li⁺/Li. In addition, distinct graphite features are observed during lithiation at ~0.21, 0.12, and 0.08 V vs. Li⁺/Li, and during delithiation at ~0.10, 0.13, and 0.22 V vs. Li⁺/Li.

Figure 1c presents the post-formation in-situ electrochemical dilatometry (ECD) voltage and thickness change profiles of the SiO_x/Gr electrode during C/30 lithiation (solid lines) and subsequent delithiation (dashed lines). The electrode reaches a maximum thickness expansion of 49% after a 10 h hold at 10 mV, followed by a contraction of 41% upon subsequent delithiation, corresponding to a reversible expansion of ~84%. Under these conditions (0.01-1.0 V Li⁺/Li with extended voltage holds), the electrode delivered a lithiation capacity of 1500 mAh g⁻¹_{SiO_x+C}, of which 91% was reversible upon delithiation (1360 mAh g⁻¹_{SiO_x+C}). The blue dotted box in **Figure 1c** highlights the capacity and expansion accessed under typical full-cell operating conditions (0.05-0.7 V vs. Li⁺/Li), corresponding to a capacity of ~850 mAh g⁻¹_{SiO_x+C}, and ~35% lithiation-

induced expansion. These values are consistent with previous reports with similar potential cutoffs.³²

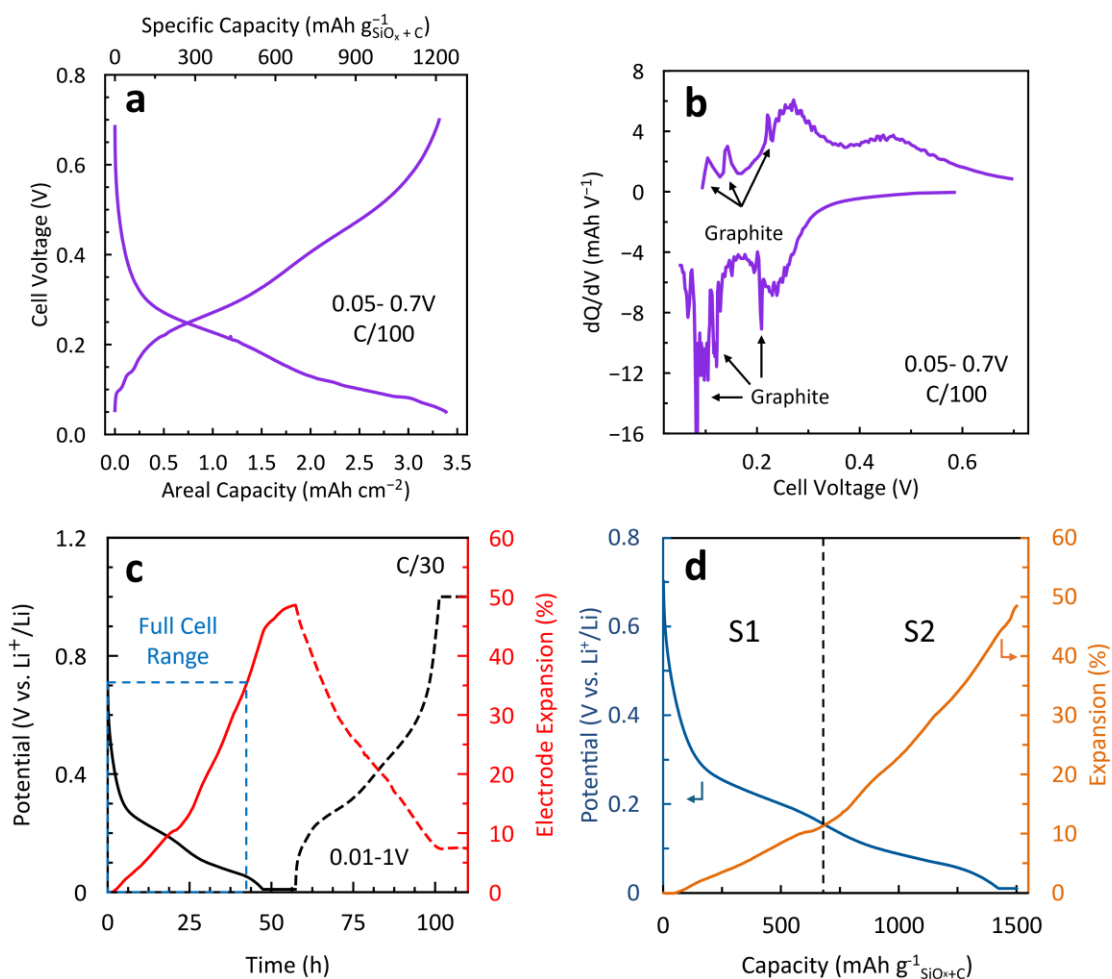


Figure 1. C/100 (a) voltage and (b) dQ/dV profiles of SiO_x/Gr; (c) C/30 voltage (black) and ECD expansion (red) profiles of SiO_x/Gr; (d) expansion as a function of cell potential (blue) and capacity (orange). All data are from cells with a Li-metal counter electrode.

The expansion behavior exhibits a two-step profile as shown in **Figure 1d**. The first step (S1, 1.0-0.15 V vs. Li⁺/Li) contributes ~10% expansion over 0-700 mAh g⁻¹_{SiO_x+C}, while the second

step (S2, 0.15-0.01 V vs. Li^+/Li) contributes $\sim 39\%$ expansion over $700\text{-}1500\text{ mAh g}^{-1}_{\text{SiO}_x+\text{C}}$. These steps correspond directly to the two silicon lithiation features observed in **Figure 1b**, indicating that the lower-potential silicon lithiation reaction induces a substantially larger volumetric response per inserted lithium than the higher-potential lithiation process. The maximum 49% electrode expansion observed here falls within the lower range of values typically reported for SiO_x electrodes.^{32–34} This lower expansion is attributed both to the presence of graphite, which itself expands by only $\sim 10\%$,³⁵ and to the high initial electrode porosity (62.9%), which provides internal void space to accommodate volume changes, as previously described.³⁶

Formation Cycle Profiles in Three-Electrode Cells

The formation cycling data were analyzed to quantify first-cycle irreversibility, evaluate the effectiveness of anode prelithiation, and establish steady-state electrode potential windows prior to long-term aging. Voltage and dQ/dV profiles during the first three cycles of a prelithiated three-electrode $\text{NMC811}||\text{SiO}_x/\text{Gr}$ cell at C/10 are shown in **Figures 2a** and **2b**, respectively. **Figures 2c–2f** show that for all cycles, cell charge terminated when the cathode potential reached 4.25 V; that is, the anode potential did not reach 0.05 V vs. Li^+/Li . Discharge terminated when the cell voltage reached 2.8 V; that is, the anode did not reach the 0.7 V vs. Li^+/Li cutoff potential.

The first cycle charge capacity of the prelithiated three-electrode cell was 3.12 mAh cm^{-2} , and the first discharge capacity was 2.74 mAh cm^{-2} , corresponding to an FCE of 87.8%. Because the SiO_x/Gr anode was prelithiated prior to formation, irreversible lithium consumption associated with SEI formation at the anode is minimized, and the observed first-cycle capacity loss can therefore be attributed primarily to the NMC811 cathode (**Figure 2c** and **2d**). This first-cycle loss is a well-known phenomenon and is attributed to a sudden decrease in lithium-ion mobility at the

oxide particle surfaces near the end of discharge when the oxide is near full-lithiation.^{37,38} Note that these first-cycle Li^+ ions are not truly “lost”, but are simply stored in the SiO_x/Gr anode.

Upon completion of cell discharge, the cathode potential profile polarizes, indicating that the cell is cathode-limited in this cycling window. The SiO_x/Gr anode potential reaches 0.06 V and 0.65 V during the 1st lithiation and delithiation, respectively (**Figures 2e** and **2f**). The lack of pronounced anode polarization at the end of discharge indicates that a portion of the prelithiation reservoir remains in the anode after formation as discussed below. In subsequent lithiation (cell charge) and delithiation cycles, the anode potentials increase to ~0.07 V and ~0.66 V vs. Li^+/Li , respectively. Aside from the first charge cycle, minimal capacity loss was observed during formation cycling, as evidenced by the closely overlapping voltage and dQ/dV profiles.

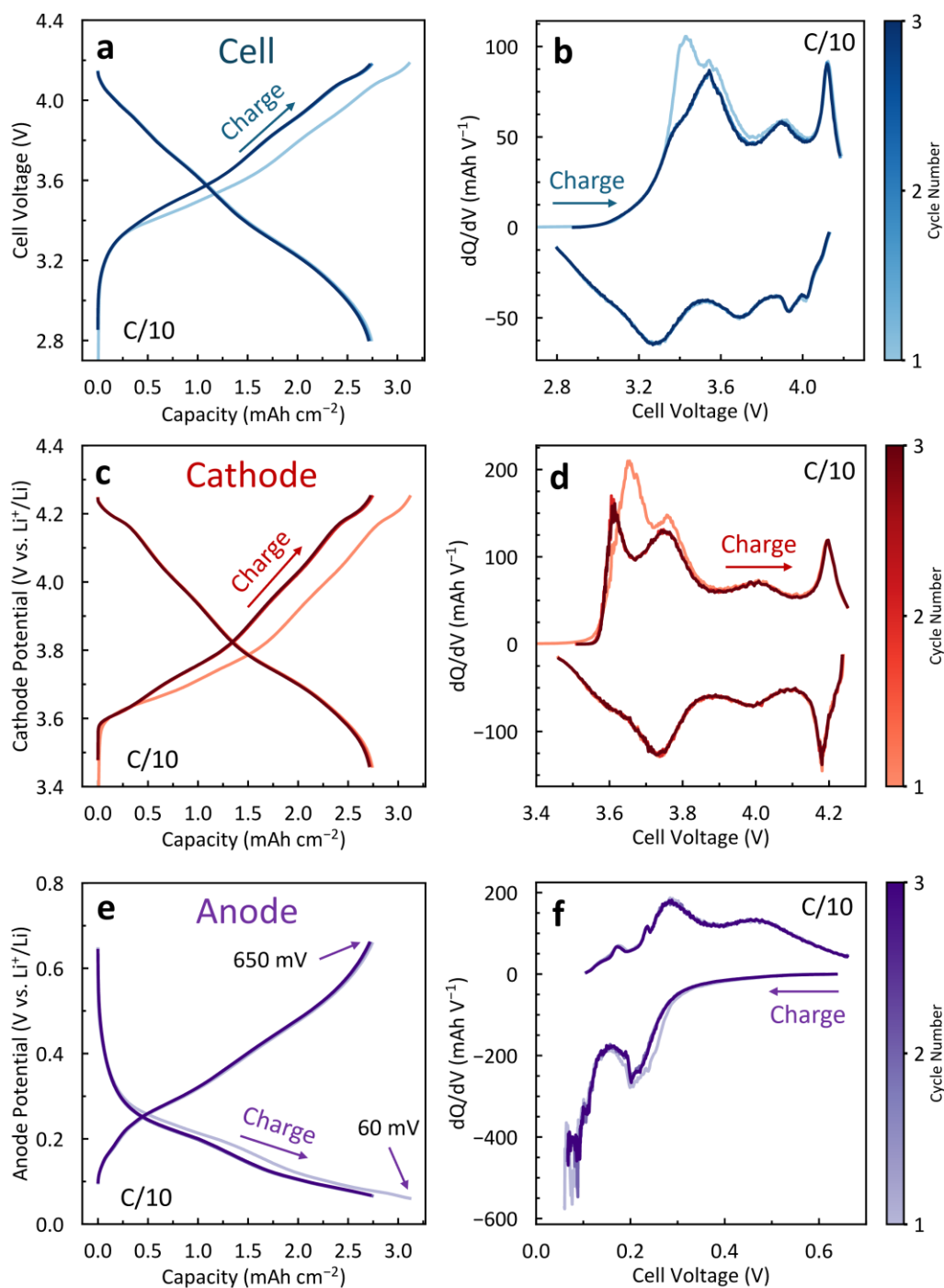


Figure 2. Voltage (left) and dQ/dV (right) profiles for the full cell (a, b, blues) at C/10; NMC811 cathode (c, d, reds); and SiO_x/Gr anode (e, f, purples) during formation cycles.

Coin Cell Cycle Aging

Coin cells with NMC811||SiO_x/Gr were prelithiated and formed as described above. The capacity vs. cycle number plot (**Figure 3a**) shows an initial C/10 discharge capacity of 2.67 mAh cm⁻². After 500 cycles, the cell capacity decreased to 2.34 mAh cm⁻², which is a loss of 0.33 mAh cm⁻² (12%). The discharge capacity corresponding to 90% retention during the C/10 RPT cycles is shown as a dashed black line in **Figure 3a**. Note that the cell gained capacity during the early C/3 cycles (**Figure 3b**). This phenomenon is attributed to a reduction in cell impedance during early aging, as discussed further below.

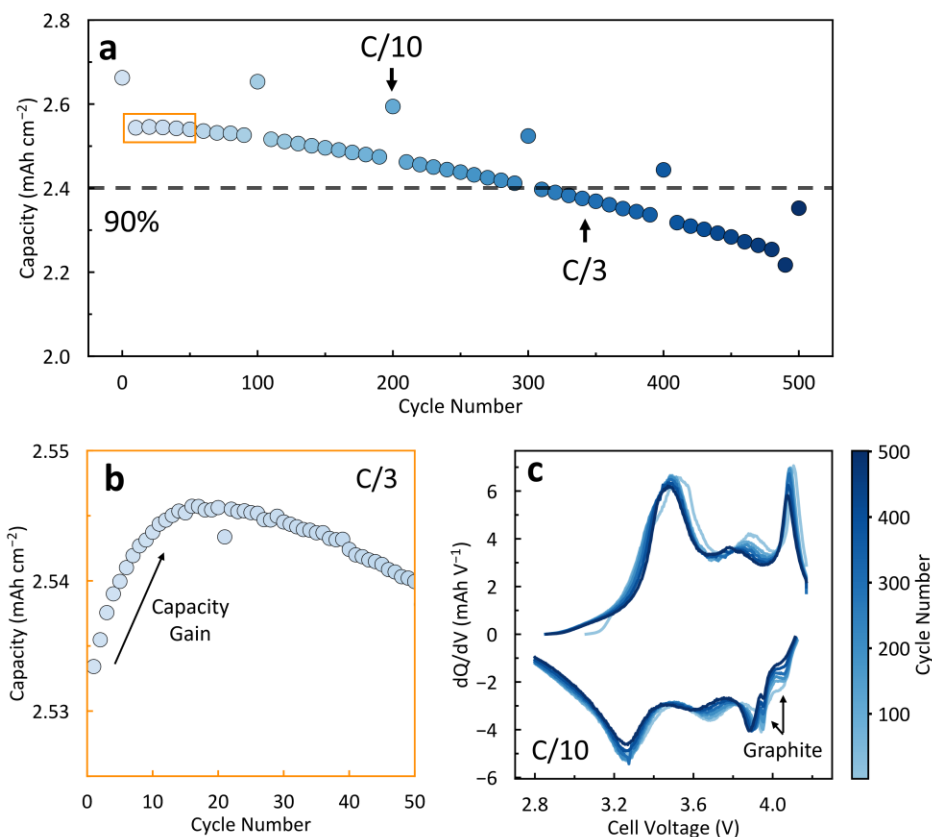


Figure 3. NMC811||SiO_x/Gr (a) capacity retention, (b) early cycle capacity gain, and (c) dQ/dV profiles over 500 cycles. The dashed line in panel (a) corresponds to the point of 90% capacity retention for the C/10 RPT cycles as a contextual aid.

The C/10 RPT dQ/dV profiles in **Figure 3c** reveal gradual shifts in several features across the voltage profile, which can be attributed to relative motion of the electrode potentials during cell aging.²⁹ The charge feature at ~ 4.1 V exhibited only minor changes over cycling but showed increased polarization near the top of charge, suggesting that the cathode approaches near-complete delithiation at this voltage. dV/dQ analysis (**Figure A2**) of analogous three-electrode data further indicates that the prelithiation reservoir is largely depleted after ~ 200 cycles, as cell polarization became progressively less dominated by the cathode.³⁹ The discharge-side dQ/dV peaks at ~ 4.05 and ~ 3.95 V monotonically decrease in intensity with cycling, consistent with an apparent loss of electrochemically accessible graphite capacity. In addition, the discharge feature at ~ 3.25 V decreased steadily in intensity with cycling. Because this feature occurs near the bottom of discharge, its attenuation is attributed primarily to loss of lithium inventory (LLI), which limits full relithiation of the cathode.

The excellent cycling stability of the cells is partially related to the relatively low expansion of the SiO_x/Gr anodes (see **Figure 1c**). Under the full-cell anode operating window of ~ 0.05 - 0.7 vs. Li⁺/Li, the electrode is expected to undergo only $\sim 35\%$ lithiation-induced expansion, based on the dilatometry measurements. This limited expansion likely mitigates common silicon degradation mechanisms, such as coating delamination and particle fracture, thereby enhancing long-term cell durability.

Three-Electrode Potential Shift and Impedance Analysis

To further elucidate the evolution of the NMC811||SiO_x/Gr voltage profile, a three-electrode cell was aged using a protocol analogous to that of the coin cells. As shown in **Figure 4a**, the full-cell voltage window remained constant throughout cycling, aside from periodic

impedance measurements every 100 cycles, during which the voltage window was expanded slightly to accommodate high-current pulses.

Because charging was limited solely by the full-cell voltage to mimic coin cell operation, the individual electrode potentials were allowed to float. As shown in **Figures 4b** and **4c**, both the cathode and anode potentials shifted progressively to higher values during cycling. This shift is attributed to capacity slippage, whereby consumption of lithium inventory through parasitic reactions prevents the electrodes from returning to their fully discharged states, causing each subsequent cycle to begin at elevated potentials.²⁹

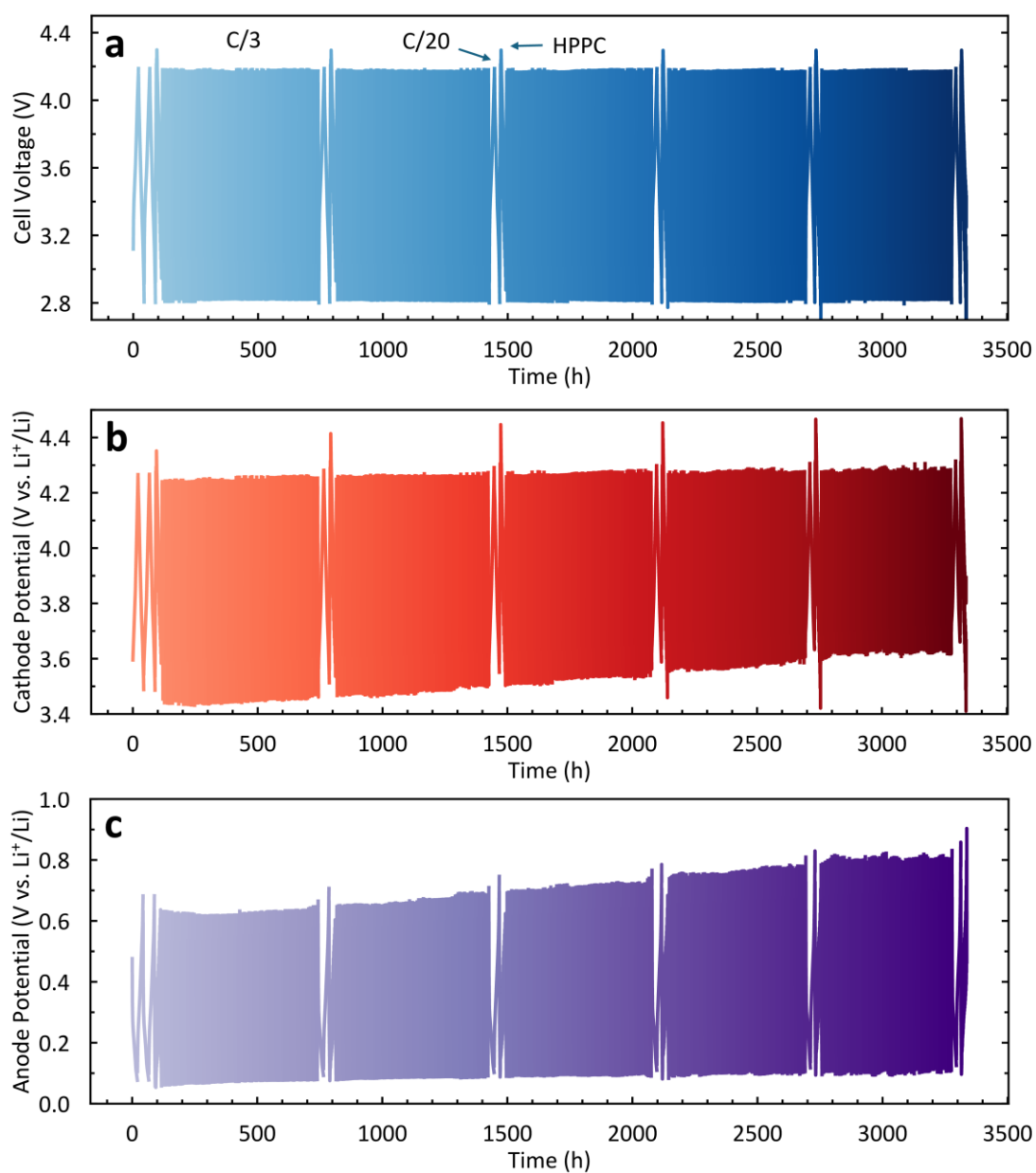


Figure 4. Continuous temporal voltage profiles over 500 cycles for the (a) full cell, (b) cathode, and (c) anode of a three-electrode cell.

Due to the constant full-cell voltage window imposed by the cycling protocol, the cathode and anode potential shifts are intrinsically coupled during both charge and discharge. Notably, the magnitude of potential shift differed between charge and discharge endpoints, as shown in **Figure 5**. The charge endpoint potentials increased by only ~ 40 mV over aging (**Figure 5a**), whereas the discharge endpoint potentials increased by ~ 182 mV (**Figure 5b**). This asymmetry arises from differences in the shapes and slopes of the respective electrode potential profiles.

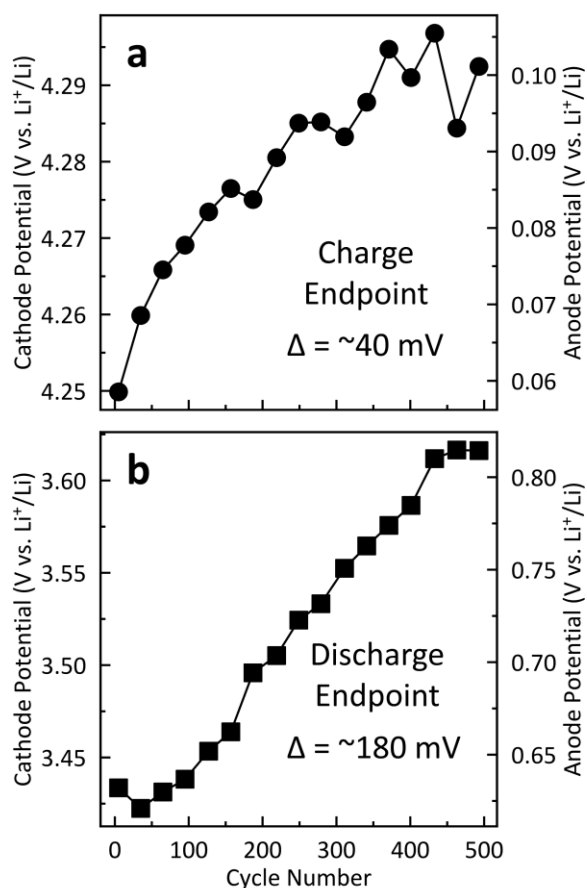


Figure 5. (a) Charge and (b) discharge voltage shift of the 3-electrode cell electrodes over 500 cycles.

In addition to the overall upward shift, a small decrease in the fully discharged electrode potentials can be observed over the first 30 cycles in **Figure 5b**. This feature indicates an increase in accessible capacity during early aging and mirrors the capacity gain observed in the coin-cell cycling data (**Figure 3b**). To probe the origin of this effect, hybrid pulsed power characterization (HPPC) measurements were performed on the three-electrode cell. As shown in **Figure 6a**, the full-cell impedance decreased at low cell voltages during early aging (cycles 1-100). Deconvolution of the impedance contributions reveals that the cathode impedance increased monotonically (**Figure 6b**), whereas the anode impedance decreased across much of its potential range (**Figure 6c**). This decrease in anode impedance accounts for the net decrease in full-cell impedance and explains the early-stage capacity gain and the transient negative shift in anode potential.

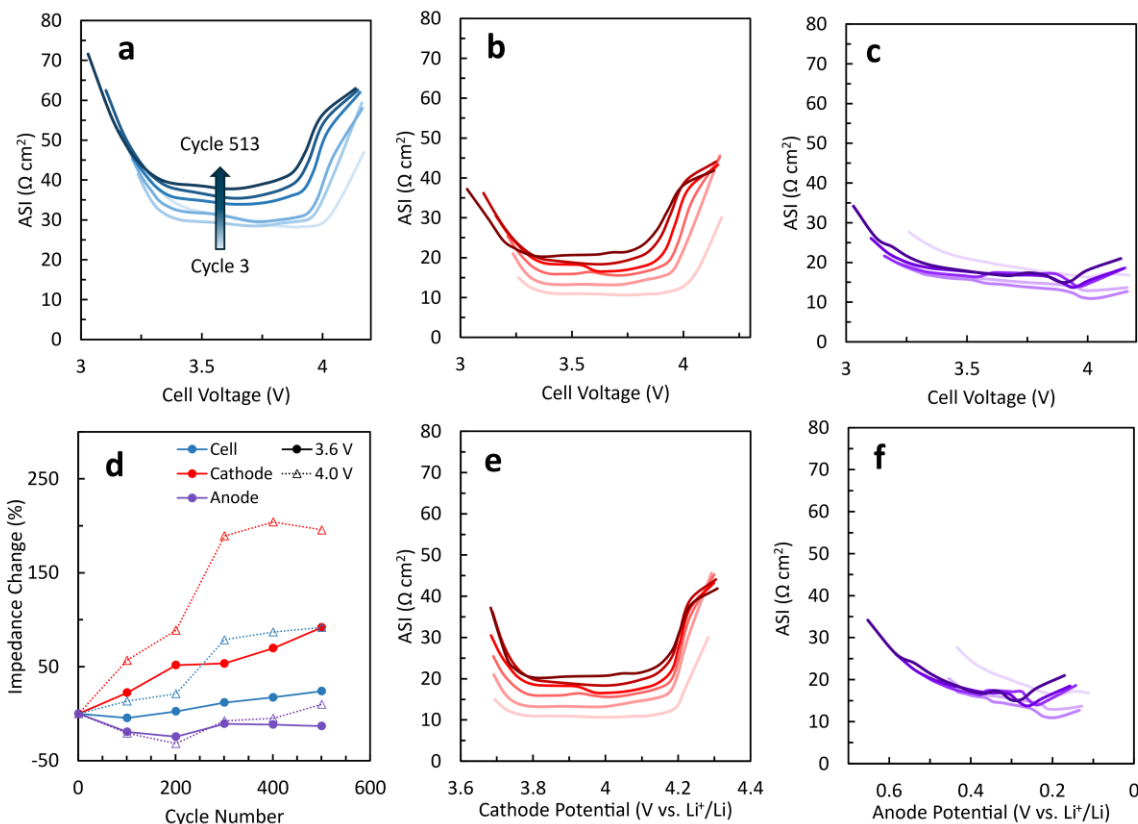


Figure 6. ASI as a function of cell voltage for the (a) full cell (blues), (b) cathode (reds), and (c) anode (purples) over the course of aging, where the earlier cycles are in light colors and the later cycles are in dark colors; (d) change in impedance for the cell (blue), cathode (red), and anode (purple) at 3.6 V (solid lines, filled circles) and 4.0 V (dotted lines, hollow triangles); (e) cathode and (f) anode impedance as a function of their respective electrode potentials over the course of cycling.

The impedance evolution of the full cell (blue), cathode (red), and anode (purple) at cell voltages of 3.6 V (solid circles) and 4.0 V (open triangles) is summarized in **Figure 6d**. The overall impedance rise during cycling is dominated by the cathode, particularly at higher voltages. In

contrast, the anode impedance decreased during early cycling and then stabilized, indicating minimal impedance-driven degradation of the SiO_x/Gr electrode over extended cycling.

To further isolate potential-dependent effects, the ASI is plotted as a function of electrode potential for both electrodes (**Figures 6e, 6f**). The cathode ASI (**Figure 6e**) increased steadily with cycling, consistent with **Figures 6b** and **6d**. The apparent leveling off above ~ 4.2 V vs. Li^+/Li at later stages of aging reflects the progressive upward shift of the cathode potential, rather than intrinsic impedance stabilization, during cycling. The increase in cathode potential at the top of charge over the course of aging results in irreversible oxygen evolution due to the energetic overlap of $\text{Co}^{3+/4+}$ redox with the O^{2-} 2p band as well as irreversible crystal structure transitions to spinel and rock-salt phases.^{40–43} These processes can induce active material loss through particle cracking and interfacial stress, ultimately accelerating electrolyte consumption and performance loss.^{42,44,45} At the anode, the apparent impedance rise observed when plotted versus cell voltage (**Figure 6c**) can be attributed to potential shifts rather than intrinsic degradation. When plotted as a function of anode potential (**Figure 6f**), the impedance remains largely unchanged at fixed potentials over most of the aging process. However, as the fully discharged anode potential shifted to higher values, the impedance increased due to conversion of metallic Li_xSi back into more resistive, lithium-deficient silicides.⁴⁶

The low-potential region of the anode impedance profile (50–300 mV vs. Li^+/Li) exhibits a distinct evolution relative to the higher-potential region (**Figure 6f**). During early cycling (cycles 1–100), the impedance in this region decreases. At later stages of aging (cycles 100–500), however, the low-potential impedance increased for a given potential. This rise correlates with the attenuation and disappearance of high-voltage dQ/dV features observed in the coin cell data

(**Figure 3c**) and suggests impedance rise associated with graphite particles within the SiO_x/Gr composite, consistent with the three-electrode anode dQ/dV profiles shown in **Figure 2f**.

Harvested Electrodes

To assess material-level changes induced by long-term cycling, aged NMC811|| SiO_x/Gr full cells were disassembled in an argon-filled glovebox, and the electrodes were reassembled into fresh coin cells against lithium metal using new separators and fresh electrolyte. These harvested-electrode cells were conditioned with three C/10 cycles, followed by a C/100 cycle to minimize kinetic limitations. Harvested SiO_x/Gr anodes were cycled between 0.05 and 0.7 V vs. Li^+/Li , while the harvested NMC811 cathodes were cycled between 2.5 and 4.3 V vs. Li^+/Li .

Upon reassembly, the open-circuit voltages were 3.6 V for NMC811 and 0.9 V vs. Li^+/Li for SiO_x/Gr cells, indicating partially (de)lithiated states for both electrodes. The OCV of the SiO_x/Gr anode is higher than expected based on the degree of capacity fade inferred from three-electrode measurements (**Figure 5b**), suggesting that additional self-discharge may have occurred during disassembly and rinsing.

Voltage and dQ/dV profiles for harvested and pristine electrodes are compared in **Figure 7**. The harvested NMC811 cathode exhibited a ~3.9% capacity loss relative to the pristine electrode, with the discharge capacity decreasing from 226 to 217 $\text{mAh g}^{-1}_{\text{NMC}}$ (**Figure 7a**). The corresponding dQ/dV profiles (**Figure 7b**) show no significant changes in feature shape or position, indicating that the observed capacity loss likely arises from loss of electronic connectivity rather than bulk structural or phase changes within the active material.

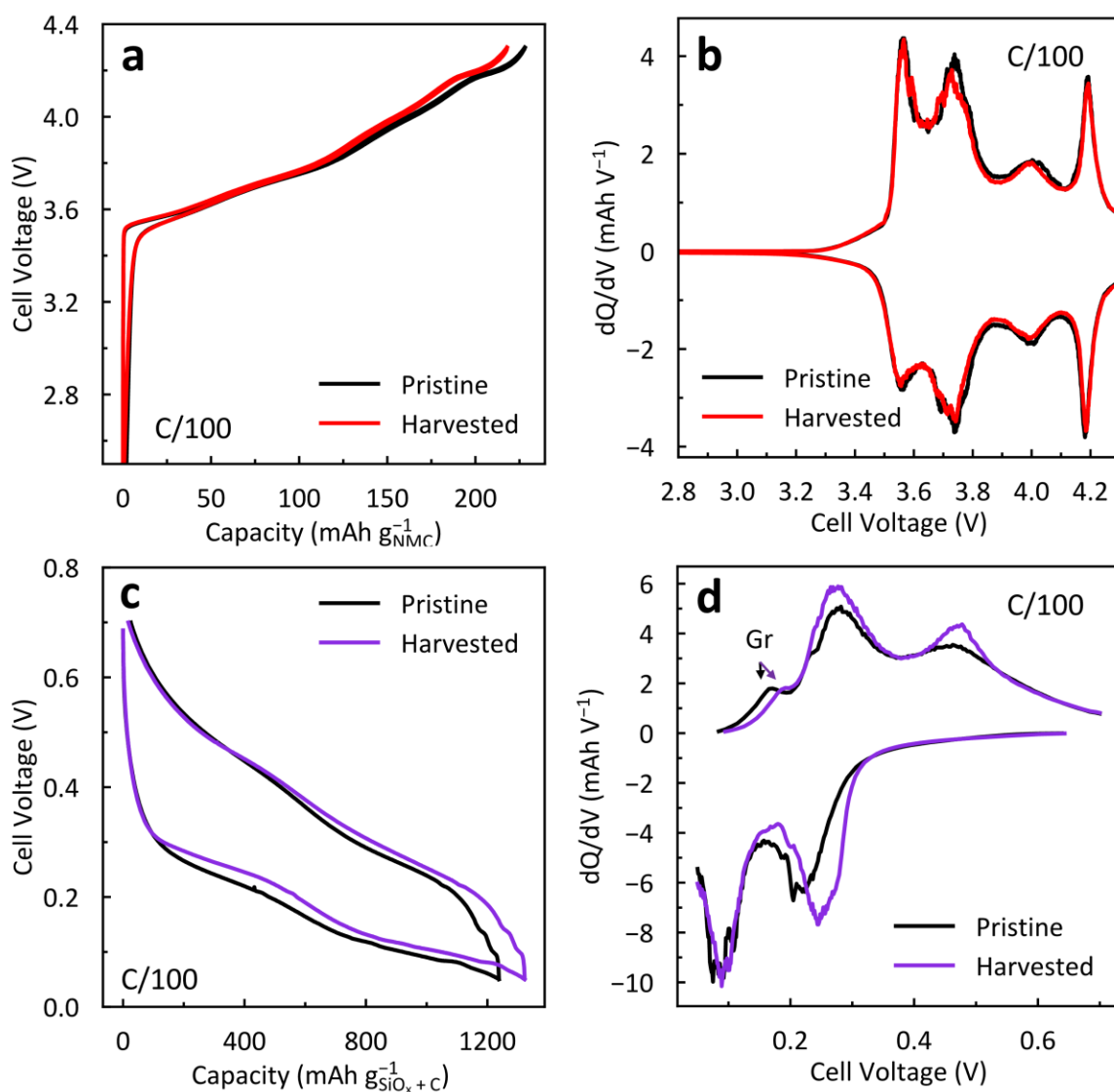


Figure 7. (a, b) NMC811||Li and (c, d) SiO_x/Gr||Li; C/100 (a, c) voltage and (b, d) dQ/dV profiles for the pristine and harvested electrodes. The pristine profiles are shown in black, while the harvested electrode profiles are shown in red and purple for the cathode and anode, respectively.

In contrast, the harvested SiO_x/Gr electrode exhibited a higher capacity (1305 mAh g⁻¹_{SiO_x+C}) compared to that of the pristine electrode (1212 mAh g⁻¹_{SiO_x+C}) when cycled between 0.05 and 0.7 V vs. Li⁺/Li at a C/100 rate (**Figure 7c**), corresponding to a 7.7% capacity gain after having

been cycled 500 times. The dQ/dV profile (**Figure 7d**) presents an explanation, as the lithiation feature near 0.2 V vs. Li^+/Li increased in area and shifted to higher potential following aging. To the best of our knowledge, such a shift has not been previously reported for silicon-containing anodes, likely because it is obscured by concurrent impedance growth and mechanical degradation resulting from coating delamination, electrode pulverization, and particle fracture.

The ~0.2 V lithiation feature in pristine amorphous SiO_x (black line, **Figure 7d**) has been attributed to the conversion of the amorphous silicon matrix into smaller silicon clusters interspersed with amorphous Li_xSi phases.^{47–49} The harvested electrode data indicate that this conversion becomes more favorable with cycling, as evidenced by the increased and fully reversible peak area. Given the slow cycling rate employed (C/100), this effect is attributed to thermodynamic rather than kinetic factors. The mechanistic origin of this enhanced conversion remains unclear. One possible explanation is improved electronic connectivity resulting from pore filling during inelastic expansion and early-stage structural rearrangement. Alternatively, this behavior may be an intrinsic characteristic of silicon that is rarely observed due to premature mechanical failure and impedance rise in less mechanically stable electrodes.

Finally, the primary graphite delithiation feature at ~0.15 V vs. Li^+/Li in the harvested SiO_x/Gr electrode, shifted to higher potentials relative to the pristine sample (**Figure 7d**). This shift suggests a change in the local graphite environment that increases the energetic barrier for lithium extraction, consistent with the impedance rise observed in the low-potential region of the anode ASI profile (**Figure 6f**).

Post-Cycling Electron Microscopy Characterization

Cross-sectional SEM was conducted to quantify thickness changes in the SiO_x/Gr anode resulting from prolonged cycling (**Figure 8**). The pristine electrode (**Figure 8a**) exhibited a coating thickness of $\sim 35\ \mu\text{m}$. After 500 cycles, the harvested electrode (**Figure 8b**) showed an average coating thickness of $\sim 60\text{--}70\ \mu\text{m}$. Because the electrode was harvested when the cell was fully discharged, this increase corresponds to an irreversible expansion of $\sim 75\text{--}100\%$. Despite this substantial electrode-level expansion, no evidence of cracking or fracture was observed in the SiO_x or graphite particles. This preserved particle integrity is consistent with the relatively modest reversible expansion of the electrode during cycling ($\sim 35\%$, **Figure 1c**).

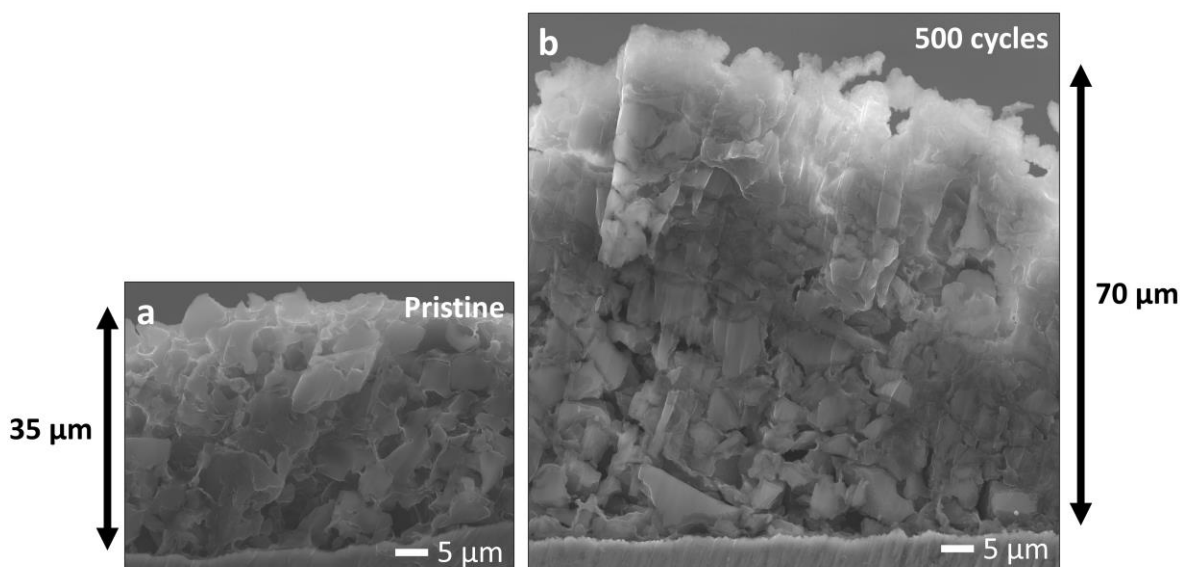


Figure 8. Cross-sectional SEM images of the (a) pristine and (b) cycled SiO_x/Gr anode.

To further elucidate the origin of the irreversible expansion, pristine and aged SiO_x/Gr electrodes were analyzed using PFIB tomography combined with EDS (**Figure 9**). The pristine

electrode (**Figure 9a**) consists primarily of silicon (red) and graphite (green) within the electrode coating, with copper (orange) originating from the current collector. The brown coloration near the electrode surface corresponds to pore space as previously described.³¹

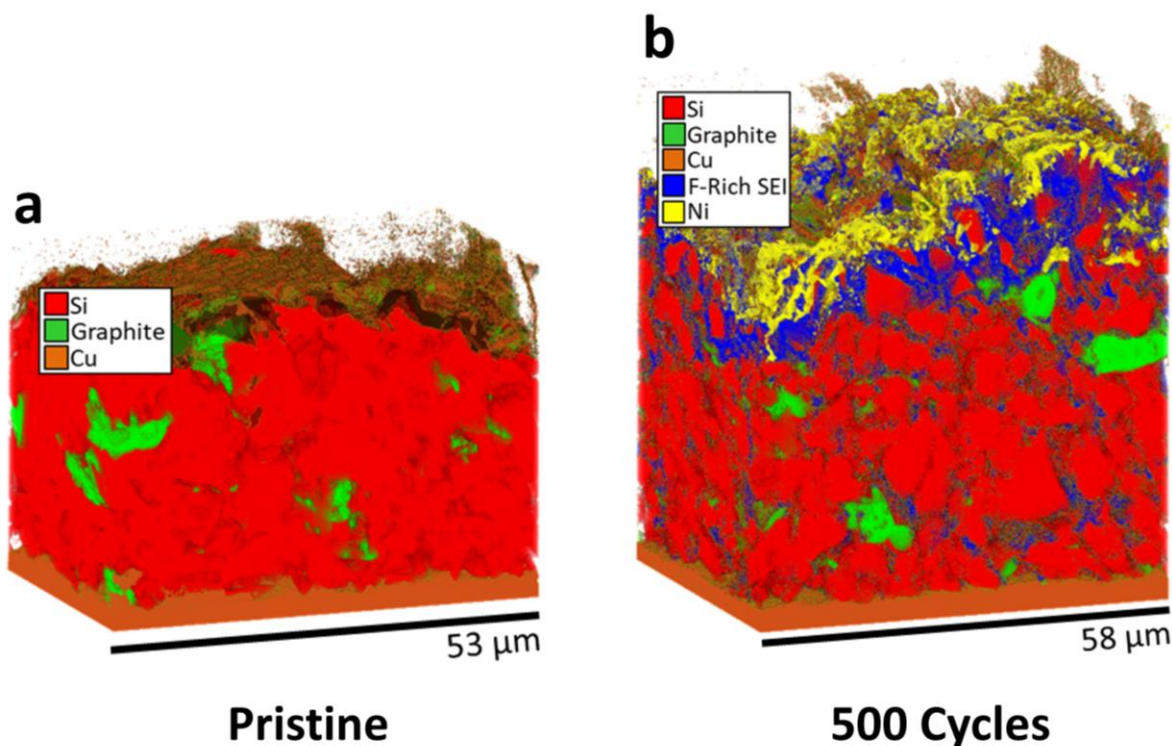


Figure 9. Cross-sectional scanning electron micrographs of the (a) pristine and (b) three-electrode SiO_x anode cycled 500 times. The ~ 150 nm thick Ni-rich surface layer in (b) is an artifact of the final cycle before cell disassembly, during which the cathode potential inadvertently exceeded 5V vs. Li^+/Li ; the Ni dissolved from the NMC811 cathode and subsequently deposited on the anode.

In contrast, the electrode harvested after 500 cycles (**Figure 9b**) exhibits pronounced thickening, consistent with the SEM observations (**Figure 8**). A fluorine signal is distributed throughout the electrode cross-section, indicating the formation of a fluorine-rich solid-electrolyte interphase (SEI) extending deep into the bulk of the SiO_x/Gr electrode. The combination of high initial porosity, widespread fluorine-containing species, and pronounced irreversible expansion

strongly suggests that continuous SEI accumulation on particle surfaces throughout the electrode is the primary driver of thickness growth. This interpretation is supported by the in-situ electrochemical dilatometry results, which show only ~16% irreversible expansion during the first cycle (**Figure 1c**), far smaller than the ~100% irreversible expansion observed by SEM and PFIB tomography after extended aging.

Cryogenic scanning transmission electron microscopy (cryo-STEM) was used to resolve the nanoscale morphology and chemistry of the SEI formed on the SiO_x/Gr electrode before and after cycling (**Figure 10**). Elemental maps of the pristine electrode (**Figures 10a-e**) show SiO_x particles with characteristic sizes of ~5 μm and graphite particles exceeding 10 μm in diameter. The strong spatial overlap between the silicon and oxygen signals confirms that oxygen is predominantly associated with SiO_x rather than the graphite, as expected.

After 500 cycles, a thin lamella extracted from a region near the copper current collector of the SiO_x/Gr electrode was analyzed (**Figures 10f-o**). The composite images (**Figures 10f, g**) show both SiO_x and Gr particles. The SiO_x particles have an inorganic-rich “shell” surrounding the particle, approximately 1 μm thick, containing both fluorine (**Figure 10l**) and phosphorus (**Figure 10m**). Complementary electron energy loss spectroscopy (EELS) data (not shown) suggest that the fluorine is primarily present as LiF. The phosphorus is likely present as Li_xPF_y and $\text{Li}_x\text{PF}_y\text{O}_z$ compounds formed from the decomposition of LiPF_6 in the electrolyte.

The oxygen signal (**Figure 10i**) extends slightly beyond the SiO_x particles, indicating incorporation of oxygen-containing species into the SEI. The concurrent presence of carbon (**Figure 10j**) suggests a mixed inorganic-organic SEI on the SiO_x particles, with the EDS intensities indicating that the fluorine-rich inorganic component is dominant. Small amounts of Ni

(**Figure 10n**) and Mn (**Figure 10o**) are seen dispersed in the SEI, indicating transition-metal (TM) dissolution from the NMC811 cathode and subsequent deposition on the anode. **Figure 10j** shows that the Gr particles also have a SEI layer, which is much thinner than that on the SiO_x particles, highlighting the preferential SEI accumulation on the latter.

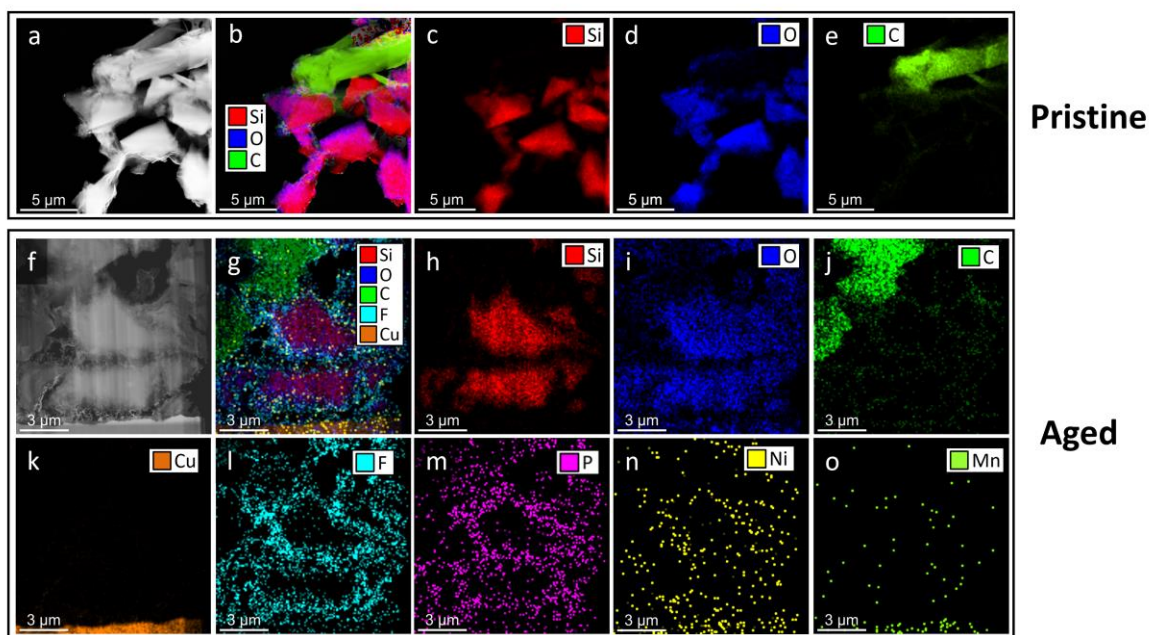


Figure 10. Cryo-STEM images and EDS elemental maps of (a-e) pristine and (f-o) aged SiO_x/Gr electrodes from a region close to the Cu current collector.

The micron-scale SEI thickness on the aged SiO_x/Gr electrodes is atypical for LIB anodes where SEI layers are more commonly reported to be tens of nanometers thick.^{50–53} The thicker SEI likely results from the relatively small reversible expansion of the SiO_x/Gr electrode compared to that of pure silicon anodes ($\sim 35\%$ vs. $\sim 300\%$). In systems with large volume changes, repeated expansion and contraction could fracture the SEI limiting its net growth, while releasing passivated lithium in the form of SEI into the electrolyte. In contrast, the modest dimensional changes in the

SiO_x/Gr electrode likely allow the SEI to remain mechanically intact, facilitating continuous accumulation as a “shell” during cycling.^{32,54} This mechanism provides a consistent explanation for the pronounced irreversible electrode thickening observed after extended aging (**Figure 8**).

Lithium-Ion Reservoir Effects on Capacity Retention

SEI growth involves the irreversible trapping of lithium ions. Thick SEI layers have previously been reported in SiO_x-based anodes and are typically associated with severe capacity fade.^{32,54} The coexistence of sizable SEI deposits (**Figures 9 and 10**) and moderate apparent capacity loss (**Figure 3a**) therefore appears paradoxical. Below, we show that this discrepancy is due to mechanisms “masking” the true extent of lithium inventory loss.

Si-based particles will rarely be fully delithiated in full-cells. Inspection of voltage profiles indicates that amorphous Li_xSi compounds require high potentials (~1.5 V vs. Li⁺/Li) for all the stored Li⁺ to be extracted.^{30,55,56} This potential is higher than that achieved by the anode at the end of discharge in many relevant cell designs, as exemplified by the ~0.65 V vs. Li⁺/Li final discharge potential at the beginning of cycling (**Figure 5b**), indicating that surplus Li⁺ is always present in the anode. These inaccessible lithium ions are placed into Si during the first cycle and are not extracted due to voltage cutoff limitations, contributing to the initial irreversibility of the cell. Hence, functionally, most Si anodes hold a *reservoir* of Li⁺. Certain prelithiation practices will temporarily add to this reservoir, contributing to a pool of lithium ions that can help offset capacity fade.³⁹

Accessing the Li⁺ stored in this reservoir simply requires the anode to experience progressively higher potentials as the cell ages.³⁹ **Figure 4c** and **Figure 5b** show that this condition is fulfilled in our cells. Thus, over time, some of the Li⁺ in the reservoir of our anodes will be

released to the cell, returning to the cathode and offsetting some of the Li^+ lost to the SEI. Consequently, this mechanism will inflate the discharge capacity measured in every cycle.

Cathodes can similarly host Li^+ reservoirs, as the end of cell charging will often occur before all cyclable lithium has been extracted from the active material. The NMC811 electrodes we used are an example, as they initially experience ~ 4.25 V vs. Li^+/Li (**Figure 5a**) but present non-negligible capacity up to 4.3 V vs. Li^+/Li (**Figure 7a**) and beyond.⁵⁷ As cathode potentials shift upward during aging (**Figure 5a**), this latent lithium inventory becomes progressively accessible, contributing further to capacity retention.

Thus, both the cathode and the anode can contribute additional capacity to the cell that can offset some of the lithium lost to the SEI, causing measured capacities to underestimate such losses.^{39,58} The use of a reference electrode enables direct tracking of electrode-specific potential shifts (**Figure 5**), allowing quantification of the lithium contribution from each electrode reservoir. After 500 cycles, the coin cells exhibited 12% of C/10 capacity fade (**Figure 3a**). The three-electrode cell experienced faster decay, reaching this same level of fade after ~ 308 cycles. At that point, performance of both cell formats is identical (**Figure 11a**) suggesting that the three-electrode cell data up to 308 cycles can be used to estimate electrode-reservoir contributions to the performance of coin cells.

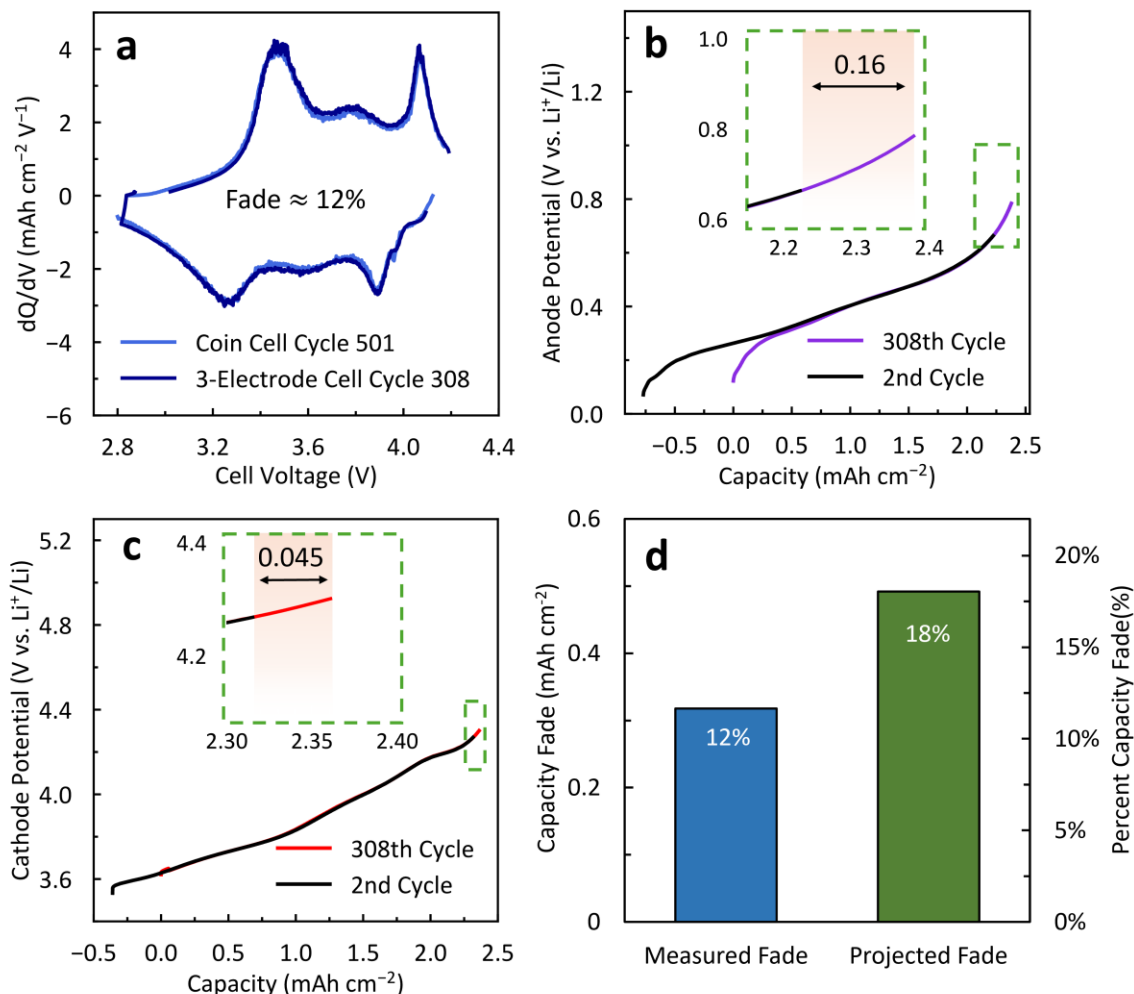


Figure 11. (a) dQ/dV profiles of the 501st cycle of the coin cell (light blue) and the 308th cycle of the three-electrode cell (dark blue) at which the capacity fade was most similar between the two cells; (b) anodic voltage profile of the three-electrode cell during the 1st (black) and 308th (purple) cycles where the 1st cycle has been shifted so that the high potential regions of the two profiles are overlaid; the inset demonstrates the capacity gained due to anode potential shift; (c) cathodic voltage profile of the three-electrode cell during the 1st (black) and 308th (red) cycles where the 1st cycle has been shifted so that the high potential regions of the two profiles are overlaid; and (d) measured capacity fade of the coin cell (blue) and the projected fade without capacity from the electrode reservoirs (green).

To visualize the capacity accessed from the reservoirs as the cells aged, the initial and final voltage profiles measured for the anode (**Figure 11b**) and cathode (**Figure 11c**) are overlaid. Additional delithiation of the anode during aging led to an additional delithiation of $\sim 0.16 \text{ mAh cm}^{-2}$, while progressive charging of the cathode accessed an extra $\sim 0.045 \text{ mAh cm}^{-2}$, for a total of $\sim 0.205 \text{ mAh cm}^{-2}$ or $\sim 6\%$ of the initial three-electrode cell capacity. This is similar to the 5% reported by Friedrich et al. for NCA||Si cells, though in their work the contributions from the cathode are larger than that from the anode.⁵⁹ The remarkable conclusion from this analysis is that although only 12% capacity fade was measured experimentally, the true amount of Li^+ consumed by the SEI actually corresponds to $\sim 18\%$ of the initial accessible Li^+ inventory of the cell (**Figure 11d**). In other words, our coin cells that apparently exhibit mild capacity fade (**Figure 3a**) have actually endured levels of degradation nearly equivalent to a cell at the end of life (20% capacity fade). Considering this argument, the extensive SEI growth revealed in the micrographs (**Figures 9 and 10**) is unsurprising.

Conclusions

In this work, the electrochemical, mechanical, and aging behavior of prelithiated SiO_x/Gr composite anodes paired with NMC811 cathodes was systematically investigated using techniques that included electrochemical dilatometry, three-electrode electrochemistry, and electron microscopy. Electrochemical dilatometry revealed that the SiO_x/Gr electrode undergoes a maximum expansion of 49% when lithiated to 10 mV, with 84% of this expansion and 91% of the capacity being reversible upon delithiation. The correlation between irreversible expansion and irreversible capacity indicates that lithium-consuming processes induce disproportionately large mechanical changes. The expansion behavior exhibits a distinct two-slope profile, with accelerated

expansion occurring at lower anode potentials. Compared with prior reports on silicon-rich electrodes, the relatively modest expansion observed here is attributed to the high initial electrode porosity and the presence of graphite, which acts as an expansion buffer.

When implemented in full cells, prelithiated SiO_x/Gr anodes paired with NMC811 cathodes exhibited relatively stable cycling, with only 12% capacity fade over 500 cycles in a coin-cell format. Post-cycling electrochemical analysis of harvested electrodes revealed that the SiO_x/Gr anode exhibited a 7.7% increase in reversible capacity, whereas the NMC811 cathode showed ~3.9% capacity loss. The anode capacity gain is primarily associated with the growth and upward shift of the lithiation feature near 0.2 V vs. Li^+/Li , suggesting that cycling facilitates increased electrochemical accessibility of SiO_x , rather than loss of active material.

Three-electrode impedance analysis showed that cell-level impedance growth is dominated by the cathode, particularly as electrode potential shifts force the cathode profile to higher voltages. In contrast, the impedance of the SiO_x/Gr anode remained largely unchanged during aging. Minor changes observed at low potentials, an initial decrease followed by a slight increase, are consistent with increased access to SiO_x domains and impedance growth associated with graphite, respectively.

Despite the apparent electrochemical stability, cross-sectional SEM, PFIB tomography, and cryogenic STEM revealed substantial irreversible thickening of the SiO_x/Gr electrode, with the coating thickness doubling from ~35 to ~70 μm after 500 cycles. This expansion was not associated with particle cracking, but rather with the accumulation of an inorganic-rich SEI permeating the electrode bulk. The modest reversible expansion of the SiO_x/Gr composite likely

allows the SEI to remain mechanically intact during cycling, enabling continuous SEI growth rather than repeated fracture and reformation.

Finally, quantitative analysis of electrode potential shifts in the three-electrode cell revealed that the apparent capacity fade of the full cell was masked by Li^+ released from the lithium reservoir in the anode and, to a lesser extent, the cathode. This finding reconciles the extensive SEI formation and irreversible electrode expansion with the modest measured capacity loss and underscores the importance of electrode-specific diagnostics when evaluating silicon-containing anodes.

Overall, these results demonstrate that low-expansion SiO_x/Gr anodes can exhibit excellent mechanical integrity and apparent cycling stability while simultaneously undergoing substantial, masked lithium inventory loss through SEI accumulation. This study highlights both the promise and hidden liabilities of prelithiation strategies and emphasizes the importance of three-electrode analysis and post-aging characterization for accurately assessing degradation mechanisms in next-generation silicon-containing lithium-ion batteries.

Appendix

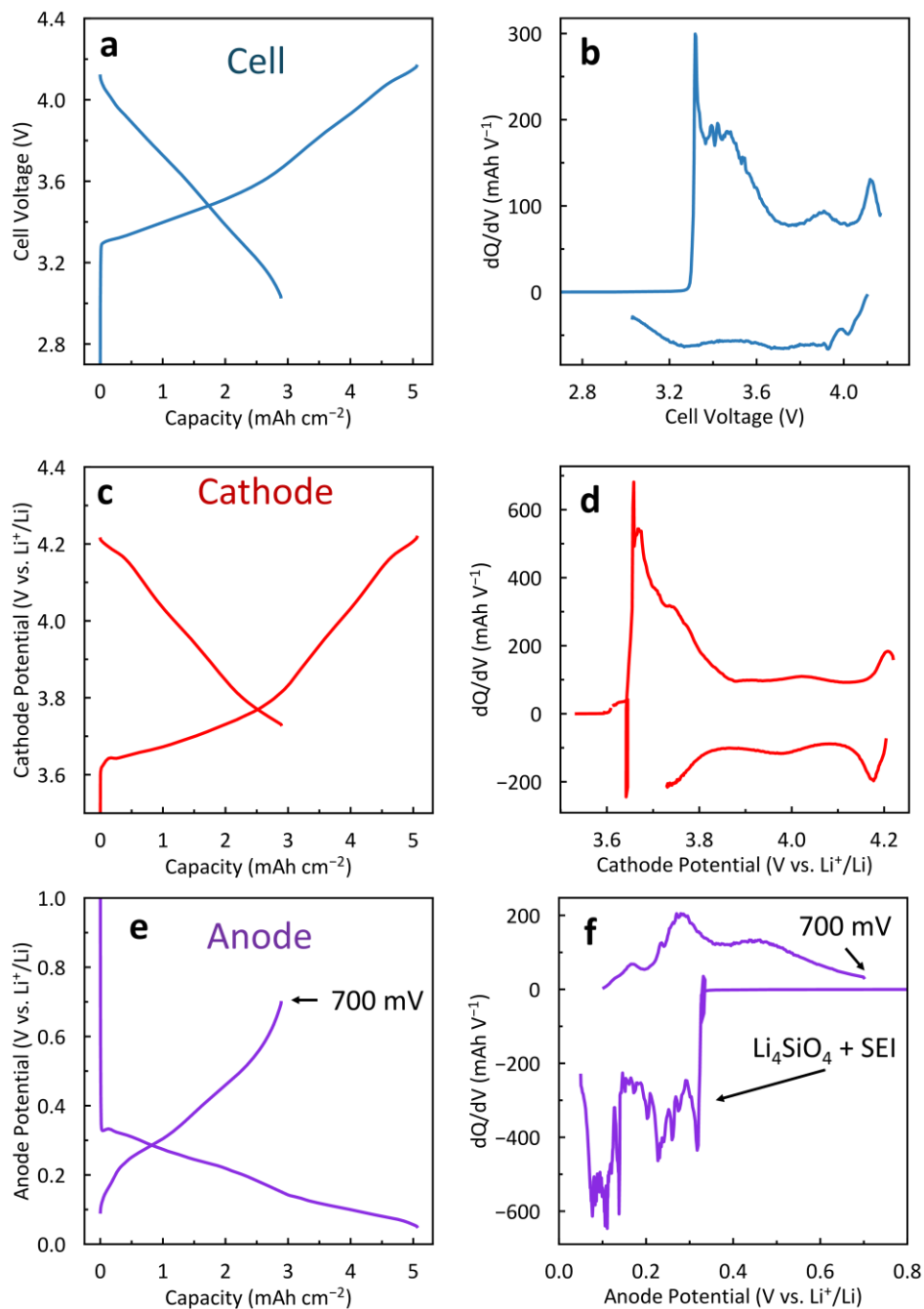


Figure A1. Prelithiation cycle (left; a, c, e) capacity-voltage profiles and (right; b, d, f) dQ/dV profiles for the (a, b, blues) cell, (c, d, reds) cathode, and (e, f, purples) anode.

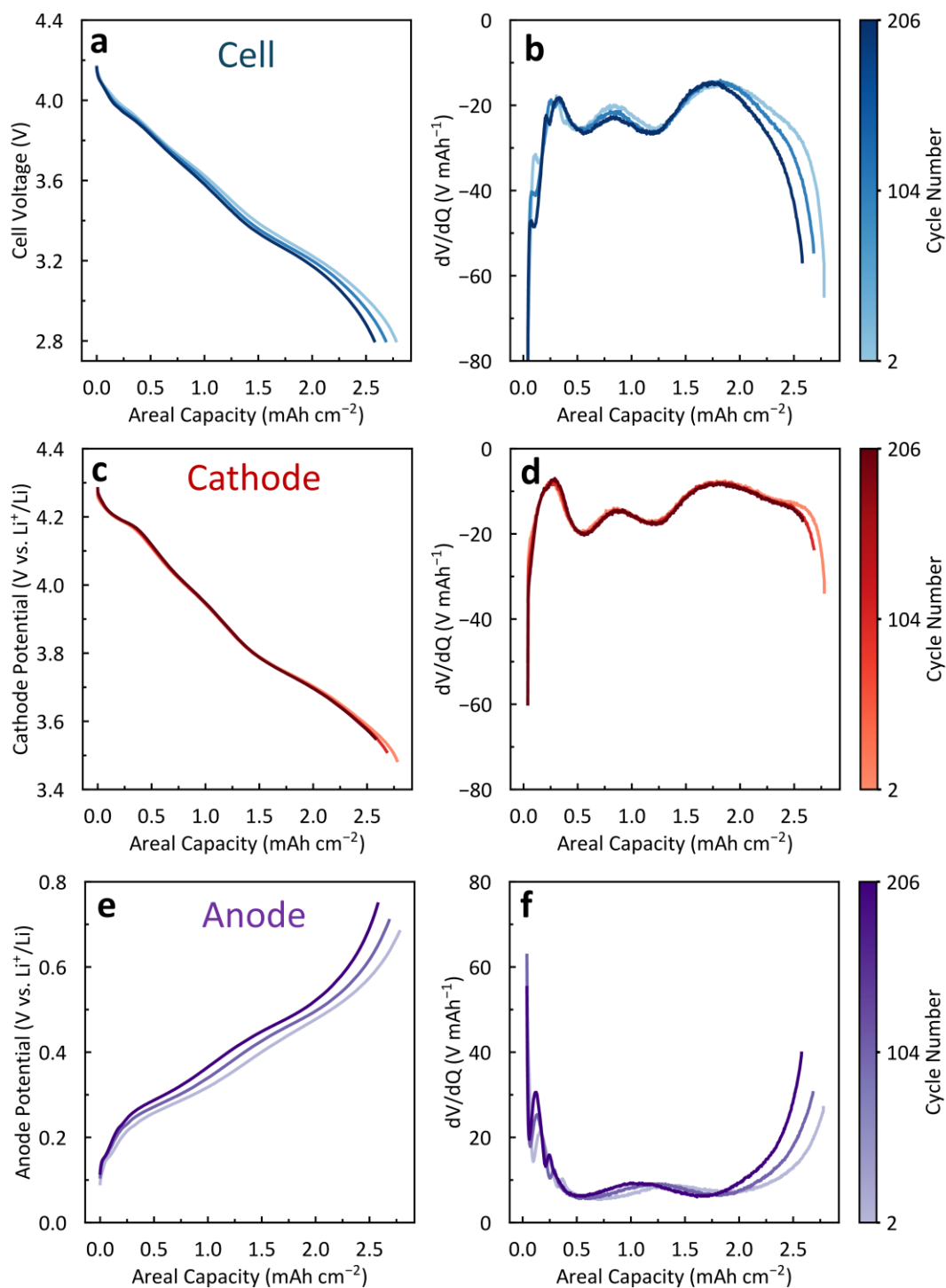


Figure A2. Discharge voltage (left) and dV/dQ (right) profiles for the three-electrode (a, b, blues) cell, (c, d, reds) cathode, and (e, f, purples) anode for the first three C/20 RPT cycles,

corresponding to cycles 2, 104, and 206. The magnitude of the dV/dQ provides a direct indication of how the voltage change of an electrode contributes to the end of discharge. In traditional graphite cells, discharge is anode-limited; that is, the $|dV/dQ, \text{anode}| \gg |dV/dQ, \text{cathode}|$. For our prelithiated cells, the $|dV/dQ, \text{cathode}|$ is slightly higher than that of the anode at the beginning of life, but this relationship reverses as the cell ages. In a previous work, we have shown that the contribution of each electrode to determine the end of discharge of the cell can be codified by the parameter λ , which is the ratio between $|dV/dQ, \text{cathode}|$ and $|dV/dQ, \text{cell}|$.³⁹ For a traditional graphite cell, $\lambda \approx 0$; for a highly prelithiated cell, $\lambda \approx 1$ and discharge ends when the cathode polarizes for being fully relithiated. For our three-electrode cell, we initially have $\lambda = 0.55$, which decreases to $\lambda = 0.42$ after 100 cycles and $\lambda = 0.22$ after 300. Typical non-prelithiated SiO_x cells built with our electrodes have $\lambda = 0.2-0.4$.^{39,58,60,61} Hence, our three-electrode cell initially presented a relatively high cathode limitation, which vanishes after ~ 100 cycles. After that point, the cell reverts to a "normal" SiO_x system, with the excess inventory provided by prelithiation extinguished. Based on the level of capacity fade (like we did in Figure 11a), that transition is expected to occur after ~ 200 cycles in our coin cells.

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CHAPTER SIX

PRINCIPLES OF CARBON SCAFFOLD SELECTION FOR
SI/C COMPOSITES

Contribution of Authors and Co-Authors

Manuscript in Chapter 6

Author: Charles McDaniel

Contributions: Fabricated cells, carried out characterization, analyzed data, and co-wrote the manuscript.

Co-Author: Ian Joyce

Contributions: Synthesized materials, carried out characterization, analyzed data, and co-wrote the manuscript.

Co-Author: Cody Morse

Contributions: Fabricated cells.

Co-Author: Nicholas P. Stadie

Contributions: Advised with the experimental direction, interpreted results, and assisted in writing and editing the manuscript.

Manuscript Information

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Abstract

Silicon/carbon (Si/C) composites are now the demonstrated successor to graphite as high-energy density lithium-ion battery (LIB) anodes due to the increased capacity of silicon and only little change to the overall charge/discharge potential and reversibility in optimized cases. However, selection of the scaffold and overall guiding principles for composite structure remain under active investigation. Herein, three carbon scaffold families spanning a broad phase space of crystallinity and surface area were employed as substrates for silane and acetylene deposition experiments to yield Si/C composites of varying structural characteristics and composition. Differential thermogravimetric analysis (DTGA) was employed using a novel method to determine the content of silicon, carbon, and silicon oxide present in each Si/C composite. The silicon environments formed in the composites could be distinctly classified as Type I (intraparticle, nanoscale) or Type II (interparticle, bulk scale) by comparison to a series of pure silicon samples. These classifications were correlated with electrochemical performance, demonstrating that Type I and Type II silicon contents could be relevant predictors for the LIB performance of present and future Si/C composite anodes.

Introduction

Graphite, the long-standing anode in commercial LIBs, has a theoretical capacity of 372 mAh g⁻¹ (LiC₆) and enables extremely reliable cycling in full-cells due to its topotactic ion storage mechanism.¹ However, to meet the ever-increasing global energy demands, LIBs with increased energy density are needed;² one strategy to achieve this end is to employ a higher capacity anode material such as silicon in the place of graphite.³ Silicon exhibits a room-temperature theoretical

capacity of 3579 mAh g⁻¹ (Li₁₅Si₄) and is also highly abundant in the Earth's crust. Unfortunately, the extremely high capacity of silicon is concomitant with a ~300% volumetric expansion upon lithiation.⁴ This expansion leads to electrode pulverization during cycling, which disrupts electrical contact between the active particles and causes a massive consumption of electrolyte through continuous solid-electrolyte interphase (SEI) formation and reformation.^{5,6}

Numerous strategies have been employed to ameliorate the detrimental effects of volume expansion in silicon-containing anodes. An already commercialized strategy is to combine silicon and carbon in an intimate composite via chemical vapor deposition (CVD) of silane (SiH₄) within the pores of a carbon-based scaffold.⁷ This approach ideally anchors the silicon phase to the conductive carbon scaffold,⁸ providing void space for expansion during cycling without disconnection from the electrical network,⁹ thereby improving electrochemical stability.^{9,10} A possible secondary effect of this method is the control (i.e., nanosizing) of the native silicon crystallite size,¹¹ which is itself a known contributor to stability of silicon-based active LIB anode materials.^{12,13} Much remains to be understood about optimal silicon content and structure to achieve higher specific capacity than graphite without compromising cyclability.

At low temperatures (<550 °C) and near-ambient pressures, thermal CVD of silane in the presence of a carbon powder leads to decomposition of the silane into silicon at the carbon interface, creating an intimate composite.^{14,15} In the case of porous carbon scaffolds, this occurs primarily within the pore network of the carbon scaffold.¹⁶ Deposition conditions and carbon scaffold characteristics both alter the mechanism of silane deposition.¹⁷ Recent work has theorized that carbon scaffold properties such as particle size,¹⁸ surface area,¹⁷ and pore volume¹⁹ impact the

structure of the deposited silicon phase, but there has not to our knowledge been a systematic experimental investigation describing their independent effects.

These gaps in knowledge related to Si/C composite battery anodes are in part caused by the non-trivial nature of characterizing the specific composition and structure of both components, especially when the silicon phase is nanosized. Typical approaches to resolving these specific details consist of microscopic and spectroscopic techniques, which only provide local information rather than bulk properties.^{17,20–23} Thermogravimetric analysis (TGA) has also been used to quantify the amount of silicon in Si/C composites, taken as the remaining mass after combustion of the composite under flowing air.²⁴ While yielding a useful estimate of average bulk composition, this simple method is limited in that it treats the initial sample as pure Si/C (i.e., oxide-free) and it generally does not yield any details about the nature of the silicon type. Ignoring the potentially significant native silicon oxide layer (SiO_x where $x \approx 2$) present on all Si/C composite, as is typically done,^{25–27} can introduce significant error (up to 25 wt% Si by our estimate) into the Si content calculation. The accuracy of this estimate is crucial to predicting the electrochemical lithiation capacity of the composite since bulk SiO_2 is electrochemically inert²⁸ and nanophase SiO_2 cannot be reversibly lithiated.^{29–31}

Herein, we present a novel application of differential TGA (DTGA) to quantify the composition of Si/C composites. A total of 18 Si/C composites were synthesized by thermal CVD of silane and then acetylene (for passivation) onto structurally distinct carbon scaffolds across a wide range of porosity and graphitic crystallinity. DTGA revealed a bimodal distribution of silicon domain types, which were classified as Type I and Type II corresponding to lower and higher thermal stability, respectively. When electrochemically lithiated/delithiated, Si/C composites with

greater Type II Si content presented a more prominent signature of $\text{Li}_{15}\text{Si}_4$ de-alloying at slow rates and generally exhibited poorer cycling stability. On the other hand, Si/C composites with greater Type I Si content exhibited higher cycling stability and diminished $\text{Li}_{15}\text{Si}_4$ signature. A series of pure silicon materials with known particle sizes were then analyzed by the same methods to contextualize the detection of Type I and Type II silicon in Si/C composites and to estimate the length-scale of the silicon environments characteristic of each type. Hence, the DTGA method described herein is a useful tool for future researchers seeking to improve the cycling stability of Si/C composites, specifically by optimizing synthesis conditions to promote Type I silicon formation.

Experimental

Materials

Three carbon materials were obtained from commercial suppliers: superactivated carbon (MSC-30, Kansai Coke & Chemicals Co.), carbon black (Super P, BR0121, MSE Supplies), and high surface area carbon black (Ketjenblack, EC600JD, MSE Supplies). Four silicon materials were obtained from commercial suppliers: plasma-enhanced chemical vapor deposition (PECVD) silicon (nano-Si, AGC Plasma Technology Solutions), fine silicon nano-powder (50 nm, 98%, 44384, lot# S17H061, Alfa Aesar), coarse silicon nano-powder (100 nm, 98%, 633097, lot# MKCM0616, Sigma-Aldrich), and silicon micro-powder (-325 mesh, 99%, 215619, lot# MKCK6629, Sigma-Aldrich).

Carbon Scaffold Heat Treatment

The commercial carbon scaffolds were subjected to heat-treatment (HT) at 1200-2000 °C under either vacuum (1200-1800 °C) or argon (2000 °C) within a graphitization furnace (RD-G, R. D. Webb Co.). In a typical treatment, 1.0 g of sample was placed into a 24 mL cylindrical graphite crucible (JA1166, MSE Supplies), subjected to vacuum overnight, and then heated to the desired set temperature (1200, 1400, 1600, 1800, or 2000 °C) at a ramp rate of 5 °C min⁻¹. After holding for 1 h, the sample was then allowed to cool under vacuum overnight. The heat-treated scaffolds are referred to by abbreviations as summarized in (see **Table 1**) thus producing three families of six scaffolds each.

Table 1. Carbon scaffold naming abbreviations as a function of parent scaffold name and HT temperature.

HT Temperature (°C)	Parent Carbon Scaffold		
	MSC-30	Ketjenblack	Super P
(none)	MSC	KB	SP
1200	MSCL	KBL	SPL
1400	MSCLM	KBLM	SPLM
1600	MSCM	KBM	SPM
1800	MSCMH	KBMH	SPMH
2000	MSCH	KBH	SPH

Synthesis of Si/C Composites

In each synthesis, 200 mg of carbon scaffold were loaded into a rectangular alumina boat (100×25×6 mm, Almath Crucibles Ltd.), which was then placed into a horizontal quartz tube (ø 51 mm) held within a single-zone tube furnace (GSL-1100X-S, MTI Corp.). The quartz tube was sealed via compression fittings within a custom stainless-steel gas manifold designed for handling

silane (Swagelok Co.). The manifold was first thoroughly purged through a series of 40 vacuum and argon filling steps to ensure a thoroughly inert atmosphere. Under flowing Ar (700 sccm), the furnace was then heated to 200 °C at a ramp rate of 5 °C min⁻¹, held for 20 min, and then further heated to 500 °C at the same rate. Upon reaching the set point, the gas flow was switched to a silane/helium mixture (5% SiH₄ in He, 6.0 purity, EFC Gases & Advanced Materials) at 50 mL min⁻¹ for 60 min using a dedicated mass flow controller (MC-Series, Alicat Scientific Inc.). The manifold was then evacuated and refilled with argon another 40 times. The gas flow was then switched to acetylene (99.6%, American Welding & Gas) at 50 mL min⁻¹ for 30 min using a dedicated mass flow controller (MC-Series, Alicat Scientific Inc.). The manifold was evacuated and refilled with argon once more, and the furnace was cooled to ambient. The product was removed under air and then transferred to an argon-filled glovebox for storage (<0.5 ppm H₂O/O₂).

Materials Characterization

Nitrogen (N₂) adsorption/desorption isotherms were measured at ~77 K using a commercial Sieverts apparatus (3Flex, Micromeritics Corp.). Samples were degassed under vacuum at 200 °C for 12 h prior to analysis. Specific surface area was calculated from the adsorption branch of the isotherms using the Brunauer-Emmett-Teller (BET) model over a relative pressure (P/P₀) range of 0.05-0.20 and applying standard consistency criteria.³² The elemental composition (CHO) of the carbon scaffolds was measured using combustion analysis (Atlantic Microlabs Inc.). Measurements were made in triplicate for each sample and averaged.

Powder X-ray diffraction (XRD) patterns were measured using a benchtop diffractometer (D2 Phaser, Bruker Corp.) in Bragg-Brentano geometry with Cu K $\alpha_{1,2}$ radiation ($\lambda = 1.54$ Å) at 30

kV and 10 mA. Scans were acquired over $2\theta = 10\text{--}60^\circ$ with a step size of 0.026° and a step time of 5 s.

Raman spectra were measured at room temperature using a Raman spectrometer (LabRAM HR Evolution, Horiba Scientific Ltd.) equipped with a confocal microscope and a 532 nm (2.33 eV) frequency-doubled Nd:YAG laser. The excitation power was 4.5 mW to avoid heating effects and spectra were collected over the range of $100\text{--}3500\text{ cm}^{-1}$ with a resolution of 1 cm^{-1} .

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) mapping were performed using a field-emission scanning electron microscope (SUPRA 55VP, Zeiss) equipped with a silicon drift detector (X-Max, 80 mm^2 , Oxford Instruments). The microscope was operated at an accelerating voltage of 15 kV with a working distance of 8.5 mm. Samples were mounted by pressing into indium foil. Elemental maps for carbon, oxygen, and silicon were measured using the characteristic EDX peaks at 0.27, 0.51 and 1.84 keV, respectively.^{33,34}

TGA was performed using a benchtop thermal analyzer (STA 449 F5 Jupiter, Netzsch-Gerätebau GmbH) under flowing air (breathing grade, American Gas & Welding) at 25 mL min^{-1} . The samples ($\sim 15\text{ mg}$) were loaded into an alumina pan, heated at a ramp rate of $5\text{ }^\circ\text{C min}^{-1}$ up to $1400\text{ }^\circ\text{C}$, and then held for 60 min. The analyzer was calibrated using copper(II) oxalate hemihydrate (98%, A15365-18, Thermo Fisher) and a pan-specific experimental blank was subtracted from each run; these corrections for buoyancy error and thorough control studies permit reporting the data as either wt% or mass%.

DTGA Methodology

Numerical differentiation of the TGA data was performed by numerically differentiating data points in 0.8s intervals to obtain raw DTGA profiles for further analysis. Each raw DTGA profile was fitted to four gaussian lineshapes by a least-squares error minimization approach. Two of the four constituent peaks, those for silicon conversion to $\text{SiO}_2(\text{s})$, were held to impart an increase in mass (positive DTGA signal) and the other two constituent peaks, those for carbon conversion to $\text{CO}_2(\text{g})$, were held to impart a decrease in mass (negative DTGA signal). In all cases herein, the two negative carbon peaks were not significantly different to permit distinct analysis and were added together to obtain the mass loss associated to carbon in the original sample, by multiplication with a factor of 1.

On the other hand, the silicon content associated with each positive silicon peak was separately multiplied by the mass ratio of solid silicon to oxygen gas of roughly 0.87766. These two individual contributions to the silicon content were summed to estimate the total silicon content of each Si/C composite. Lastly, the initial SiO_2 content present in each composite prior to TGA (i.e., inherent to the original Si/C composite) was estimated by subtraction of the fully oxidized Si content from the final mass of the sample at the end of the TGA experiment according to:

$$wt\%_{\text{SiO}_2} = wt\%_{\text{final}} - wt\%_{\text{Si}} \cdot 2.1394 \quad (1)$$

where $wt\%_{\text{SiO}_2}$ is the original SiO_2 content in the sample prior to TGA, $wt\%_{\text{final}}$ is the final weight of the sample after TGA, $wt\%_{\text{Si}}$ is the original silicon content in the sample prior to TGA, and 2.1394 is the mass ratio of SiO_2 to Si (to convert the original silicon content into final SiO_2 content).

Electrode Fabrication

All 18 Si/C composites were prepared as active electrode materials for further characterization using standard slurry casting techniques. First, the Si/C composite powder was homogenized by grinding using a mortar and pestle for 15 min. Then, a slurry was prepared by combining 80 wt% active material, 10 wt% carbon black conductive additive (Super P, EQ-Lib-SuperP, MTI Corp.), 10 wt% binder, and deionized (DI) water (0.5-1 mL to achieve desirable slurry consistency). The binder was a 1:1 mixture of carboxymethyl cellulose (CMC, $\geq 99.5\%$, batch #0011912, MTI Corp.) and styrene butadiene rubber (SBR, 50 wt% in DI H₂O, CR0128, batch #19925A1, MTI Corp.). The slurry was twice homogenized using an automatic mixer (AR-100, Thinky Corp.) for 3 min at 2000 rpm. The homogenized slurry was cast onto copper foil (9 μm thickness, MTI Corp.) using a doctor blade with a wet gap of 165 μm . Drying was carried out in three steps: first for 8 h under ambient conditions, then for 8 h under air at 80 °C, and finally for 10 h under rough vacuum (~ 5 mbar, Chemstar Dry 2071B, Welch Vacuum) at 100 °C. After cooling, electrodes ($\varnothing$ 10 mm) were punched out in air and stored in an argon atmosphere glovebox (≤ 0.1 ppm H₂O/O₂). Active material loadings were measured by subtracting the mass of the foil from each electrode mass and dividing by 0.8, varying from 0.5-1.2 mg cm⁻² within all electrodes investigated herein. The pure silicon electrodes were fabricated as previously described³⁵ and the only difference was the use of pure CMC instead of a CMC/SBR mixture as the binder.

Electrochemical Cell Fabrication

Coin-type cells (2032 format, Hohsen Corp.) were assembled in a glovebox under argon atmosphere (≤ 0.1 ppm H₂O/O₂) with a lithium chip ($\varnothing$ 16 mm, 99.9%, MTI Corp.), glass fiber separator (0.26 mm thickness, $\varnothing$ 17 mm, Whatman, GF/C), working electrode, conical spring, and

two stainless steel spacers (0.5 mm thickness, $\varnothing$ 16 mm, Hohsen Corp.). The cell was flooded with 100 μ L of electrolyte, consisting of 1M LiPF₆ in a 1:1 mixture (by weight) of ethylene carbonate (EC, battery grade, Tomiyama Pure Chemical Industries Ltd.) and dimethyl carbonate (DMC, battery grade, Tomiyama Pure Chemical Industries Ltd.) with a 10 wt% addition of fluoroethylene carbonate (FEC, battery grade, Tomiyama Pure Chemical Industries Ltd.).

Electrochemical Characterization

After assembly, all cells were rested for 24 h prior to further characterization. Galvanostatic charge/discharge (GCD) cycling was performed in a temperature-controlled incubator (KB 53, Binder GmbH) at 25 °C using a battery cycler (CT30001A, Landt Instruments). Slow-rate voltage profiles were obtained by cycling once between 0.01-1.5 V vs Li⁺/Li at a rate of 20 mA g⁻¹. Cycling stability was measured by cycling once between 0.05-0.7 V vs. Li⁺/Li at a rate of 100 mA g⁻¹, followed by 49 cycles between 0.05-0.7 V at 1 A g⁻¹. This 50-cycle protocol was repeated twenty times for a total of 1000 cycles. The 100 mA g⁻¹ “slow” cycle is referred to as a reference performance test (RPT).

Results and Discussion

Carbon Scaffold Structural Variation

Three distinct commercial carbon scaffolds were selected as precursors for a wide range of scaffolds with systematically varying textural and crystalline properties, as shown in **Figure 1**. The first parent scaffold, referred to herein as MSC (**Figure 1a**), is a high surface area activated carbon (BET surface area: 3244 m² g⁻¹) comprised of large particles with a characteristically broad distribution of micropores and small mesopores giving rise to a distinct, sloping knee in its N₂

adsorption isotherm (**Figure 1d**). The second, Ketjenblack, referred to herein as KB (**Figure 1b**), is a modestly high surface area ($1405 \text{ m}^2 \text{ g}^{-1}$) but also highly conductive carbon comprised of small particles and a broad distribution of pore sizes from micropores to large mesopores and macropores. The third parent scaffold, Super P, referred to herein as SP (**Figure 1c**), is a low surface area ($62 \text{ m}^2 \text{ g}^{-1}$) carbon black comprised of small particles with a characteristically textured surface, used as an industry standard conductive additive in LIBs. Thus, the three parent scaffolds exhibit a systematically varying set of properties from highly porous and poorly conductive to nonporous and highly conductive. To generate a larger set of scaffolds with an even wider range of properties, each parent scaffold was annealed under inert conditions at five different set

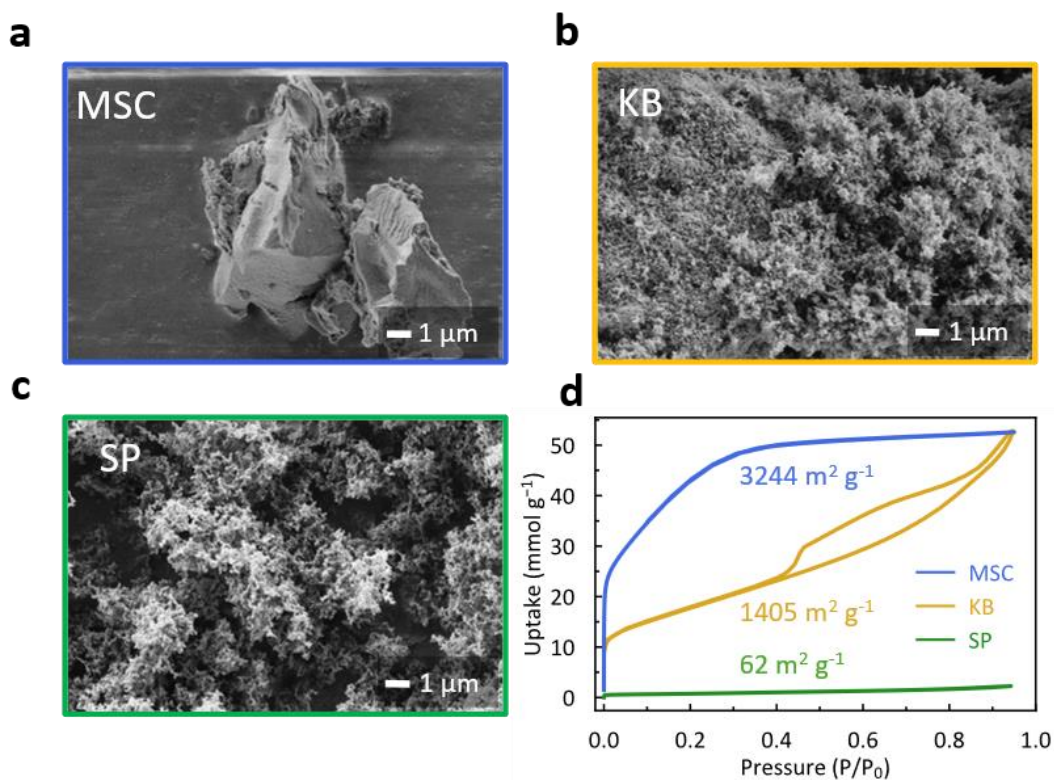


Figure 1. SEM micrographs of (a) MSC-30 (MSC), (b) Ketjenblack (KB), and (c) Super P (SP) parent carbon scaffolds. (d) N_2 adsorption/desorption isotherms of MSC (blue), KB (gold), and SP (green) at 77 K, and corresponding BET surface areas.

temperatures between 1200-2000 °C (see **Table 1**) thus producing three families of six scaffolds each.

The evolution of scaffold properties over the course of heat-treatment (HT) for all three carbon families is shown in **Figure 2**. The initial surface areas of MSC, KB, and SP were measured to be 3244, 1405, and 62 m² g⁻¹, respectively, and all three families exhibited decreasing surface area with increasing HT temperature (**Figure 2a**). Similar trends are observed in total pore volume and pore size distributions (**Figure S1**). The MSC and KB heat-treatment families experienced large (94% and 71%, respectively) decreases in N₂-accessible surface area over the entire course of HT, which can be attributed to gradual micro- (<2 nm) and mesopore (2-20 nm) closure during

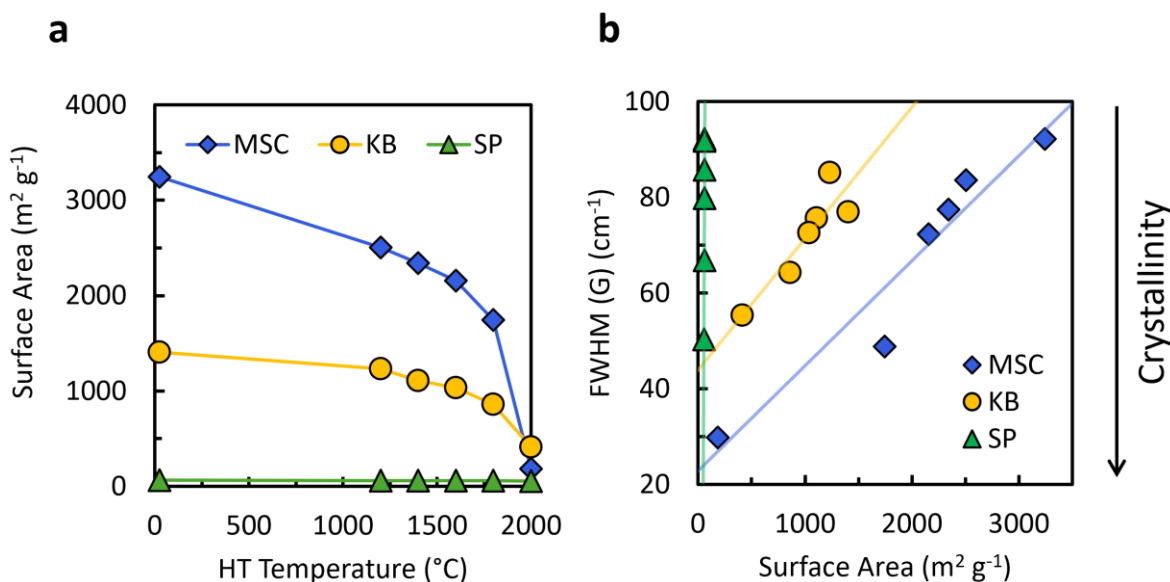


Figure 2. (a) N₂-accessible (BET) surface area as a function of HT temperature and (b) FWHM of the Raman G peak as a function of surface area for all carbon scaffolds, organized by color according to the parent carbon scaffold.

graphitization. On the other hand, the surface area of SP only decreased by 13% over the entire course of HT (from 62 to 54 m² g⁻¹ from SP to SPH, respectively). The surface areas of all carbon scaffolds are tabulated in **Table S1**.

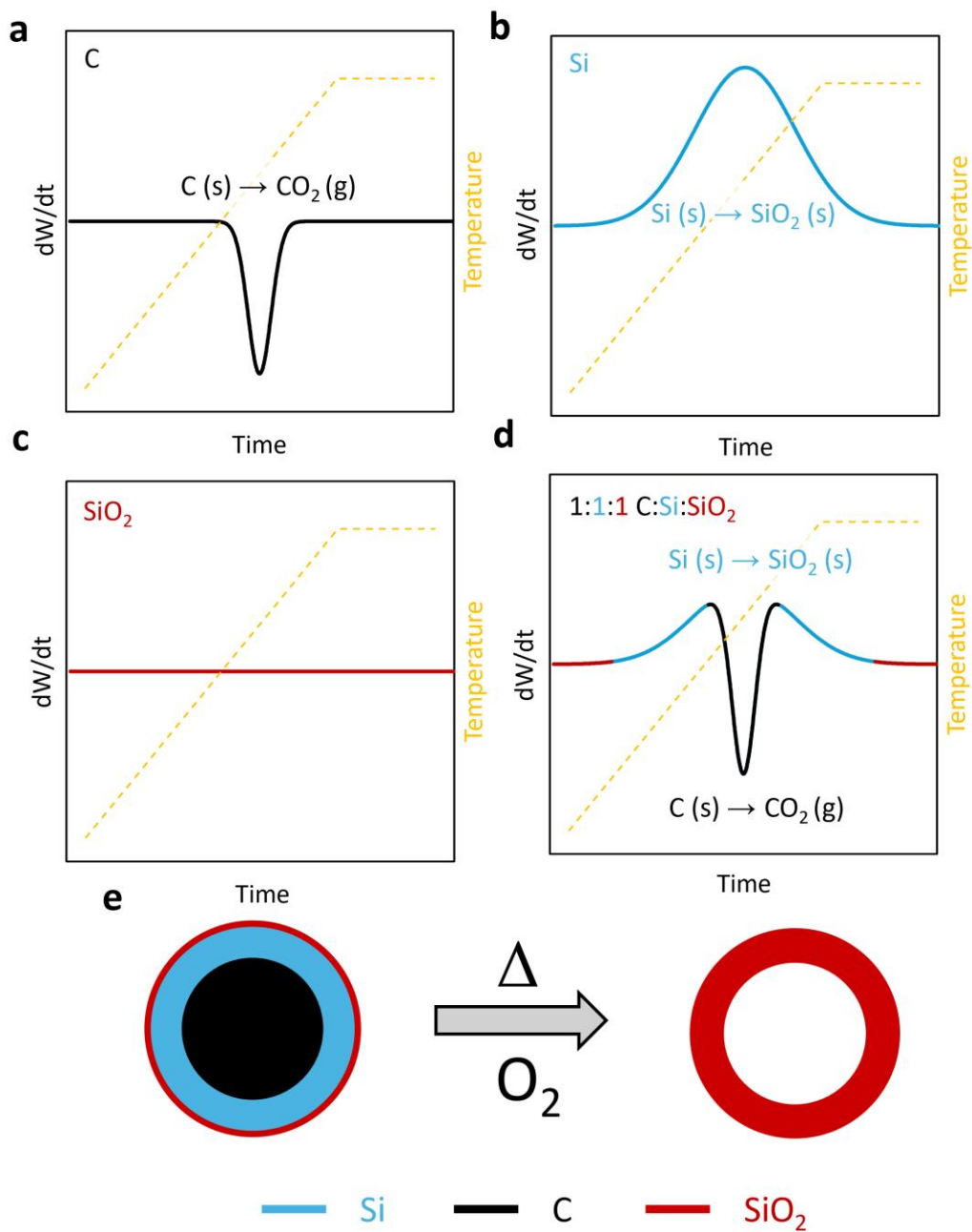
The powder XRD patterns and Raman spectra for all of the carbon scaffolds evolve with clear, systematic trends as expected for the graphitization of disordered carbons, as shown in **Figure S2**. The position and full-width at half-maximum (FWHM) of the Raman-active D and G modes of each scaffold are tabulated alongside the corresponding D:G intensity ratio (I_D/I_G) in **Table S2**. The FWHM of the G mode in the Raman spectra is a more direct indicator of graphitic crystallinity than the I_D/I_G ratio due to the wavelength-dependent dispersion effects on the intensity and position of the D mode in graphitic carbons.^{33,36} In this work, each family of carbon scaffolds undergoes a monotonic narrowing of the G mode in their respective Raman spectra as a function of HT temperature, serving as a quantitative guide for the progression of graphitization. In general, the 18 scaffolds cover a similar range in “graphite-like” crystallinity, from very low (especially MSC) to nanocrystalline graphite (especially MSCH and SPH); however, because of their variability in surface area, a remarkably wide range of phase space is represented by the set of scaffolds investigated in this work (**Figure 2b**). Hence, this set of scaffolds serves as an ideal landscape for investigation of the role of scaffold properties on subsequent Si/C composite properties and electrochemical performance in LIBs.

Si/C Composite Materials Characterization

All 18 scaffolds within the three parent scaffold families were subjected to silane deposition under identical conditions at 500 °C and subsequent acetylene deposition (also at 500 °C) for passivation, based on a method inspired by Magasinski and coworkers²² and broadly

reflective of widely-used methods to produce Si/C composite anode powders (see the Experimental section for details). The resulting compositions of the so-obtained Si/C composites, comprised of the original carbon (and its inherent CHO composition, **Figure S3**), the deposited silicon, possible silicon oxide interfacial layer, and newly deposited carbon (via acetylene deposition), were characterized by a novel DTGA deconvolution method.

A summary of the theoretical outcome of DTGA experiments on Si/C composites is shown in **Scheme 1**, which depicts the expected change in mass of a representative set of relevant materials upon combustion under flowing air: pure C (**Scheme 1a**), pure Si (**Scheme 1b**), pure SiO₂ (**Scheme 1c**), and an arbitrary mixture of all three (**Scheme 1d**). Corresponding TGA schematics are shown in **Figure S4**. Pure carbon (e.g., graphite) and other forms of carbonaceous material (e.g., activated carbon) combust completely within a short window of time once the combustion temperature has been reached to produce gaseous products (marked by a sharp negative peak indicating a *decrease* in mass); no mass remains at the end of the TGA experiment. Contrastingly, pure silicon (28.085 g mol⁻¹) combusts completely to form solid SiO₂ (60.085 g mol⁻¹), generally a slower (and hence less sharp) *increase* in mass since the product remains on the balance at the end of the TGA experiment, as denoted by a broad, positive DTGA peak. A third case, pure SiO₂ is already fully oxidized and thus does not change in mass upon heating in the presence of flowing air. The combustion of an equimass mixture of these three phases leads to at least two unambiguous features (a steep mass decrease and a less steep mass increase), yielding quantifiable “C” (i.e., carbonaceous) and Si contents, respectively, and the content of SiO₂ can be determined by the difference from 100%. A visual schematic showing the combustion of a core-



Scheme 1. DTGA profiles of (a) pure carbon, (b) pure silicon, (c) pure SiO_2 , and (d) a 1:1:1 mixture of carbon, silicon, and SiO_2 . (e) Schematic representation of the combustion of a Si/C composite leaving pure SiO_2 as the sole solid phase product.

shell model of Si/C is shown in **Scheme 1e**, where the carbon disappears due to conversion to CO₂ gas, and the Si converts to SiO₂.

The TGA profiles of the 18 Si/C composites synthesized herein are shown in **Figure S5** and the corresponding DTGA profiles in **Figure 3**. Most of the composites exhibited four distinct DTGA features: a low-temperature mass increase event (corresponding to the oxidation of a relatively unstable form of silicon, referred to herein as Si Type I), two mass decrease events (corresponding to carbon combustion), and a high-temperature mass increase event (corresponding to the oxidation of a relatively stable form of silicon, referred to herein as Si Type II). The DTGA profiles of these events could be accurately fitted by overlapping four Gaussian line shapes; this enabled the deconvolution and quantification of the individual component phases within each composite. As an example, the DTGA profile of a representative Si/C composite with well-separated Type I and Type II silicon oxidation events is shown in **Figure 3d**.

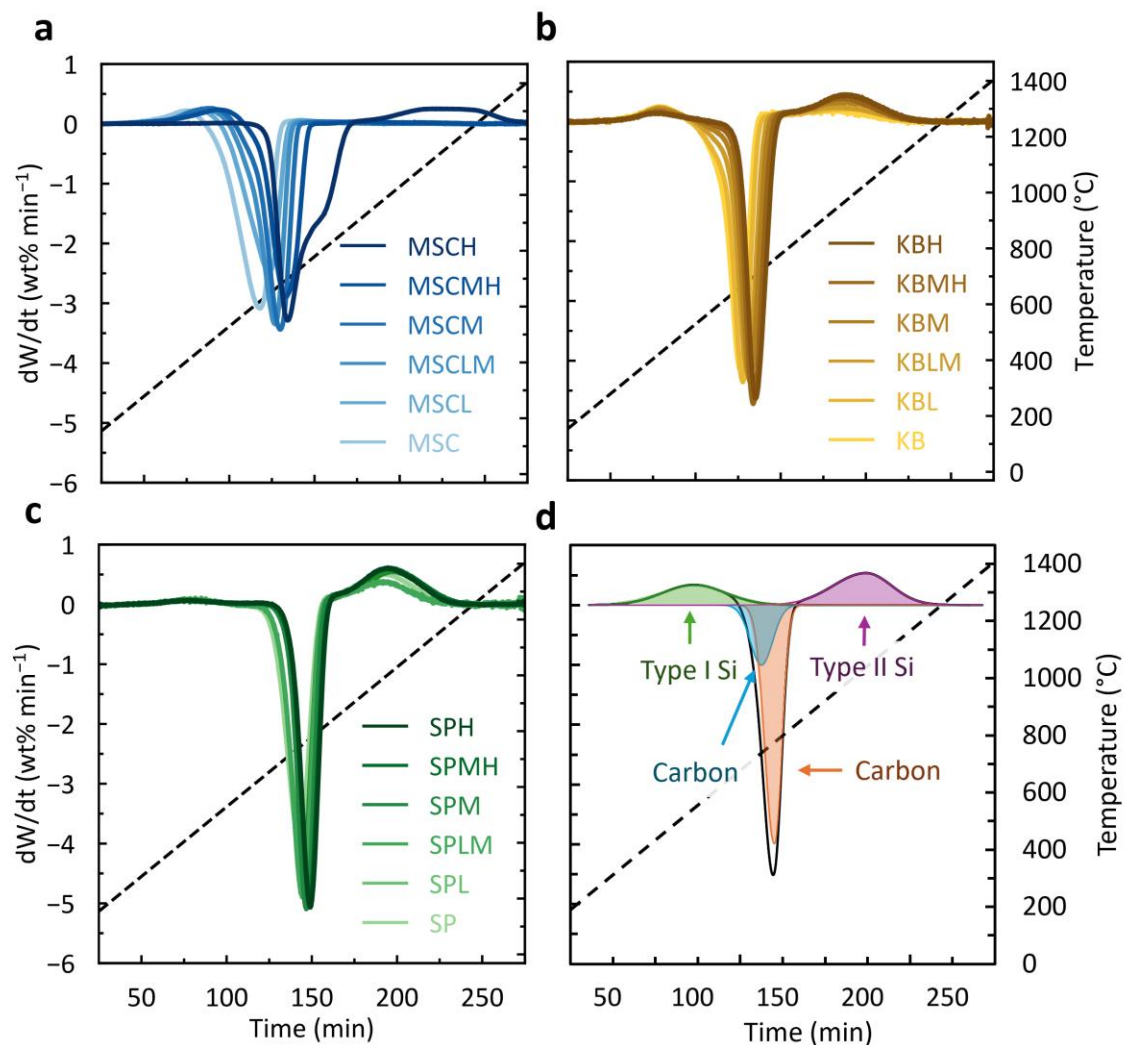


Figure 3. DTGA profiles of experimental materials within the (a) MSC, (b) KB, and (c) SP families of Si/C composites, and (d) a representative Si/C composite, showing the four labeled deconvoluted contributions found in most samples.

Several trends among the DTGA profiles of the Si/C composites could be seen directly, most importantly that the carbon oxidation events typically moved to higher temperature as a function of scaffold HT temperature and that the silicon oxidation events were reduced in intensity within the same series evolution. These results confirm the general expectations that the scaffold

itself becomes more stable (graphite-like) at higher HT temperatures and that the samples with lower porosity (due to HT) carry lower contents of silicon, respectively. The quantified deconvolution of the DTGA profiles for all Si/C composites is tabulated in **Table 2** and select trends are shown in **Figure 4**. Interestingly, Type I and Type II silicon contents follow distinctly unique trends for each of the three scaffold families, as shown in **Figure 4a** and **Figure 4c**. The highest surface area and most microporous scaffolds (MSC family) favored the formation of the highest content of Type I silicon (up to 18 wt% for MSCL), followed by the KB family (up to 14 wt% for KB) and the SP family (containing ~2 wt% for all Si/C composites derived from SP-type scaffolds). The slight increase in Type I silicon content from the MSC to MSCL scaffolds, despite a reduction in surface area and microporosity, is perhaps attributable to a more effective acetylene passivation on the MSC-derived Si/C composite relative to those derived from more graphitized scaffolds, preventing conversion of Type I silicon into SiO₂ (**Figure S6**).

To control for the effects of overall composition, the absolute mass of Type I silicon (determined using the absolute difference in mass of the Si/C composite compared to the original scaffold, measured after synthesis) for each composite is shown in **Figure 4b**. The amount of Type I silicon deposited during silane deposition at 500 °C is directly correlated to the surface area of the scaffold.

On the other hand, the Type II silicon content across all composites shows almost the opposite trend as that for Type I silicon, as shown in **Figure 4c**. The SP family of composites preferentially forms Type II silicon, up to the highest value measured herein of 23 wt% for SPMH. The KB family contains the next highest Type II content, up to 18 wt% for the KBH-derived Si/C composite, while the MSC family does not exhibit any discernible Type II silicon from MSC to

MSCLM; MSCM, which has a BET surface area of $2157 \text{ m}^2 \text{ g}^{-1}$, is the first MSC scaffold in the increasing HT temperature series to host Type II silicon. The highest Type II silicon content within the MSC family is that for the MSCH-derived composite (16.5 wt%), though it exhibits no Type I silicon content. Notably, the total Si content (Type I + Type II) does not significantly differ across any composite within a parent scaffold family, indicating that the primary effect of scaffold HT processing is interconversion between readiness for Type I or Type II silicon deposition (**Figure S7**). The higher total Si content of the KB (and SP) scaffold families suggests that silicon deposition efficiency for any carbon scaffold is controlled by factors beyond crystallinity and porosity, such as particle size or surface functionality.

Table 2. Compositional analysis of Si/C composites as a function of carbon scaffold, estimated using the DTGA method. The error is determined by the difference of the sum from 100%.

Carbon Scaffold	Type I Si (wt%)	Type II Si (wt%)	Total Si (wt%)	C (wt%)	SiO ₂ (wt%)	Error (wt%)
MSC	14.2	0.0	14.2	76.5	9.8	0.5
MSCL	18.0	0.0	18.0	64.5	13.9	3.5
MSCLM	16.1	0.0	16.1	65.2	18.7	0.1
MSCM	16.6	0.6	17.2	61.7	21.7	0.6
MSCMH	13.1	1.6	14.7	58.0	25.4	1.9
MSCH	0.0	14.4	14.4	81.0	5.9	1.2
KB	13.8	10.5	24.3	69.1	7.9	1.3
KBL	10.9	12.3	23.2	65.9	11.7	0.8
KBLM	13.8	10.9	24.7	67.7	9.9	2.3
KBM	10.6	16.1	26.6	61.9	11.5	0.1
KBMH	10.8	15.9	26.7	65.2	8.1	0.0
KBH	7.9	18.1	26.0	63.0	11.1	0.2
SP	1.8	20.8	22.7	63.8	11.3	2.2
SPL	2.0	20.0	22.1	65.2	12.0	0.7
SPLM	2.1	19.7	21.8	65.4	8.3	4.5
SPM	2.0	22.8	24.8	64.2	13.2	2.1
SPMH	2.1	23.4	25.5	60.7	13.8	0.0
SPH	2.2	22.6	24.8	63.0	12.0	0.2

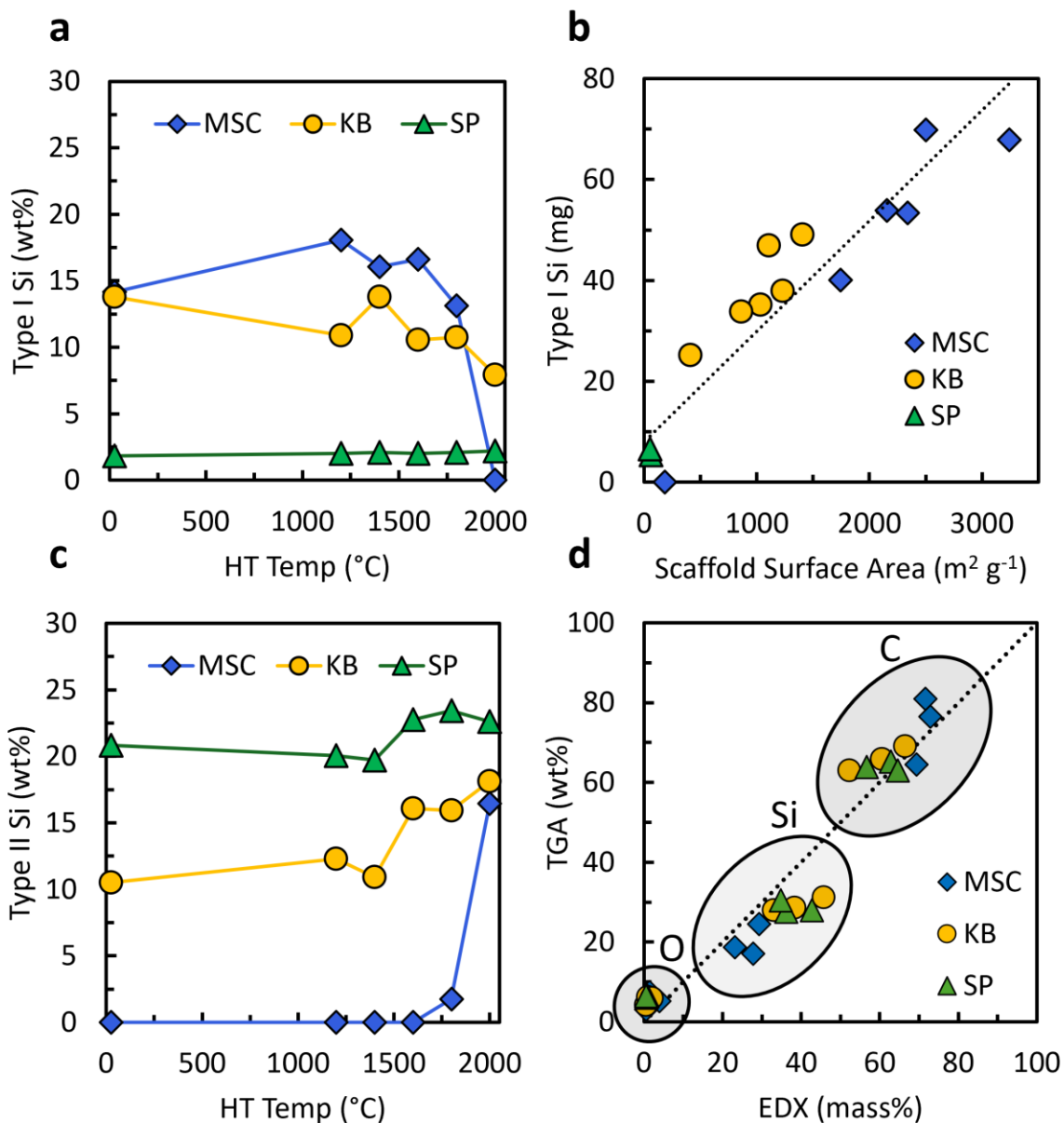


Figure 4. Compositional analysis of the MSC (blue), KB (gold), and SP (green) Si/C composite families: (a) relative Type I Si, (b) absolute Type I Si, (c) and relative Type II Si as determined by DTGA deconvolution, and (d) correlation of total Si, C, and O content as resolved by TGA and EDX analysis.

To validate the DTGA quantification method of compositional analysis, 9 Si/C composites derived from scaffolds comprising the parent, -L, and -H variants of each family were subjected to EDX mapping experiments over large areas ($>1 \text{ mm}^2$) to quantify the overall content of Si, C, and O (**Figures S8-S10**). The correlation between the DTGA results and those measured using EDX is shown in **Figure 4d**; there is high statistical consistency between the two methods ($R^2 = 0.93$). The systematic errors (under-estimation of carbon and over-estimation of silicon by EDX) are attributable to the difference in scattering cross-sections between C and Si,^{37,38} implying that DTGA could in fact be even more accurate than EDX. This is also supported by an analysis of the error provided by summing the various independent components of the Si/C compositions as resolved by the DTGA method (**Figure S11**).

The pre-existing SiO_2 content of each scaffold (prior to TGA, as estimated by DTGA analysis) is plotted in **Figure S12**. This oxide content remains low ($<10 \text{ wt\%}$) for both KB- and SP-derived Si/C composites, regardless of scaffold HT temperature. On the other hand, MSC-derived composites exhibit a monotonic increase in SiO_2 content from MSC to MSCMH (RT to $1800 \text{ }^\circ\text{C}$), suggesting that the cumulative effects of heat-treatment could inhibit subsequent acetylene passivation under these conditions.

Si/C Composite Electrochemistry

To understand the electrochemical lithiation/delithiation properties of Type I and Type II silicon within Si/C composites, two extreme samples were chosen for primary analysis: the Type I silicon-dominant MSCL- and Type II silicon-dominant SPL-derived composites. Two experiments were conducted in lithium half-cells: (i) slow rate, deep-lithiation GCD cycling to

assess the full capacity and near-equilibrium lithiation/delithiation potentials (20 mA g⁻¹, 0.01-1.5 V vs. Li⁺/Li) and (ii) faster rate GCD cycling within a narrower potential range to assess long-cycling stability (1 A g⁻¹, 0.05-0.7 V vs. Li⁺/Li, with an RPT at 100 mA g⁻¹ every 50 cycles), as shown in **Figure 5**.

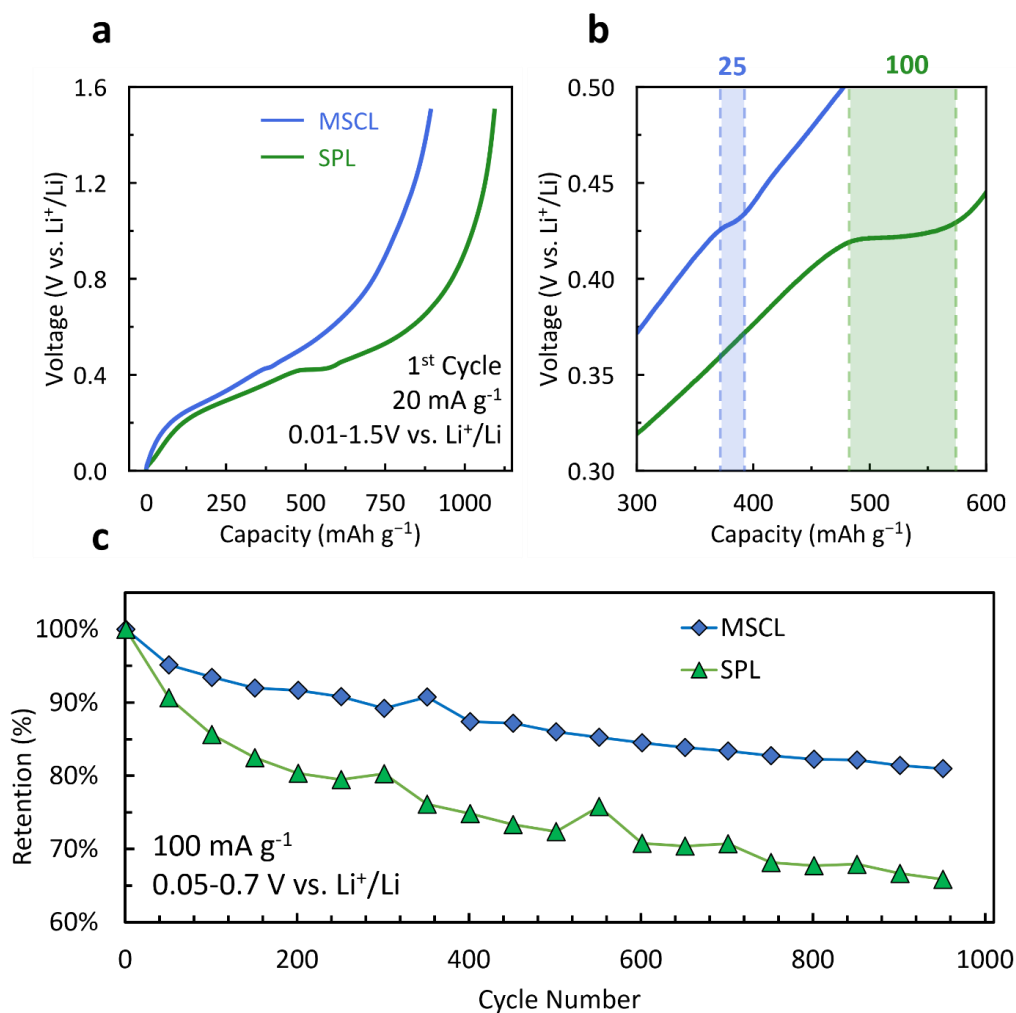


Figure 5. Electrochemical characterization of MSCL- (Type I Si-dominant, blue) and SPL- (Type II Si-dominant green) derived Si/C composites: (a) full and (b) plateau region of the 1st cycle delithiation voltage profile at 20 mA g⁻¹, and (c) lithiation capacity retention during 100 mA g⁻¹ RPT cycles over long-cycling at 1 A g⁻¹.

Under slow-rate cycling, the MSCL- and SPL-derived Si/C composites exhibit 1st cycle delithiation capacities of 893 and 1093 mAh g⁻¹, respectively, as shown in **Figure 5a**. These capacities are proportional to the total silicon content (Type I + Type II) for the two composites (18 and 22 wt%, respectively), following a consistent trend across all Si/C composites studied herein. Based on the DTGA total silicon content alone, the theoretical silicon-based capacity of each Si/C composite is 644 and 787 mAh g⁻¹, respectively (assuming an ultimate lithiation state of Li₁₅Si₄).⁴ The remaining capacity must be owed to SiO₂ (rather, SiO_x with $x < 2$) and/or carbon within the composite. We note that it would generally not be useful to perform the control experiment (electrochemical lithiation of only the scaffold prior to silane deposition) in order to measure the lithiation capacity of the scaffold itself; surface site blockage during the CVD process would certainly change the landscape of available lithiation sites.

A distinct plateau attributable to Li₁₅Si₄ de-alloying³⁹ can be observed in the 1st cycle delithiation profile of both composites (**Figure 5b**). Notably, the plateau capacity of the SPL-derived Si/C composite is ~4 times longer than that of the MSCL-derived composite (~100 vs. ~25 mAh g⁻¹, respectively). This indicates that while both materials contain silicon domains that are sufficiently large enough to support the 2-phase de-alloying reaction,³⁹ the prevalence of such domains is far greater in the SPL-derived (Type II silicon-dominant) composite. Hence, we attribute a decidedly “bulk” character to the Type II silicon content within Si/C composites.

The GCD cycling stability for both Si/C composites over 1000 cycles is shown in **Figure 5c** (all cycling data including both the 1 A g⁻¹ standard and 100 mA g⁻¹ RPT cycles for both composites are shown in **Figure S13**). The stability of the MSCL-derived composite is significantly higher than that of the SPL-derived composite, especially in the first 200-300 cycles.

Based on the RPT cycles, the ultimate cycling retention for each composite after 1000 cycles is 81% and 66%, respectively, representing a near-two-fold improvement in the loss of capacity by incorporating Type I Si instead of Type II Si. This effect is consistent across all scaffolds investigated herein, and is not dependent on the total silicon content. For example, higher-capacity MSCL-derived Si/C composites synthesized with a longer silane deposition time exhibit similar capacity retention character to lower-capacity analogs (~80% capacity retention despite a two-fold increase in total silicon content, see **Figure S14**). These results demonstrate that Type I silicon is a more desirable silicon environment than Type II for improved cycling stability at modest current rates.

Classification of Silicon Domain Types in Si/C Composites

To provide context to the above findings, a series of pure silicon materials of increasing nominal particle size (PECVD nano-Si, 50 nm, 100 nm, and 44 μm) were characterized under identical conditions to the Si/C composites: TGA/DTGA compositional analysis followed by slow-rate, deep lithiation GCD cycling (**Figure 6**). SEM imaging confirms the increasing particle size of the pure Si materials (**Figure S15**). The DTGA profiles of the four materials are shown in **Figure 6a**, revealing a clear, monotonic increase in oxidation onset temperature as a function of increasing particle size.^{40,41} Likewise, the primary oxidation events are centered at 930, 1020, 1180, and 1400 $^{\circ}\text{C}$ for PECVD (highest peak), 50 nm, 100 nm, and 44 μm silicon, respectively. These serve as a rough calibration for the oxidation events measured on Si/C composites. We note that the 44 μm silicon micropowder never fully completed oxidation during the TGA experiment. A similar micron-sized silicon powder (1 μm nominal particle size, not shown) was subjected to long-duration TGA and did not plateau in weight even after up to 96 h at 1400 $^{\circ}\text{C}$. This is due to the

slow diffusion of oxygen through the large, crystalline silicon domains inherent to this silicon micropowder. By comparison to the Si/C composites produced in this work, fortunately none of the composites seem to contain such large Si domains and the DTGA method remains a viable approach.

Additional observations made based on the pure silicon DTGA analysis are important to note. First, multiple peaks are present in the DTGA profile of the PECVD silicon, indicating that it possesses a range of particle sizes, predominantly in the limit of smallest (and therefore lowest stability) particle size. Secondly, there is a monotonic trend in the final masses of the PECVD, 50 nm, and 100 nm silicon materials: 157, 172, and 181 wt%, respectively, while the 44 μm silicon micropowder did not complete oxidation (**Figure S16a**). This demonstrates that the smaller particle size silicon materials exhibit a higher content of native oxide (SiO_2), calculated to be 41 wt%, 27 wt%, and 17 wt% for the PECVD, 50 nm, and 100 nm Si samples, respectively.

The DTGA profiles of the MSCL- and SPL-derived Si/C composites, shown in **Figure 6c**, exhibit primary oxidation peaks centered at 540 and 1030 $^{\circ}\text{C}$, respectively. The peak centered at 1030 $^{\circ}\text{C}$ for the SPL-derived composite (which contains predominantly Type II silicon) most closely resembles that of the 50 nm pure silicon material, which corroborates previous reports of the size of silicon domains in other Si/C composites made from carbon black.²² Interestingly, the MSCL-derived Si/C composite oxidizes at an even lower temperature than any of the primary features of the pure silicon materials explored herein; the primary oxidation event for the MSCL-derived composite most closely resembles a minor event observed in the profile of PECVD silicon. This indicates that microporous scaffolds such as MSCL harbor silicon domains (referred to herein as Type I) that are similar to or smaller than even those inherent to PECVD silicon, which typically

exhibits domains on the scale of 2-10 nm depending on synthesis conditions.^{42,43} Hence, Type I and Type II silicon exhibit clearly distinct domain size, and extremely small domain size (as in Type I) is preferable for long-cycling electrochemical stability.

Slow rate, deep lithiation cycling of the pure silicon materials provides an additional comparison to the Si/C composites synthesized herein; the 1st cycle delithiation profile for all four silicon materials is shown in **Figure S16b**. The corresponding differential capacity (dQ/dV) voltage profiles of the silicon materials are shown in **Figure 6b**, and those for MSCL- and SPL-derived Si/C composites are shown in **Figure 6d**. As the particle size of the pure silicon materials increases, the main delithiation event (de-alloying of $\text{Li}_{15}\text{Si}_4$) both narrows and increases in relative capacity, providing an additional calibration method for determining silicon domain size in the Si/C composites. By comparison to the pure silicon materials, the $\text{Li}_{15}\text{Si}_4$ de-alloying peak of the SPL-derived composite most closely resembles that of the 100 nm pure silicon nanopowder, in contrast to the DTGA analysis above. Thus, we conclude that Type II silicon is likely to be within the range of 50-100 nm in silicon domain size. The $\text{Li}_{15}\text{Si}_4$ de-alloying event of the MSCL-derived composite (containing dominantly Type I silicon) perhaps resembles that of the PECVD silicon, confirming its extremely small Si domain size, significantly smaller than that of Type II silicon-dominant composites.

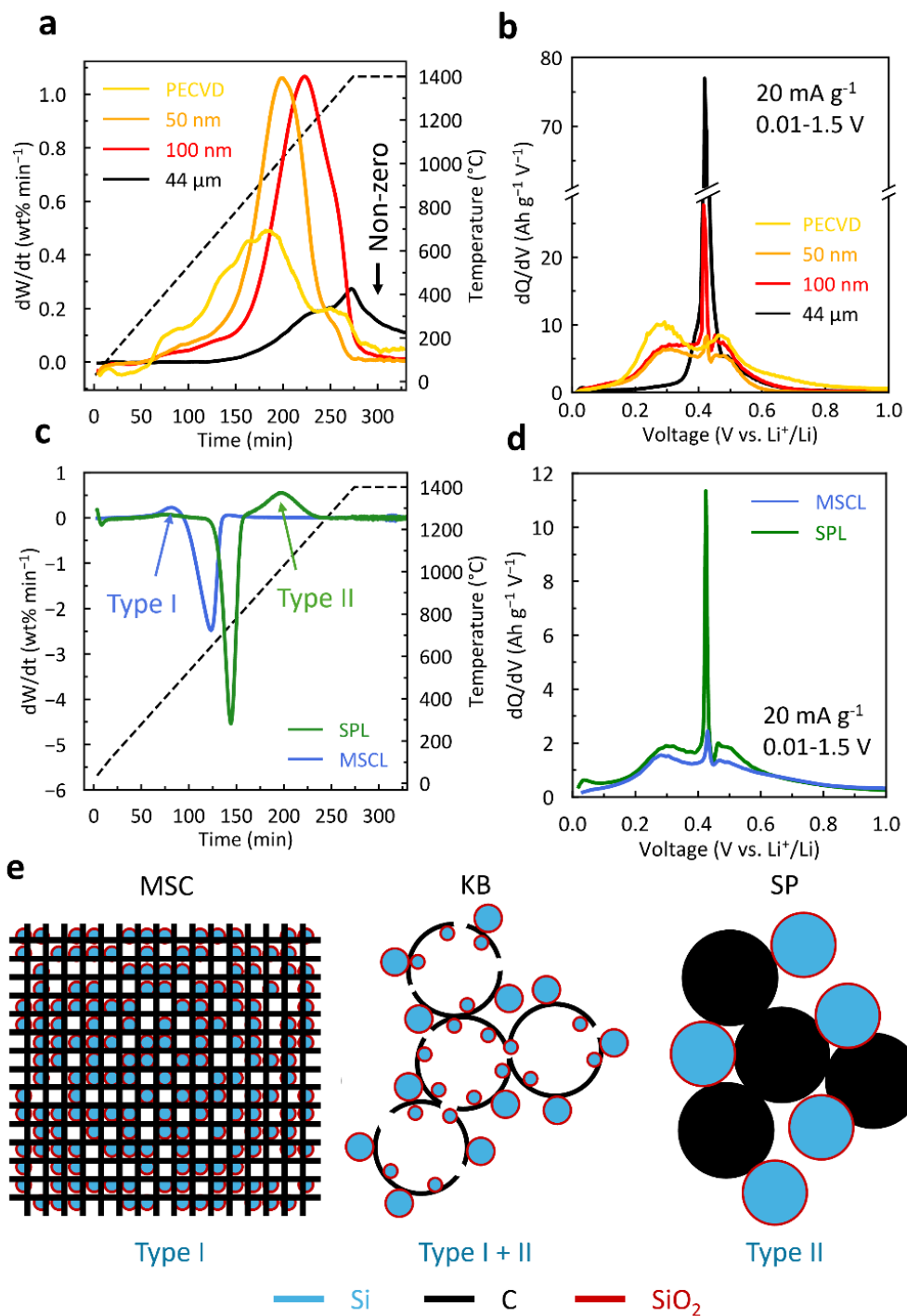


Figure 6. (a) DTGA and (b) dQ/dV profiles for PECVD (yellow), 50 nm (orange), 100 nm (red) and 44 μm (black); (c) DTGA and (d) dQ/dV profiles for MSCL- (blue) and SPL- (green) Si/C composites. (e) proposed morphological compositions for (left) MSC-, (middle) KB-, and (right) SP- Si/C composites comprised of carbon (black), Si (blue), and SiO₂ (dark red).

Taken together, the comparative DTGA and dQ/dV analyses presented in **Figures 6a-6d** indicate that the low silicon oxidation temperature and diminished $\text{Li}_{15}\text{Si}_4$ de-alloying character of Type I silicon are correlated with small silicon domain size. When combined with the materials and electrochemical properties of all of the Si/C composites presented in **Figures 1-5** and **Figure S7**, a summarizing schematic depiction of the role of the carbon scaffold in favoring the distinct silicon domain types (Type I and Type II) is given in **Figure 6e**. The nonporous, small particulate nature of SP and its family of scaffolds favors the formation of large (50-100 nm, Type II) silicon nanoparticles on its outer particle surfaces, as previously reported.²² In contrast, the mesoporous, small particulate nature of KB and its family of scaffolds favors the formation of both small (Type I) and larger (Type II) silicon nanodomains. Finally, the almost exclusively microporous and large particulate MSC family of scaffolds strongly favors the formation of small (Type I) silicon nanodomains, preventing any significant $\text{Li}_{15}\text{Si}_4$ de-alloying. Little or no presence of Type II silicon in the MSCL-derived Si/C composite lend it significantly higher electrochemical stability. Future work should focus on increasing the content of Type I silicon in Si/C composites to achieve both high capacity and long-cycling stability; this work implies that the scaffolds needed for such composites contain a preponderance of micropores.

Conclusions

In this work, we demonstrate that carbon scaffold structural and textural properties play a predictable role in the resulting Si/C composite structure and composition, and hence electrochemical performance (e.g., capacity and cycling stability). A novel DTGA deconvolution method presented herein reveals the presence and permits the quantification of two distinct silicon

domain types across the 18 Si/C composites synthesized. The first, Type I silicon, is favorably formed within the micropores of high surface area carbon scaffolds such as activated carbon MSC-30; it is characterized by low temperature oxidation under flowing air (500-600 °C), little or no $\text{Li}_{15}\text{Si}_4$ de-alloying under slow-rate delithiation, and extremely small domain size (similar to or smaller than PECVD silicon). The second, Type II silicon, is favorably formed on the surfaces of nonporous scaffolds such as Super P carbon black; it is characterized by higher temperature oxidation under flowing air (~1000 °C), significant $\text{Li}_{15}\text{Si}_4$ de-alloying under slow-rate delithiation, and larger “bulk-like” silicon nanodomains (similar to those found in 50-100 nm silicon nanopowders).

Interconversion between the likely formation of Type I and Type II silicon is possible for a given carbon scaffold through heat-treatment. In general, Type I silicon exhibits higher electrochemical cycling stability (e.g., 81% lithiation capacity retention after 1000 cycles for the MSCL-derived Si/C composite) than Type II silicon (e.g., 67% lithiation capacity retention after 1000 cycles for the SPL-derived Si/C composite). This serves as guidance for future work to select appropriate carbon scaffolds for both high capacity and long-lasting Si/C composite anode materials for LIB applications.

Acknowledgements

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Supporting Information

Table S1. BET surface area, oxygen content, and hydrogen content of MSC-, KB-, and SP-derived carbon scaffolds. Carbon comprises the remainder of the composition.

HT Temp (°C)	BET Surface Area (m ² g ⁻¹)			Oxygen Content (wt%)			Hydrogen Content (wt%)		
	MSC	KB	SP	MSC	KB	SP	MSC	KB	SP
(none)	3244	1405	62	4.96	2.03	0.59	0.11	0.21	0.15
1200	2503	1231	60*	2.32	1.66	-	-	-	-
1400	2340	1110	59*	1.78	1.34	-	-	-	-
1600	2157	1035	57*	1.94	1.09	-	-	-	-
1800	1745	861	56*	1.76	0.57	-	-	-	-
2000	185	413	54	0.95	0.66	0.32	-	-	-

* The BET surface areas of the intermediate HT temperature SP scaffolds were not individually measured but rather estimated by linear interpolation.

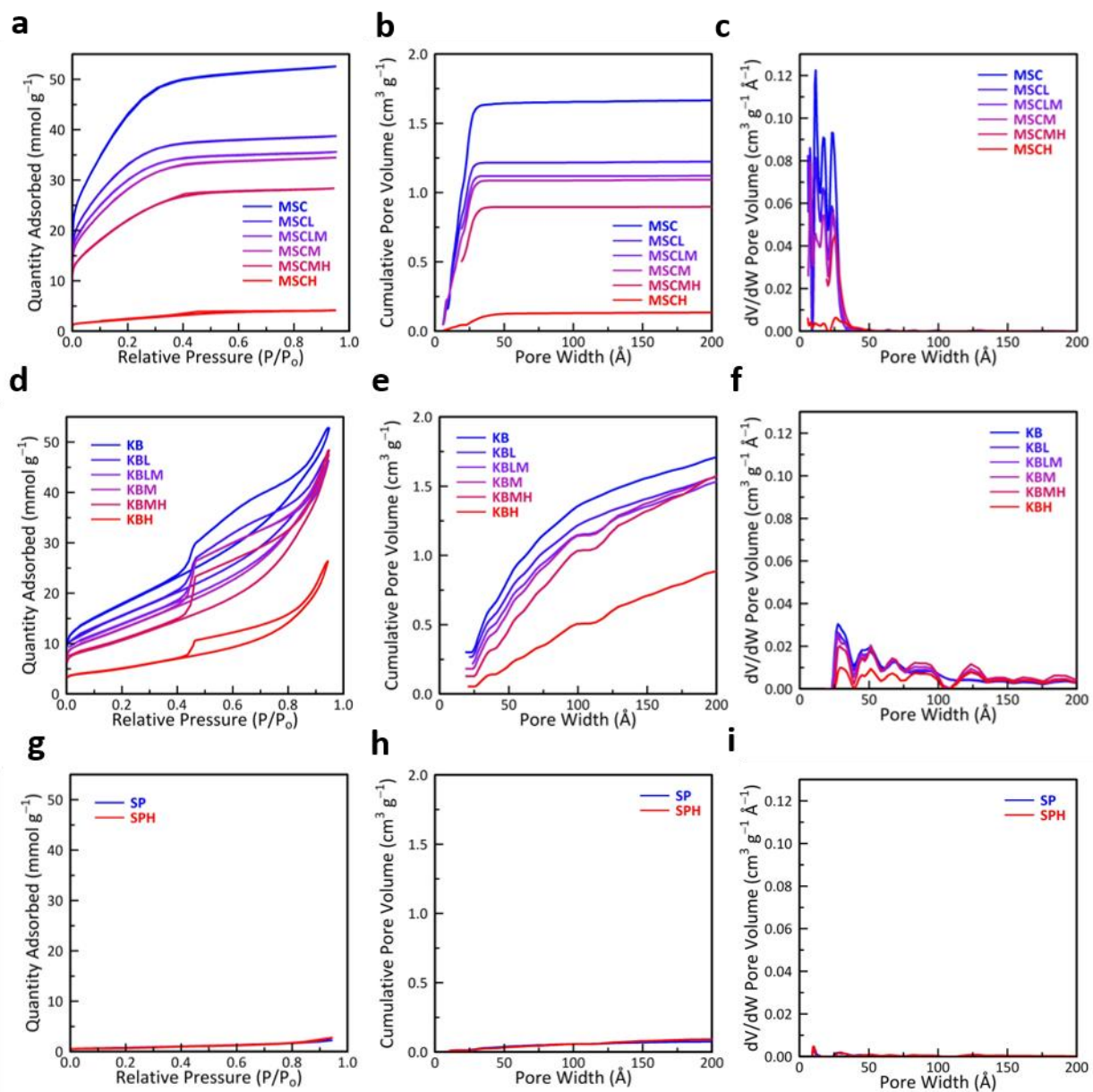


Figure S1. (a, d, g) N₂ adsorption/desorption isotherms at 77 K, and the corresponding (b, e, h) cumulative pore volume and (c, f, i) pore size distributions for MSC- (a-c), SP- (d-f), and KB- (g-i) derived carbon scaffolds (prior to silane deposition).

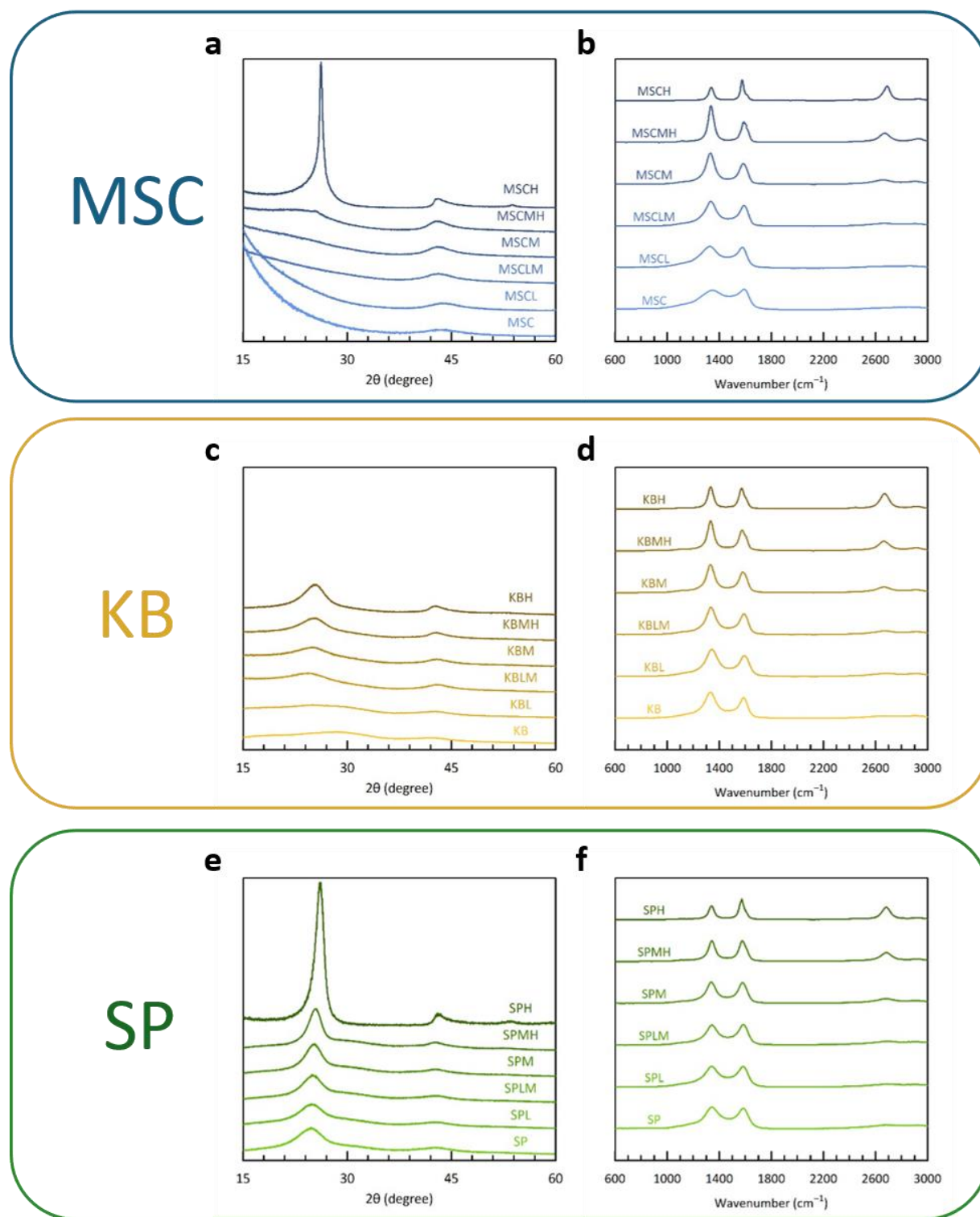


Figure S2. (a, c, e) XRD patterns and (b, d, f) Raman spectra of (a, b) MSC- (blue), (c, d) KB- (gold), and (e, f) SP- (green) derived carbon scaffolds (prior to silane deposition).

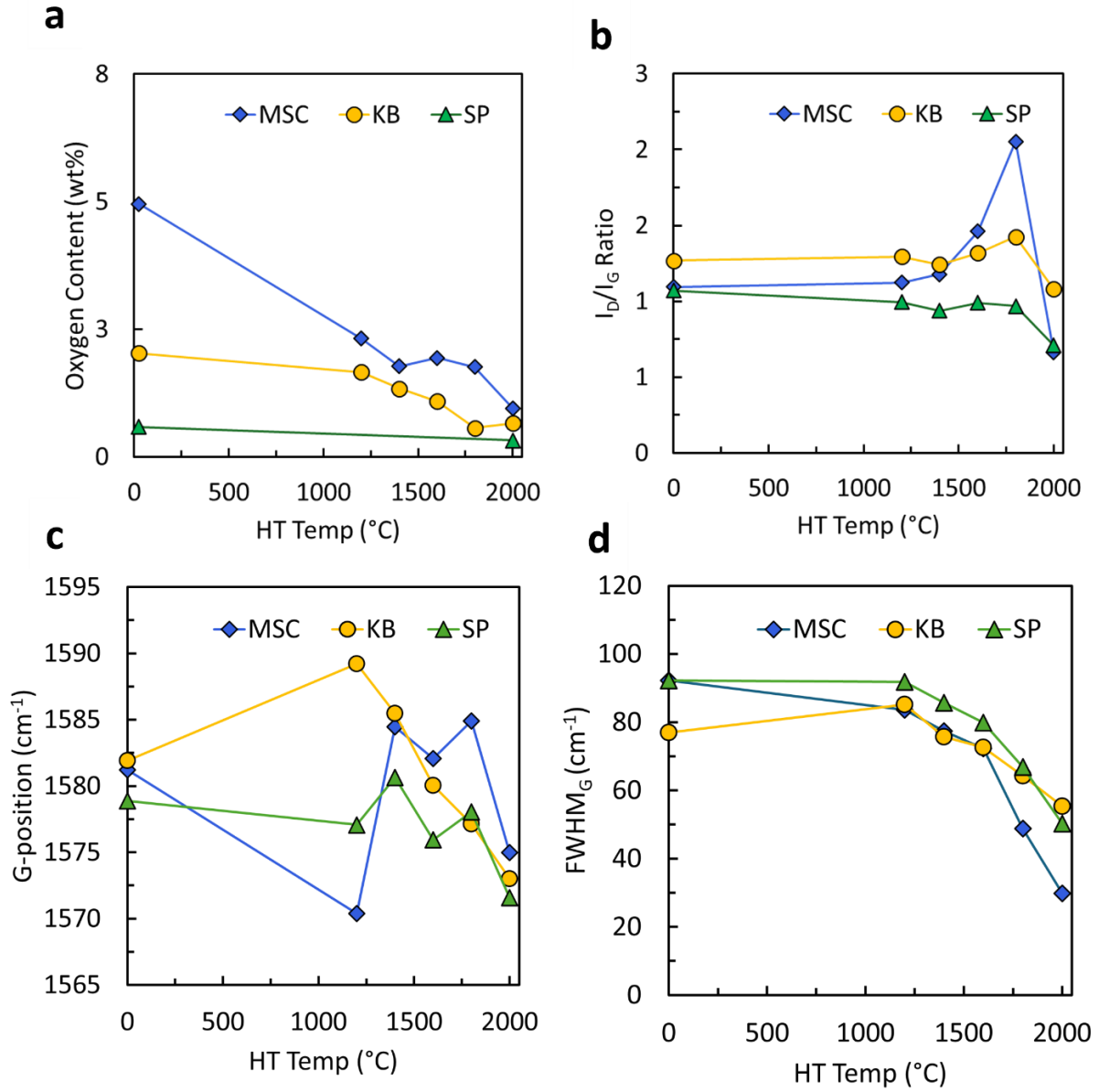


Figure S3. (a) Oxygen content (from combustion analysis), (b) Raman I_D/I_G ratio, (c) Raman G-peak position, and (d) G peak FWHM of MSC- (blue), KB- (gold), and SP- (green) derived carbon scaffolds as a function of HT temperature (prior to silane deposition).

Table S2. Raman analysis of MSC-, KB-, and SP-derived carbon scaffolds.

Scaffold	Pos D (cm⁻¹)	FWHM D (cm⁻¹)	Pos G (cm⁻¹)	FWHM G (cm⁻¹)	I_D/I_G
MSC	1349.4	237.0	1581.2	92.2	1.09
MSCL	1326.1	196.1	1570.4	83.6	1.12
MSCLM	1334.0	123.4	1584.5	77.4	1.18
MSCM	1330.3	84.7	1582.1	72.2	1.46
MSCMH	1335.7	52.0	1584.9	48.8	2.05
MSCH	1337.3	44.8	1575.0	29.8	0.66
KB	1331.0	122.9	1581.9	76.9	1.27
KBL	1342.0	124.3	1589.2	85.2	1.30
KBLM	1333.8	109.1	1587.0	75.7	1.24
KBM	1332.0	79.6	1580.0	72.6	1.32
KBMH	1330.6	61.9	1574.3	64.3	1.43
KBH	1332.6	51.3	1573.0	55.4	1.08
SP	1346.2	156.5	1578.9	92.2	1.07
SPL	1342.2	156.7	1577.1	91.8	0.99
SPLM	1343.6	144.2	1580.6	85.7	0.94
SPM	1338.0	100.6	1575.9	79.8	0.99
SPMH	1340.3	70.3	1578.0	66.9	0.97
SPH	1339.1	53.2	1571.6	50.3	0.71

Note: all Raman metrics were calculated using a fitting procedure as detailed elsewhere.³³

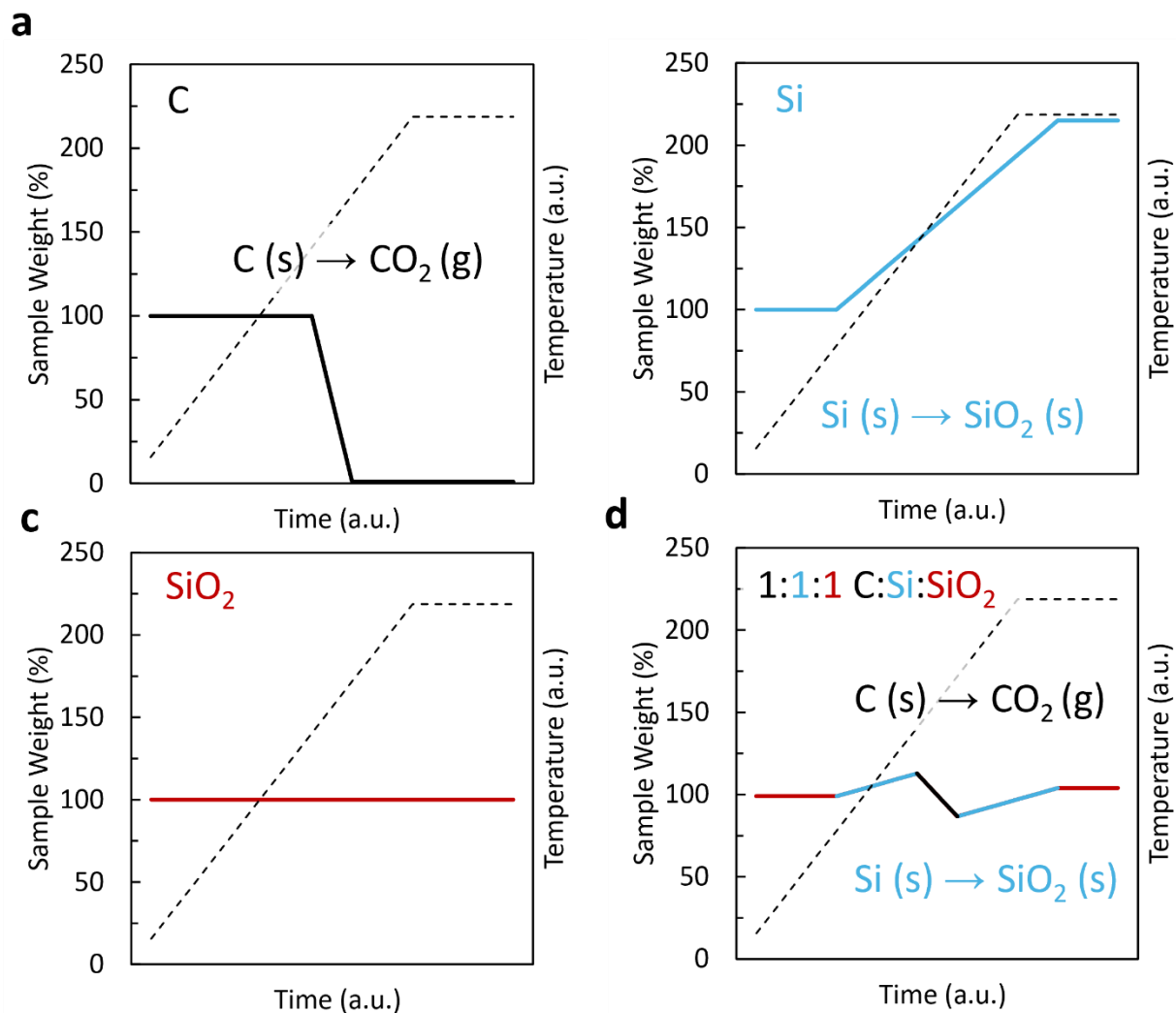


Figure S4. Schematic TGA profiles of (a) pure carbon, (b) pure silicon, (c) pure SiO₂, and (d) a 1:1:1 mixture of carbon, silicon, and SiO₂.

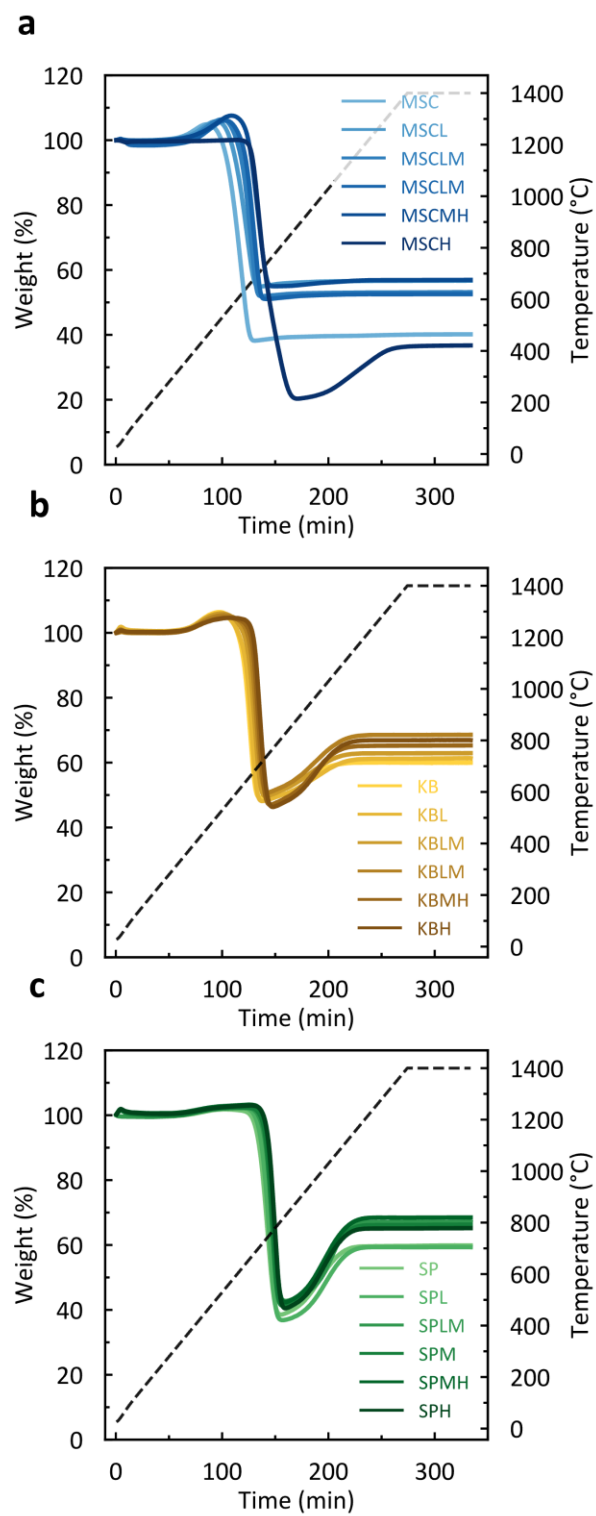


Figure S5. TGA profiles of (a) MSC-, (b) KB-, and (c) SP-derived Si/C composites.

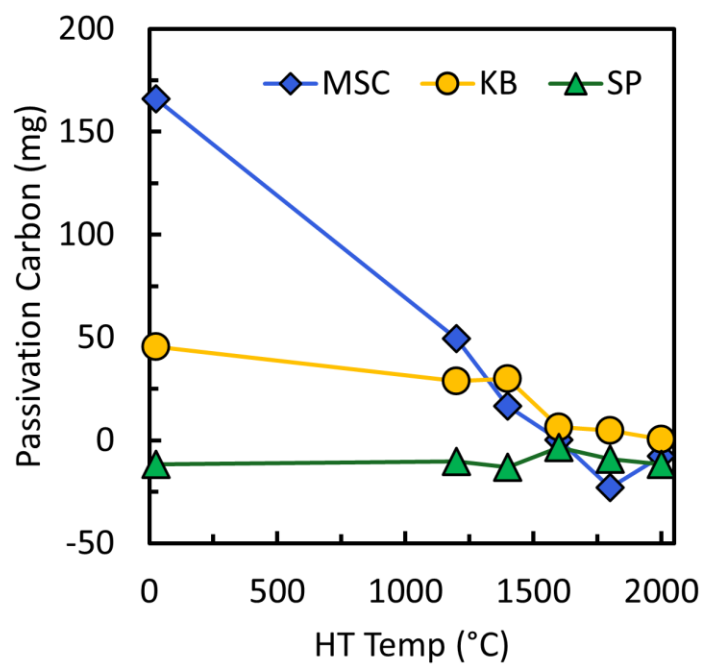


Figure S6. Estimated passivation carbon content of MSC- (blue), KB- (gold), and SP- (green) derived Si/C composites. Passivation carbon was estimated by subtracting the original scaffold mass before silane deposition (200 mg) from the total carbon mass of the Si/C composite (determined by DTGA deconvolution). Negative values are attributed to analysis error (e.g., the presence of other, neglected carbon-bearing phases such as silicon carbide).

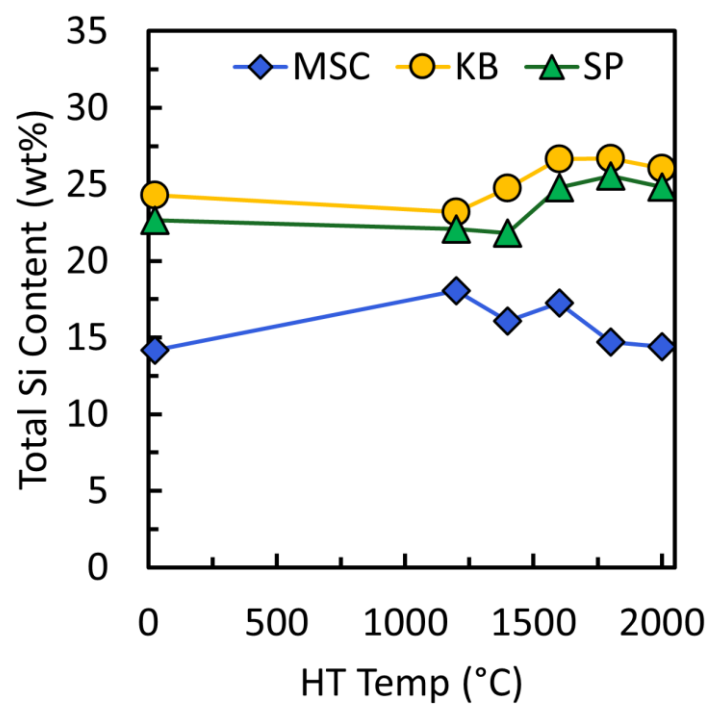


Figure S7. Total silicon content (determined by DTGA deconvolution) of MSC- (blue), KB- (gold), and SP- (green) derived Si/C composites.

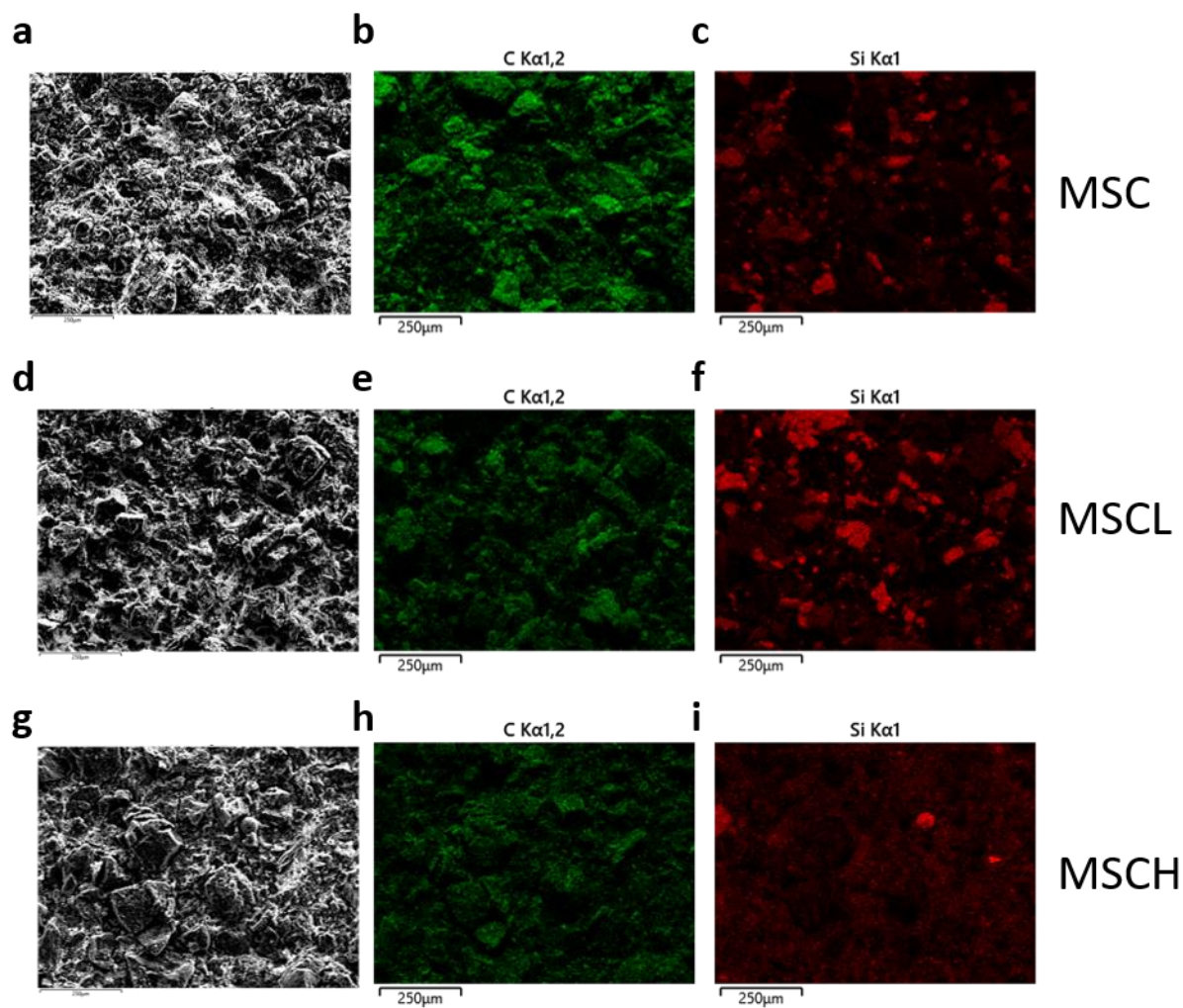


Figure S8. EDX mapping of MSC-, MSCL-, and MSCH-derived Si/C composites: C (green) and Si (red).

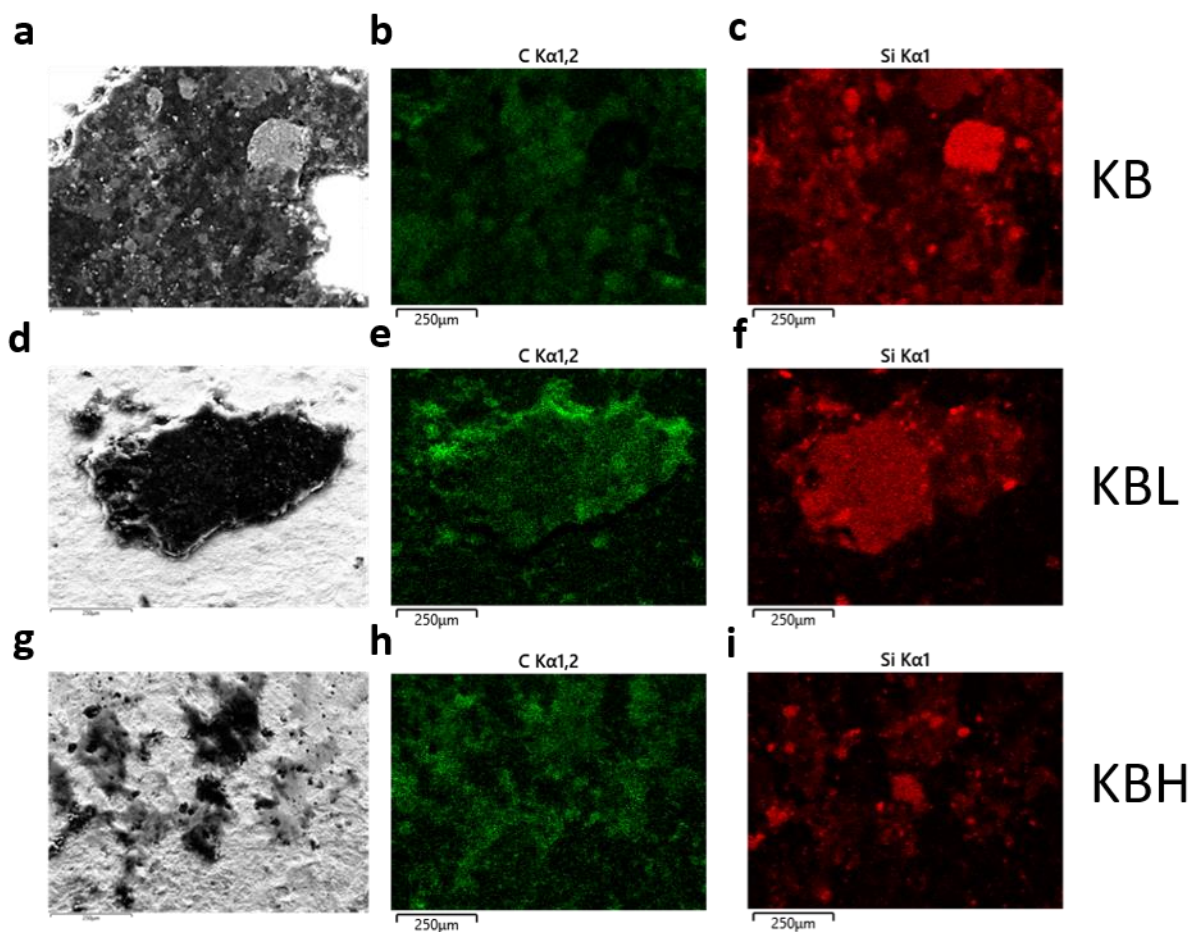


Figure S9. EDX mapping of KB-, KBL-, and KBH-derived Si/C composites: C (green) and Si (red).

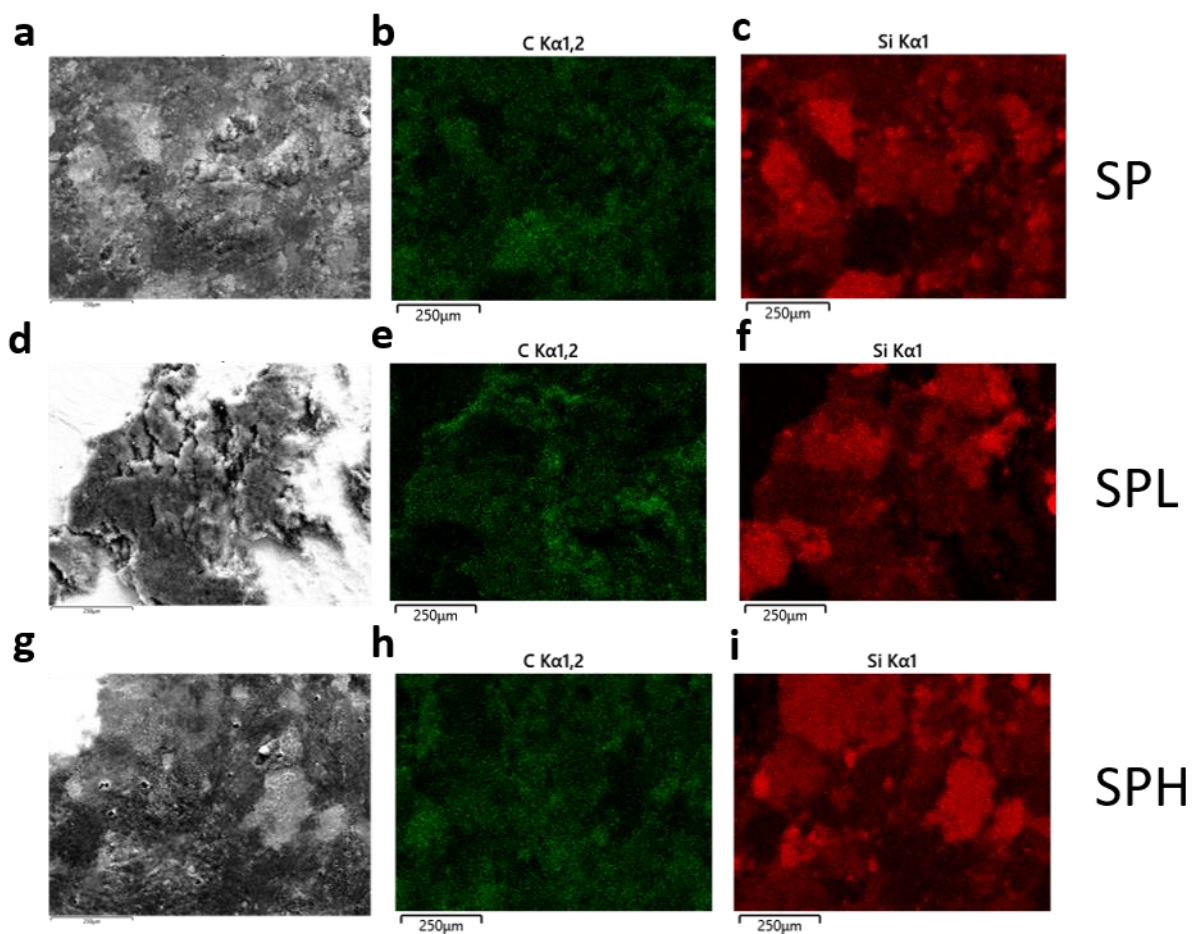


Figure S10. EDX mapping of SP-, SPL-, and SPH-derived Si/C composites: C (green) and Si (red).

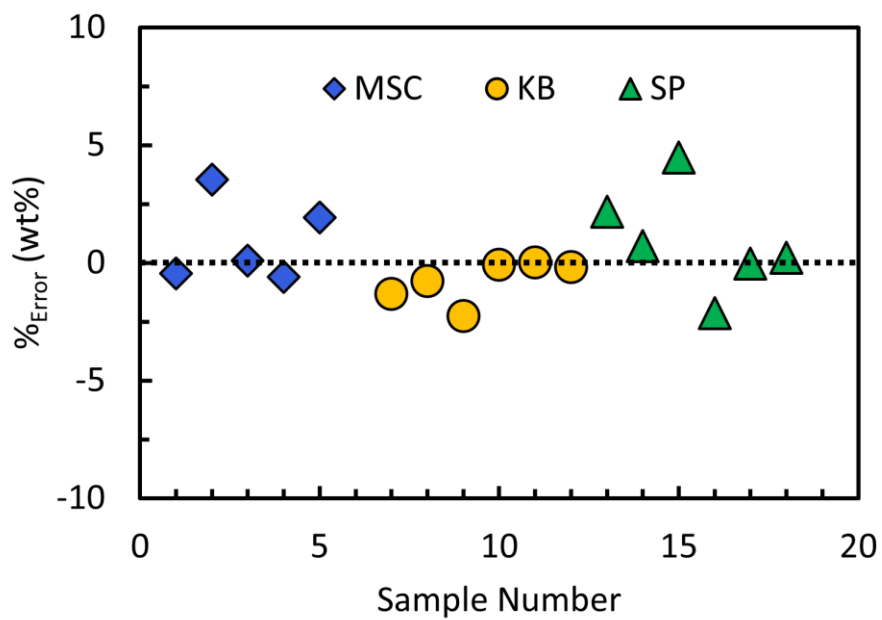


Figure S11. Error analysis of the composition of Si/C composites as determined using the DTGA deconvolution method.

Error is calculated by taking the difference between the sum of the compositional elements (C, Si, and SiO₂) from the theoretical value (100%), revealing an average error of only 1.2 wt% and a standard deviation of 1.3 wt% across all samples and phase components.

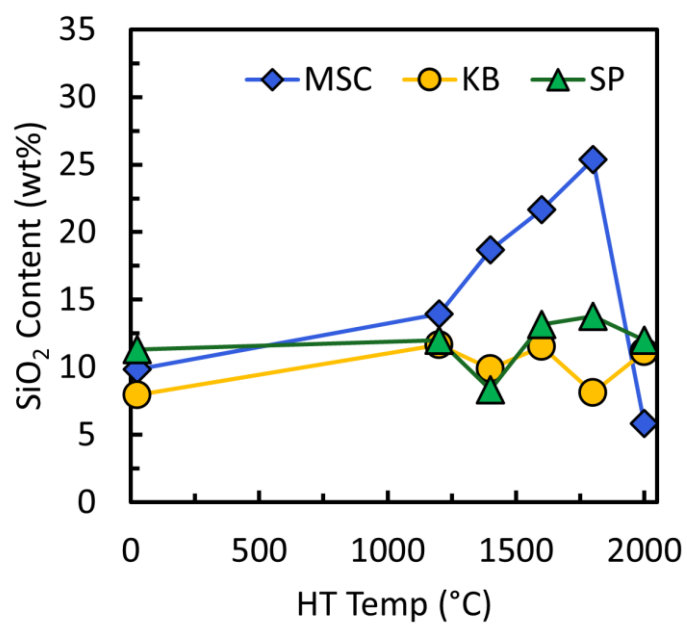


Figure S12. SiO₂ content (determined by DTGA deconvolution) of MSC- (blue), KB- (gold), and SP- (green) derived Si/C composites.

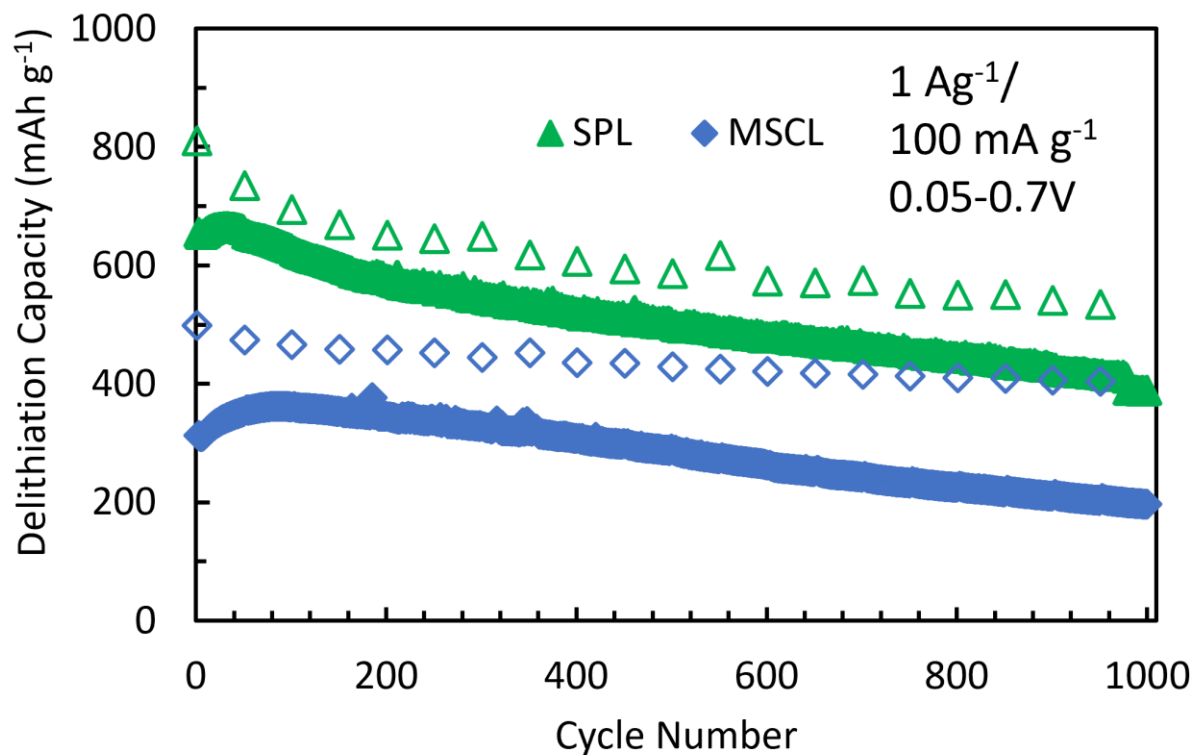


Figure S13. Delithiation capacity of the SPL- and MSCL-derived Si/C composites over 1000 cycles between 0.05-0.7 V vs. Li⁺/Li: standard cycles at 1 A g⁻¹ (closed symbols) and RPT cycles at 100 mA g⁻¹ (open symbols).

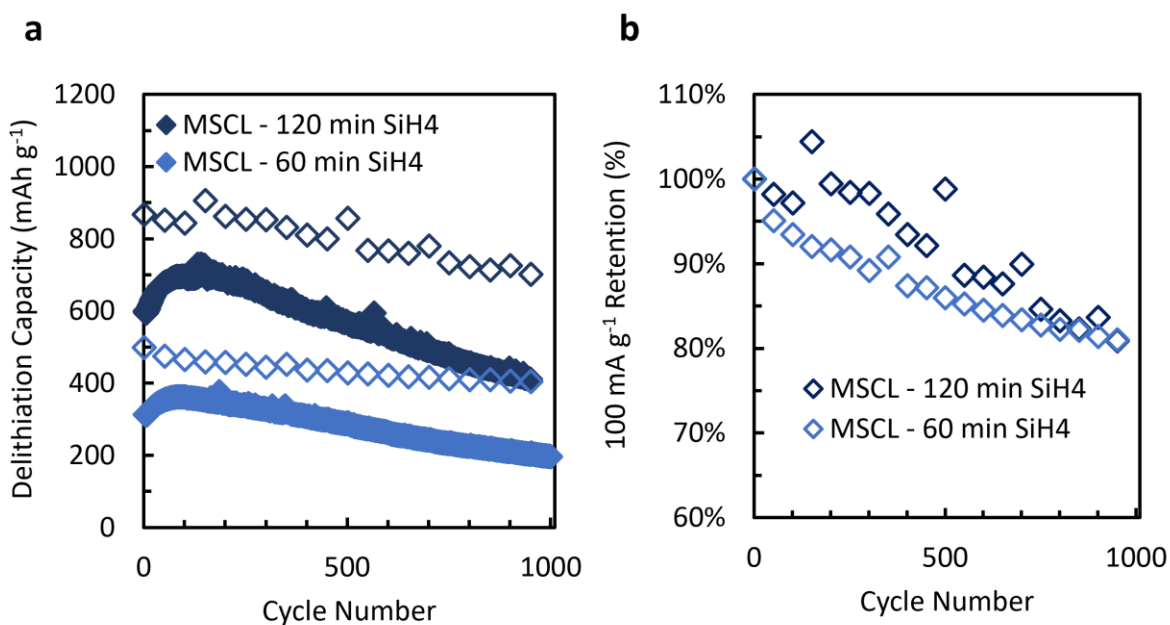


Figure S14. (a) Delithiation capacity of two MSCL-derived Si/C composites over 1000 cycles between 0.05-0.7 V vs. Li⁺/Li: standard cycles at 1 A g⁻¹ (closed symbols) and RPT cycles at 100 mA g⁻¹ (open symbols). (b) Capacity retention of the same two MSCL-derived Si/C composites over 1000 cycles between 0.05-0.7 V vs. Li⁺/Li using the RPT cycles at 100 mA g⁻¹. The standard MSCL-derived composite was synthesized under silane CVD for 60 min (light blue, 18 wt% Si) and a non-standard composite was synthesized under identical conditions except under silane CVD for 120 min (dark blue, 27 wt% Si).

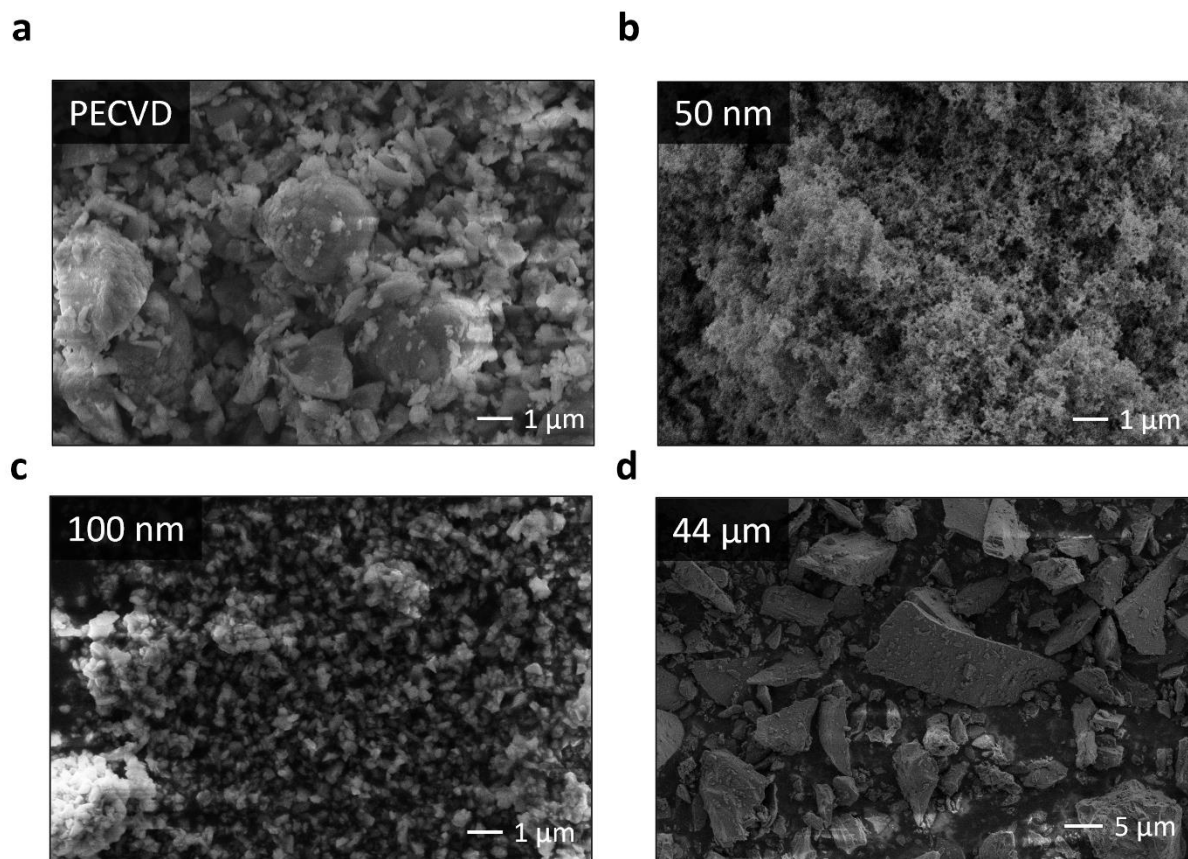


Figure S15. SEM micrographs of (a) PECVD, (b) 50 nm, (c) 100 nm, and (d) -325-mesh (44 μm) pure silicon materials. Note: the large structures in the PECVD silicon are agglomerated secondary particles. The texture of the primary PECVD particles is finer than the resolution of the instrument.

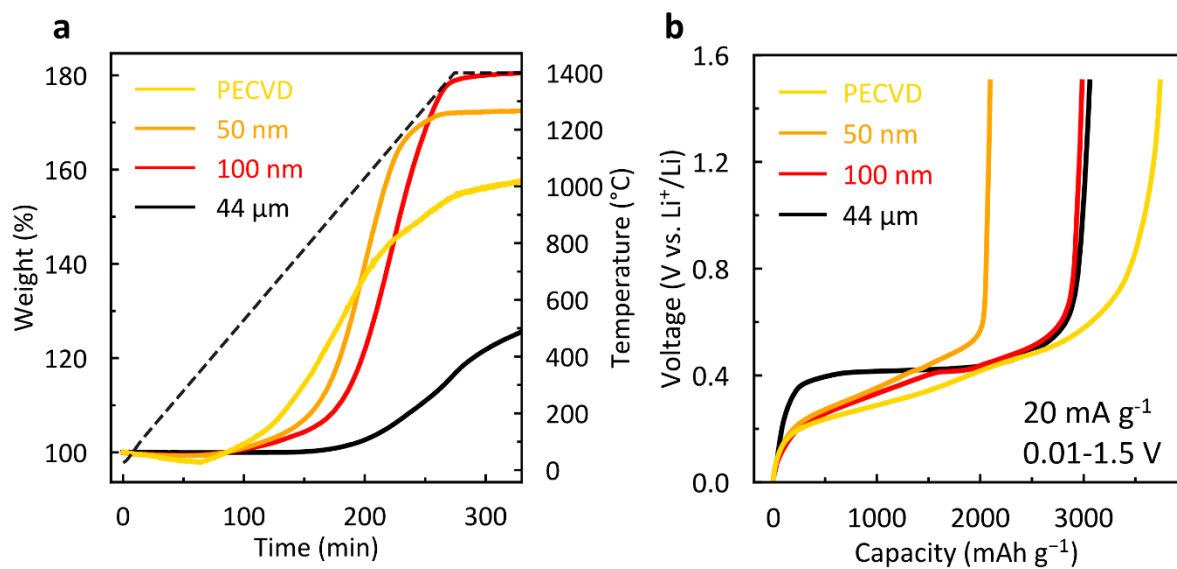


Figure S16. (a) TGA and (b) slow-rate delithiation voltage profiles of PECVD (yellow), 50 nm (orange), 100 nm (red), and 44 μm (black) pure silicon materials.

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CHAPTER SEVEN

CONCLUSIONS

Summary of Results

This dissertation presents mechanistic insights on the electrochemical lithiation of hexa-peri-hexabenzocoronene (HBC), silicon oxide (SiO_x), and silicon carbon (Si/C) composite anodes with the goal of advancing the global scientific community's understanding of both high-energy and high-power applications for next-generation LIB materials. Collectively, we sought to answer three questions across carbon and silicon LIB anode systems: where are lithium atoms residing within the host lattice, how are those sites accessed, and what does the (de)lithiation reaction leave behind? To this end, *operando* and *in-situ* techniques were employed alongside a suite of standard characterization methods. Our progress toward the objectives outlined in **Chapter 1** is detailed below.

Progress Towards Thesis ObjectivesObjective 1:

Elucidation of Lithiation Mechanism and Pseudocapacitive Rate Capability in Crystalline

Molecular Hydrocarbons

Through the synthesis and characterization of four systematic HBC analogs in **Chapter 4**, we demonstrated a clear structure-function relationship between the HBC herringbone crystal structure and rapid lithiation kinetics, establishing guidelines for realizing an entire new class of intercalative pseudocapacitive materials. *Operando* diffraction experiments unveiled that there are two lithiation mechanisms in the herringbone structure of HBC: edge site storage (at molecular

intersections) and π - π storage (in the stacking direction of the HBC molecules). A complementary set of electrochemical techniques confirmed that edge-site storage was in fact pseudocapacitive in the herringbone structure (r-HBC), but diffusion-limited in the hexagonal columnar structure (h-HBC), indicating that the specific structure of the herringbone lattice led to pseudocapacitance in these materials.

Objective 2:

Characterization of Hidden Electrochemical Degradation and Chemical Markers in SiO_x Cells

In **Chapter 5**, characterization of an SiO_x/graphite (Gr) composite electrode coupled with full cell two- and three-electrode studies revealed minimal capacity fade in the measured SiO_x/Gr||LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) system. The stability of the cell was partially attributed to the relatively low volumetric expansion of the SiO_x/Gr electrode at full state of charge (49%), which helped mitigate several degradation mechanisms that generally result in loss of active material for silicon anodes, such as particle fracture and delamination. The small degree of cell capacity fade was coupled with an increase in capacity at the anode, as measured by harvested electrode studies. Electrolyte reduction at the SiO_x anode and resultant loss of lithium inventory (LLI) accounted for most of the capacity fade in the cell. Some loss of active material (LAM) was detected at the cathode - likely caused by LLI-induced electrode potential shifts, whereupon the cathode potential is pushed up to unsustainable degrees of delithiation. The modest capacity fade was contrasted by large amounts of fluorine-rich electrolyte reduction products visualized at the anode, which prompted the study of a reservoir effect in the prelithiated SiO_x/Gr electrode. This led to the discovery of a capacity fade masking mechanism caused by release of the SiO_x lithium reservoir into the cell due to electrode potential shifts during cycling.

Objective 3:Determination of Carbon Scaffold Structure Effects on Silicon Domain Formation in Si/C

Differential thermogravimetric analysis (DTGA) was applied to ascertain the structural composition and quantity of silicon in several families of synthesized Si/C composites in **Chapter 6**. It was discovered that the temperature of silicon oxidation could be correlated to its length-scale by way of a calibration study on pure silicon. In doing so, relative amounts of Type I (nanoscale) and Type II (bulk) silicon could be deconvoluted for all 18 Si/C composites presented. Type I silicon was directly correlated with surface area of the scaffold, which decreased over the course of scaffold graphitization. It was found that mesoporous scaffolds supported a combination of Type I and Type II silicon growth, whereas microporous and non-porous scaffolds only supported Type I or Type II silicon, respectively. The $\text{Li}_{15}\text{Si}_4$ de-alloying plateau in the silicon voltage profile was used as a reporter for the presence of bulk silicon and was shown to increase in relative contribution in a colinear fashion with Type II silicon, which correlated to particle size in the pure silicon calibration study. The electrochemical stability of representative Si/C composites with predominantly Type I or Type II silicon was compared, and Type I silicon was shown to be more electrochemically stable than Type II silicon.

Future Work

Many research questions arose during this work that could not be explored within this dissertation, mainly owing to a lack of time. Each of these questions yields numerous suggested experiments that could be used to answer them, and the answers to these questions could be impactful to future progress in LIB anode research.

HBC Analogs For Structure-Derived Pseudocapacitance

The structural origins of pseudocapacitance inherent to the herringbone structure of HBC were investigated and reported in detail in **Chapter 4**. It is possible that such sites were also previously lithiated when investigating the lithiation of coronene,¹ though no such evidence was collected. In comparison, the potential of intercalation differs by several hundred mV between coronene and HBC, and neat, crystalline coronene was not reversibly lithiable (preventing diffraction studies). Thus, the question of when and how these pseudocapacitive storage sites are lithiable across the whole family of herringbone PAH structures remains unanswered. This question is further complicated by the thermal treatment required for their polymerization, which may occur at higher temperature than the decomposition of the crystal structure itself (for smaller PAHs) due to the weaker magnitude of van der Waals forces between the molecules. However, the applications for ultrafast rate capability LIB anode materials with tunable potentials are numerous, and should be explored thoroughly.

Investigating Anomalous Capacity Gain in SiO_x Anode Materials Over Aging

In **Chapter 5**, it was shown that the SiO_x/Gr anode increased in capacity over the course of 500 cycles as measured in a harvested coin cell. This was partially attributed to a decrease in impedance. However, one of the lithiation features in the thermodynamic (C/100) voltage profile of the SiO_x/Gr anode shifted to higher potentials, indicating the facilitation of small lithium silicide cluster formation, which cannot be kinetic in nature.^{2,3} Preliminary differential voltage analysis (DVA) also shows that the capacity increase occurs later in life, only beginning after cycle 200 for this aging protocol. Some of the capacity increase can be attributed to enhanced connectivity in the electrode due to formation of ionically conductive buffering phases of Li₂O and lithium silicate.

However, those mechanisms cannot describe the observed change in the thermodynamics of lithiation, leaving it an open question.

Si Composition Determination and Structure-Function Relationships for Si-rich Si/C Composites

All Si/C composites explored in **Chapter 6** contained a modest silicon content of ~15-25 wt%. However, industrially relevant Si/C materials would likely be closer to 50-60 wt% silicon. Several research questions remain surrounding what types of silicon would form in this more saturated regime, and what effect those silicon types would have on the electrochemical cycling stability. Preliminary studies have shown that the Type I sites of microporous carbon scaffolds become saturated and cannot accept more silicon, whereas mesoporous or non-porous scaffolds can accommodate a seemingly unlimited amount of silicon. Additionally, the silicon deposition mechanism can be further interrogated by studying scaffolds capable of both Type I and Type II silicon deposition to see if one type of silicon domain is deposited preferentially, or if they form simultaneously. Finally, other types of scaffolds could be investigated to try and measure the effect of pore size on resultant silicon domain size by silane deposition. For example, would a nanoporous scaffold be capable of silicon deposition into such small pores, or would deposition be limited by mass diffusion? What is the maximum pore size before Type I silicon is no longer formed, and the intraporous silicon is effectively a bulk particle?

Broader Impacts

The work presented in this dissertation, in combination with the entire body of existing literature on this topic, implies that there is not a single battery chemistry that can solve all the challenges presented in **Chapter 2**. The strengths and weaknesses of HBC, Si/C, and SiO_x are

compared to benchmark graphite and silicon nanoparticle materials in **Figure 1**, representing the extremes of stability and energy density, respectively. The low energy density of graphite stems from its high chemical stability, limiting the density of lithium ions that the structure can accommodate. That same chemical stability makes graphite an extremely reversible anode material for Li^+ ion insertion. That electrochemical stability and natural abundance-driven cost-efficiency have made graphite into the default anode material for most LIBs in operation today. On the other hand, silicon nanoparticles have extremely high energy density, as lithium can insert itself in between Si-Si bonds at relevant chemical potentials for operation – resulting in extremely high theoretical capacities of up to $\sim 3600 \text{ mAh g}^{-1}$. The main drawback of silicon as an LIB anode is that the large stoichiometry of inserted lithium swells the Li_xSi crystal structure, resulting in unsustainable degrees of expansion and contraction upon cycling, which are deleterious for electrochemical stability.

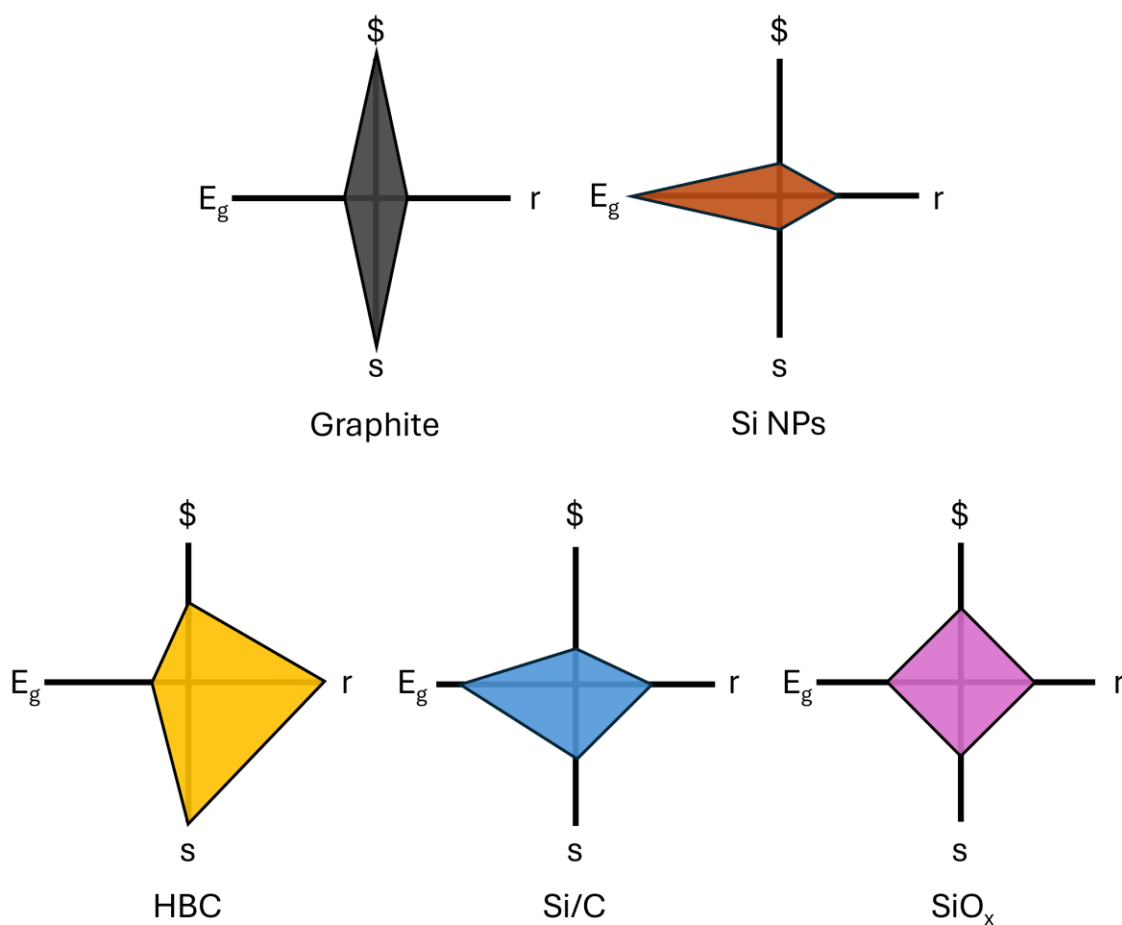


Figure 1. Spider plots comparing cost-efficiency (\$), rate capability (r), electrochemical stability (s), and gravimetric energy density (E_g) for benchmark graphite (grey) and silicon nanoparticles (Si NPs, dark orange) nanoparticle LIB anodes; and the three material classes explored in this work: HBC (yellow), Si/C (blue), and SiO_x (purple).

The properties of HBC, Si/C, and SiO_x are all contextualized by these two model materials.

HBC has a similar energy density to graphite due to a similar topotactic mechanism of lithium intercalation. While the cost efficiency is lower due to the requirement of chemical synthesis or additional processing, the rate capability is significantly faster due to rapid lithium diffusion

through the herringbone crystal structure. Si/C and SiO_x both have greater energy densities than graphite, but lower than silicon due to the presence of lower capacity phases within their respective structures. Both Si/C and SiO_x are more stable than pure silicon due to the presence of buffering phases (carbon for Si/C and Li₂O/Li_xSi_yO_z for SiO_x), which ameliorate expansion issues. Silane is expensive, causing Si/C to be less cost effective than SiO_x; however, SiO_x has a lower initial coulombic efficiency, decreasing the energy density of the system unless prelithiated.

The strengths and weaknesses of each material suit them to different applications. While HBC may be appropriate as a high-power material for AI datacenters, its low energy density makes it less appropriate for electric vehicle applications. Conversely, the high energy density of Si/C could be useful for mobile electronics but could be outcompeted by the cost-efficacy of SiO_x for grid storage applications. Hopefully, the work outlined in this document sheds light on the underlying chemical mechanisms that cause these property tradeoffs in modern lithium-ion battery anodes and can assist in the discovery of next-generation materials for future energy storage challenges.

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APPENDIX

LITHIUM-ION BATTERIES WITH LITHIUM MANGANESE IRON PHOSPHATE
CATHODES AND LITHIUM TITANATE ANODES: LINKING ELECTRODE DYNAMICS
TO CELL PERFORMANCE



Lithium-Ion Batteries with Lithium Manganese Iron Phosphate Cathodes and Lithium Titanate Anodes: Linking Electrode Dynamics to Cell Performance

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This study examines the electrochemical performance, impedance behavior, and aging mechanisms of lithium-ion cells pairing lithium manganese iron phosphate ($\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$, LMFP64) cathodes with lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) anodes. LMFP64 half-cells display distinct Fe and Mn redox plateaus at ~ 3.5 and ~ 4.1 V, respectively, and deliver excellent rate capability. Three-electrode measurements show that LMFP64 dominates cell impedance, which changes sharply across the Fe–Mn redox transition and decreases with increasing temperature (30°C – 50°C). Voltage hysteresis arises mainly from the cathode, with higher C-rates shortening redox plateaus and broadening the transition region. Elevated temperature lowers impedance, especially near the Mn-redox and transition regions, but accelerates capacity fade. Post-cycling analyses of electrodes confirm structural stability of LMFP64 and indicate loss of lithium inventory (LLI) as the source of capacity fade. This LLI causes potential slippage between the LMFP64 and LTO electrodes, which decreases the Fe-redox plateau width. Long-term cycling highlights the critical role of electrode overhang: cathode overhang mitigates capacity fade by buffering lithium loss, whereas anode overhang cells experience faster capacity decline due to uncompensated lithium depletion. These results clarify LMFP64/LTO battery impedance evolution, thermal effects, and degradation pathways and provide insights for their applications in electric vehicles.

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Supplementary material for this article is available [online](#)

Lithium-ion batteries (LIBs) containing lithium manganese iron phosphate (LMFP) cathodes have higher energy densities than those containing lithium iron phosphate (LFP) electrodes, making them more attractive for electric vehicle applications.^{1–4} These cathodes do not contain nickel and cobalt, both of which are supply-constrained and expensive. LMFP has an olivine-type crystal structure similar to that of LFP, with a general formula of LiMePO_4 ($\text{Me} = \text{Fe, Mn}$). The structure comprises PO_4 tetrahedra that provide structural stability, iron and manganese ions that serve as active redox centers, and lithium ion channels that allow for the reversible insertion and extraction of Li^+ ions. The higher content of Mn in LMFP increases its average working voltage relative to LFP because of the higher redox potential of $\text{Mn}^{3+}/\text{Mn}^{2+}$ (~ 4.1 V vs Li/Li^+) compared to $\text{Fe}^{3+}/\text{Fe}^{2+}$ (~ 3.4 V vs Li/Li^+).^{5,6}

However, despite advantages such as better safety and long cycle life, widespread adoption of LMFP materials has been limited by their high resistivity, necessitating the use of smaller particles and carbon coatings to enhance electronic conductivity.^{7,8} The smaller particles reduce packing density of active materials in the electrode, and the need for precise coating strategies increase manufacturing costs. Most research articles on LMFP focus on reducing the material resistance through strategies that include changing the Fe/Mn ratio, utilizing various doping elements, and with approaches such as particle nanostructuring.^{9–11} Few reports exist on the changes in LMFP resistivity during lithium extraction and insertion.¹² Also, to the best of our knowledge, reports of LMFP electrode impedance at higher temperatures and during long-term aging in LIB cells, do not exist in the research literature.

To address this knowledge gap we investigated cells containing $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ (LMFP64) cathodes and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anodes: the latter has excellent structural stability and less electrolyte reduction because of its higher electrode potential (1.55 V vs Li).^{13,14}

Impedance measurements at different temperatures were obtained from three-electrode cells with a microprobe reference electrode, while long-term cycling data came from two-electrode 2032-type coin cells. After test completion, electrodes harvested from the cells were examined using electrochemical methods, X-ray diffraction (XRD), scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and Inductively Coupled Plasma / Mass Spectroscopy (ICP/MS). Some of the data are contained in the Supporting Information (SI); these have the designator S (such as Fig. S1) when referred to in this text.

The results demonstrate that the impedance of the LMFP64 electrode is strongly dependent on electrode potential, exhibiting sharp changes during the Fe-to-Mn redox transition in both charge and discharge. These trends are consistent across 30, 40, and 50°C , with lower impedance values observed at higher temperatures. Capacity fade is primarily attributed to lithium loss at the LTO electrode, while impedance growth originates from the LMFP64 cathode. The resulting loss of lithium inventory (LLI) leads to potential slippage between the LMFP64 and LTO electrodes and a contraction of the Fe-redox plateau. Furthermore, electrode configuration significantly influences capacity retention: cells with a cathode (LMFP) overhang exhibit lower capacity fade because Li^+ ions from the overhang compensate for the LLI, whereas cells with an anode (LTO) overhang show higher capacity fade due to additional Li^+ losses to the overhang region. These results highlight the coupled electrochemical and geometric factors governing impedance evolution and capacity retention in LMFP/LTO lithium-ion cells.

Experimental

Materials and electrodes.—The LMFP64 and LTO electrodes were fabricated at Argonne's Cell Analysis Modeling and Prototyping (CAMP) facility. The LMFP64 powder used to fabricate the electrode was obtained from a commercial source; product information provided by the supplier (Table S1) indicates a

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Table I. Composition and constitution of the LMFP64 and LTO electrodes.

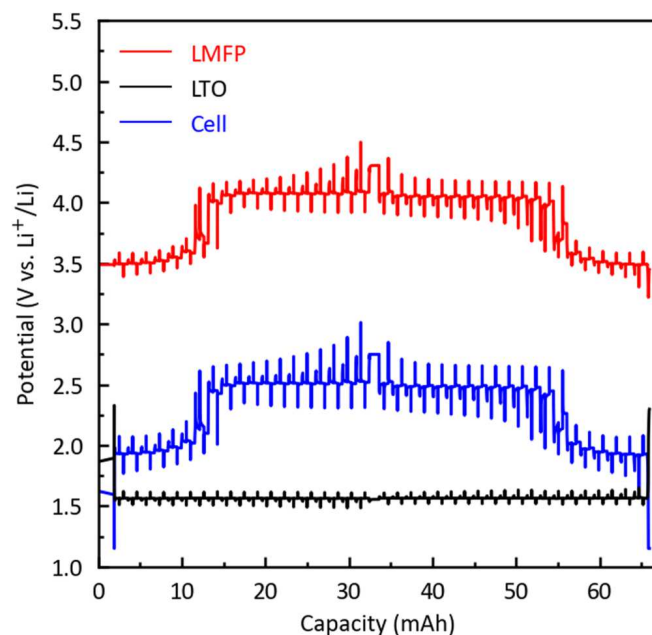
Electrode composition	LiMn _{0.6} Fe _{0.4} PO ₄	Li ₄ Ti ₅ O ₁₂
Active material (wt%)	92	92
C45/SWCNT (wt%)	3.9/0.1	3
PVdF Binder (wt%)	4	5
Current collector thickness (μm)	“primed” Al, 18	Al, 20
Total electrode thickness (μm)	95	88
Coating thickness (μm)	77	68
Electrode porosity (%)	44.3	40.4
Coating density (g cm ⁻³)	1.83	1.93
Coating Loading, (mg cm ⁻²)	14.08	13.13
Active Loading, (mg cm ⁻²)	12.95	12.08

carbon-coated material with a particle size (D_{50}) of 0.91 μm. The electrode slurry consisted of LMFP64, C-45 carbon, single-walled carbon nanotubes (SWCNTs), and a polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP) solvent (Table I); this slurry was cast onto an 18 μm thick “primed” Al foil current collector (Armor Battery Films, grade EnSafe 20). The LTO slurry consisted of lithium titanate particles, C-45 carbon, and PVDF binder in NMP solvent: the slurry was cast onto a 20 μm thick standard Al foil current collector (Table I). The electrodes were dried after casting, then calendered to achieve the desired porosity. SEM images of the LMFP64 electrode show monolithic LiMn_{0.6}Fe_{0.4}PO₄ particles with no obvious secondary particle structure (Fig. 1a), whereas the LTO electrode shows sub-micron primary particles aggregated into micron-sized secondary particles (Fig. 1b).

Cell assembly and electrochemical testing.—Our tests were conducted either in three-electrode cells containing a Li micro-reference electrode¹⁵ or in 2032-type coin cells. All cells were assembled in an Ar-atmosphere glovebox, with electrodes re-dried at 110 °C under vacuum before assembly. Celgard 2500 and 1.2 M LiPF₆ in EC:EMC (3:7 w/w) served as the separator and electrolyte, respectively.

The three-electrode cells contained LMFP64 cathodes and LTO anodes, separated by two separators. Some had equal electrode areas (20.3 cm²), while others had a *cathode overhang* (LMFP64 area 22.9 cm², LTO area 20.3 cm²); see Table S2. The reference electrode (RE) was formed by in situ Li deposition onto the exposed tip of a 25 μm diameter insulated Cu wire placed between the separators.¹⁶

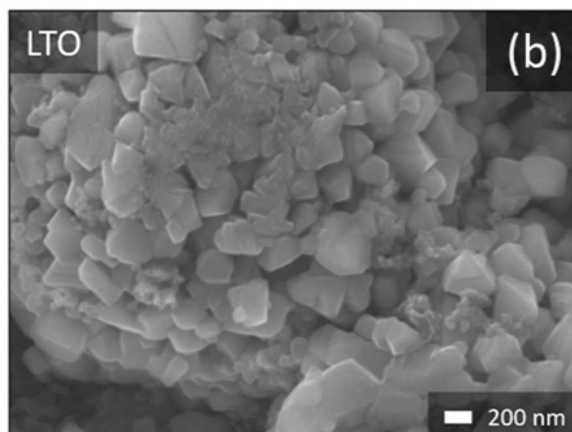
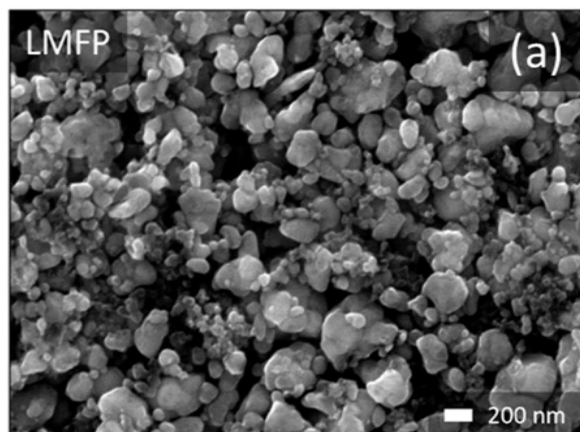
Coin cells (Table S2) were assembled with either a cathode overhang (15 mm LMFP, 14.2 mm LTO) or an anode overhang (15 mm LTO, 14.2 mm LMFP). Half-cells (LMFP64/Li and LTO/Li) were also fabricated to determine areal capacities and rate capabilities: the working electrode (LMFP64 or LTO) and counter electrode (Li-metal) in these cells were 14.2 mm and 15 mm in diameter,

**Figure 2.** Cell voltage and individual electrode potentials as a function of time during the experiment used to determine area-specific impedance across the charge and discharge segments of the cycle.

respectively. We determined the LTO/LMFP64 capacity ratios (n:p) to be ~0.94 and ~1.17 for the cathode overhang and anode overhang configurations, respectively.

Electrochemical cycling was performed on a MACCOR Series 4000 test system. The LMFP64/Li and LTO/Li cells were cycled between 2.5–4.4 V and 1.35–1.75 V, respectively. The LMFP64/LTO three-electrode cells were conditioned at 30 °C between 0.95–2.85 V at C/10, then subjected to rate capability testing: after charging to 2.85 V, cells were discharged to 0.95 V sequentially at C/20, C/10, C/5, C/2, 1 C, 1.5 C, and 2 C, with recharging to 2.85 V between discharges. Area-specific impedance (ASI) was determined from 3 C, 10 s charge/discharge current pulses applied at selected points along the voltage profile (Fig. 2). Capacity-limited steps were used along the voltage plateaus, while voltage-limited steps were applied in the LFP ↔ LMP transition regions for some cells to obtain higher resolution impedance data.

The LMFP64/LTO coin cell aging tests (Fig. S1a) included five initial C/10 conditioning cycles, 3 reference performance measurements (C/25 cycling and hybrid pulse power characterization, HPPC), and C/2 cycling between 1.15–2.75 V. In the HPPC cycles (Fig. S1b), the cells were charged to 2.75 V; then 3 C, 10 s current pulses were applied at various locations along the discharge curve.

**Figure 1.** SEM images of the pristine (a) LMFP64 and (b) LTO electrodes.

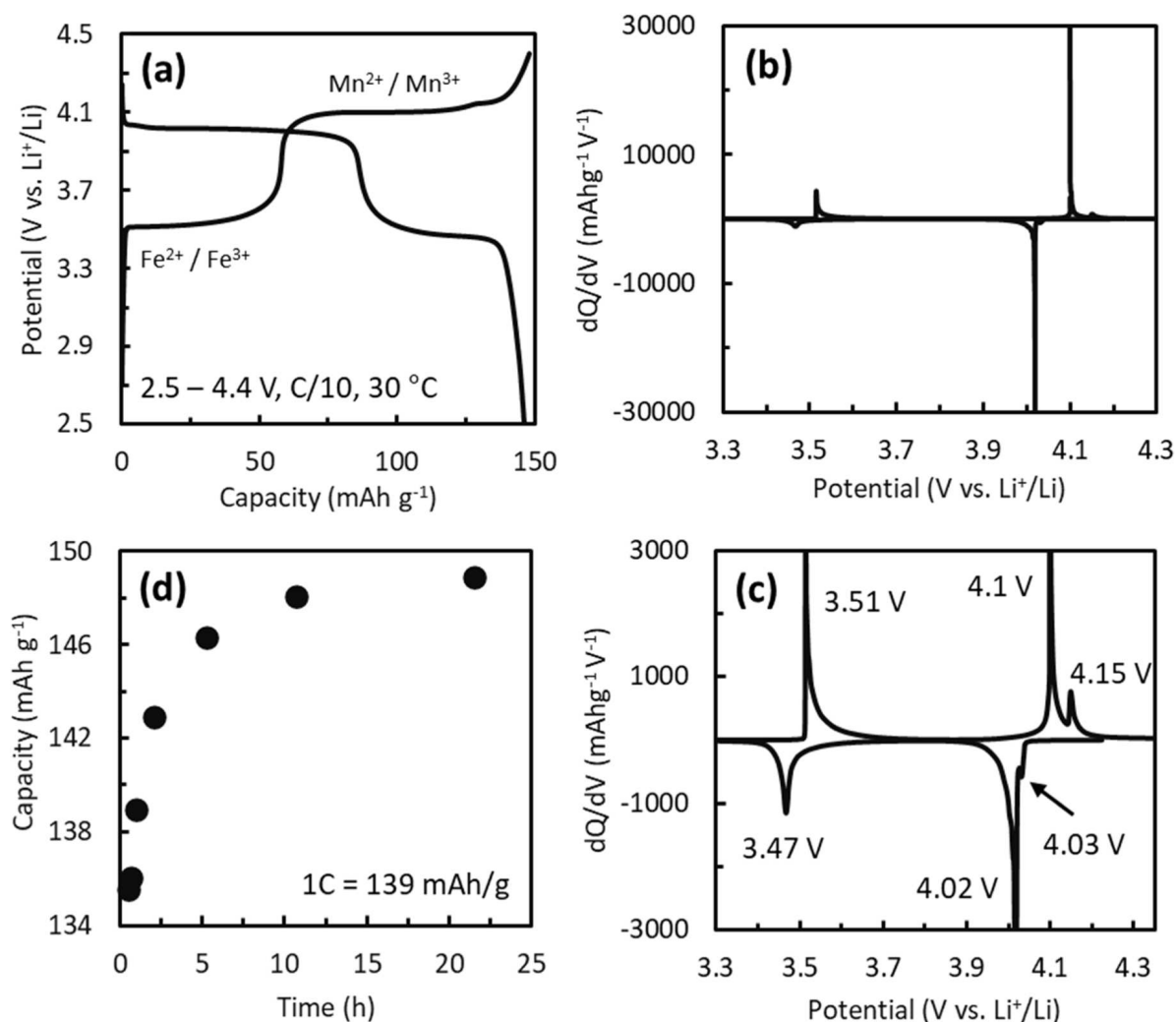


Figure 3. (a) Capacity voltage profile from the 2nd cycle of a LMFP/Li cell. (b) Differential capacity plots in the 3.3–4.3 V range; (c) is an expanded version of (b) showing peak locations. (d) Discharge capacity as a function of time taken to complete the discharge.

Harvested electrode characterization.—After cycling, selected coin cells were disassembled in an Ar-filled glovebox and electrodes harvested for post-test studies. Some of these electrodes were re-assembled into half-cells with Li metal, fresh separators, and fresh electrolyte, and cycled between 2.5–4.4 V (LMFP) or 1.35–1.75 V (LTO). Cycling-induced structural changes in the electrode materials were probed by X-ray diffraction (XRD) using a Bruker D2 diffractometer with Cu $\text{K}\alpha_{1,2}$ radiation ($\lambda = 1.54 \text{ \AA}$) in reflection geometry. LTO electrodes were scanned from 10° – 60° 2θ , and LMFP from 10° – 80° 2θ , in 0.02° steps with 1 s dwell time.

Surface chemistry of the pristine and aged LTO electrodes were examined by Auger electron spectroscopy (AES) using a Physical Electronics Auger Nanoprobe System 510 with a field emission source at 10 keV and 10 nA under $< 10^{-6}$ Torr UHV. SEM images were acquired with $5 \mu\text{m}$ and $10 \mu\text{m}$ fields of view for pristine and aged samples, respectively. Data were analyzed using PHI Multipak software.

ICP-MS measurements were performed at Argonne's Analytical Chemistry Laboratory (ACL) as described previously.¹⁷ Briefly, coatings from fresh and cycled LTO electrodes were scraped from the Cu foil, weighed, rinsed with deionized (DI) water, dried, ignited to remove organics, dissolved in DI water–HCl–HNO₃ under reflux, and treated with additional HNO₃ and HF for complete dissolution. The solutions were transferred to polypropylene tubes, diluted with DI water, and analyzed by ICP-MS.

Results

LMFP64/Li and LTO/Li cells.—Figure 3a shows a representative capacity–voltage profile of an LMFP64/Li cell cycled at C/10 and 30 °C. The first-cycle delithiation and lithiation capacities are approximately 152 and 146 mAh g⁻¹, respectively (where *g* refers to grams of LMFP64 in the cathode), corresponding to a coulombic efficiency (CE) of 96%. The voltage profiles exhibit plateaus associated with the Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺ redox reactions, separated by a sharp transition region. These plateaus appear as peaks in the differential capacity plots (Figs. 3b, 3c). In these plots, the Fe-redox peaks occur at 3.51 V and 3.47 V, while the main Mn-redox peaks appear at 4.10 V and 4.02 V during delithiation and lithiation, respectively. Smaller Mn-redox peaks at 4.15 V and 4.03 V are also observed: these peaks indicate distinct Mn micro-environments that have been reported for the olivine structure.^{18,19} Rate capability was assessed by discharging the cell between 4.4 and 2.5 V at varying rates. The discharge capacity as a function of discharge time (Fig. 3d) indicates a 1 C capacity of 139 mAh g⁻¹. The capacity ratio between 1 C and C/20 rates is 0.93, demonstrating excellent rate capability of the LMFP electrode.

Corresponding data for LTO/Li cells are presented in Fig. S2. These cells exhibit first-cycle lithiation and delithiation capacities of approximately 166 and 165 mAh g⁻¹, respectively, with a CE of 99.4%. The capacity–voltage profile (Fig. S2a) shows plateaus at 1.54 V and 1.58 V vs Li during lithiation and delithiation,

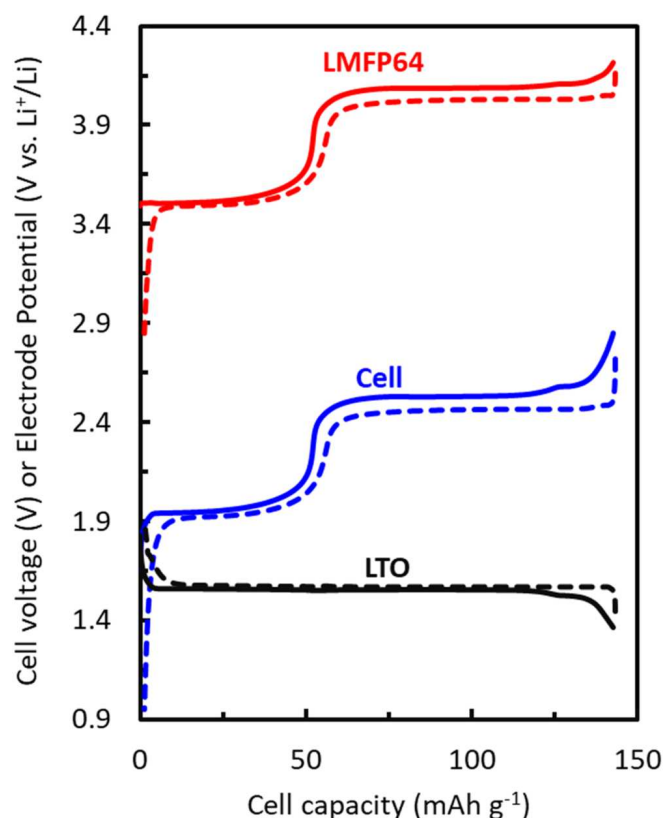


Figure 4. Capacity-voltage profiles for the LMFP64/LTO cell (blue), LMFP64 electrode (red) and LTO electrode (black) collected from a 3-electrode cell with a Li reference electrode. The data were obtained at a C/20 rate and 30 °C. The charge and discharge segments are shown as solid and dotted lines, respectively. This cell contained same-sized LMFP64 and LTO electrodes.

respectively, corresponding to the $\text{Li}_4\text{Ti}_5\text{O}_{12} \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$ structural transition. The 1 C capacity (Fig. S2b) is 159 mAh g^{-1} and the ratio between 1 C and C/20 rates is 0.97, confirming the excellent discharge rate capability of LTO electrodes.

Three-electrode cell data.—Voltage profiles.—Representative voltage profiles for the full cell and individual electrodes in LMFP64/LTO cells are shown in Fig. 4. The LMFP64 electrode exhibits Fe- and Mn-redox plateaus consistent with the half-cell data (Fig. 3a). The shape and hysteresis in the cell data can largely be attributed to the LMFP64 as the LTO electrode potential is relatively flat with minimal hysteresis, except near the limits of (de)lithiation. Observe that the voltage hysteresis in LMFP64 is more pronounced in the Mn-redox region than in the Fe-redox region.

Figure 5a–5c present cell voltage and electrode potentials during discharge at rates from C/20 to 2 C. LMFP64 voltage profiles closely follow the cell voltage trend; LTO electrode contributions become significant only at higher rates and near full discharge. Plateaus in the LMFP profiles become shorter, and the transition regions get longer and more sloped, as the applied current increases. Voltage polarization limits the cell discharge capacity, with LMFP64 contributions dominating at rates above 1 C. The discharge capacities plotted versus time (Fig. 5d) yield a 1 C capacity of $\sim 136 \text{ mAh g}^{-1}$; the ratio between 1 C and C/20 capacities is 0.96, higher than that observed for the LMFP/Li cells (Fig. 3d).

Area specific impedance.—Area specific impedance (ASI) for the full cell and individual electrodes was measured as a function of cell voltage using the protocol in Fig. 2. ASI values during charge and discharge pulses are shown in Figs. 6a and 6b, respectively. Key

observations from the plots include the following: (1) The LMFP64 electrode is the primary contributor to cell ASI; the LMFP64 ASI exceeds that of LTO, which shows relatively uniform values except near the charge and discharge segment boundaries.

(2) Charge and discharge ASI values largely overlap; minor differences arise from voltage hysteresis. Missing data in the transition region are a consequence of the test protocol.

(3) In the transition region, LMFP64 ASI is substantially higher than in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ plateaus.

(4) ASI profiles for charge and discharge pulses differ in the LMFP64 transition region. Charge pulses show a sharp ASI increase between cell voltages of 2.05 and 2.12 V, then a gradual decrease until ~ 2.5 V. Discharge pulses exhibit a gradual ASI increase from 2.05 to 2.4 V followed by a sharp decline. These behaviors are also apparent when the LMFP64 ASI is plotted as a function of its potential (Fig. S3). The ASI differences between the charge and discharge pulses are related to the voltage hysteresis displayed by the LMFP64 material (Fig. 4).

Another view depicting the correlations between cell capacity, LMFP electrode potential, and ASI during cell discharge is shown in Fig. 7. At the beginning of discharge, the LMFP64 electrode is fully delithiated and both Mn and Fe are in the 3+ oxidation states. As the electrode is lithiated, and the Mn oxidation state changes to 2+, the impedance decreases until the transition region begins, at which point the ASI starts to rise. Partway through the transition, the ASI reaches a maximum value and then starts to decrease. The ASI is lowest at the Fe-plateau as the Fe oxidation state changes to 2+. After this is completed, the ASI rises again as no further Li^+ can be inserted into the material.

Effect of increasing temperature on ASI and capacity.—As stated earlier, we examined the effect of temperature on the ASI profiles. An increase in temperature from 30 °C–50 °C caused a bigger ASI decrease at the higher cell voltages than at the lower voltages (Fig. 8a). This trend is apparent in the LMFP64 electrode ASI profiles (Fig. 8b). At elevated temperatures, ASI decreases significantly in the Mn-redox and transition regions but remains nearly unchanged in the Fe-redox region, indicating distinct impedance mechanisms across redox processes.

Figure 9 shows the effect of progressive high-temperature exposure, with all data collected at 30 °C. Cell capacity loss of approximately 16% is observed (Figs. 9a,b). Differential capacity plots reveal a reduction in Fe-redox peak intensity (Fig. 9c) while Mn-redox peaks remain relatively unchanged (Fig. 9d). A small increase in cell impedance following the thermal exposure (Fig. 9e) is mainly attributed to changes in the LMFP64 cathode (Fig. 9f).

Characterization of harvested electrodes from the 3-electrode cells.—Electrochemistry: Following thermal aging, LMFP64 and LTO electrodes were harvested and reassembled into half-cells. The LMFP64 electrodes had capacity comparable to that of pristine samples (Fig. 10a), indicating no loss of lithium occupancy sites. The harvested LTO data (Fig. 10b) shows a small decrease in capacity, suggesting either isolation or some minor damage to the active particles.

XRD: X-ray diffraction patterns on the temperature-aged LMFP64 electrode (Fig. 11a), Fig. S4a) show peak shifts relative to the pristine material. The pattern for the relithiated sample is almost identical to that of the pristine sample, indicating that peak shifts observed for the temperature-aged electrode are simply a consequence of Li-loss from the material. The LTO anode patterns (Fig. 11b, Fig. S4b) show little change after the high-temperature exposure, indicating that the bulk-material crystal structure is intact: some small, broad features in the aged-electrode patterns can be attributed to the presence of LiF in the electrode.

AES: Auger Electron Spectroscopy measurements were conducted on LTO electrodes to determine the cause(s) of the small capacity decrease observed for the aged harvested (unwashed) electrode. The

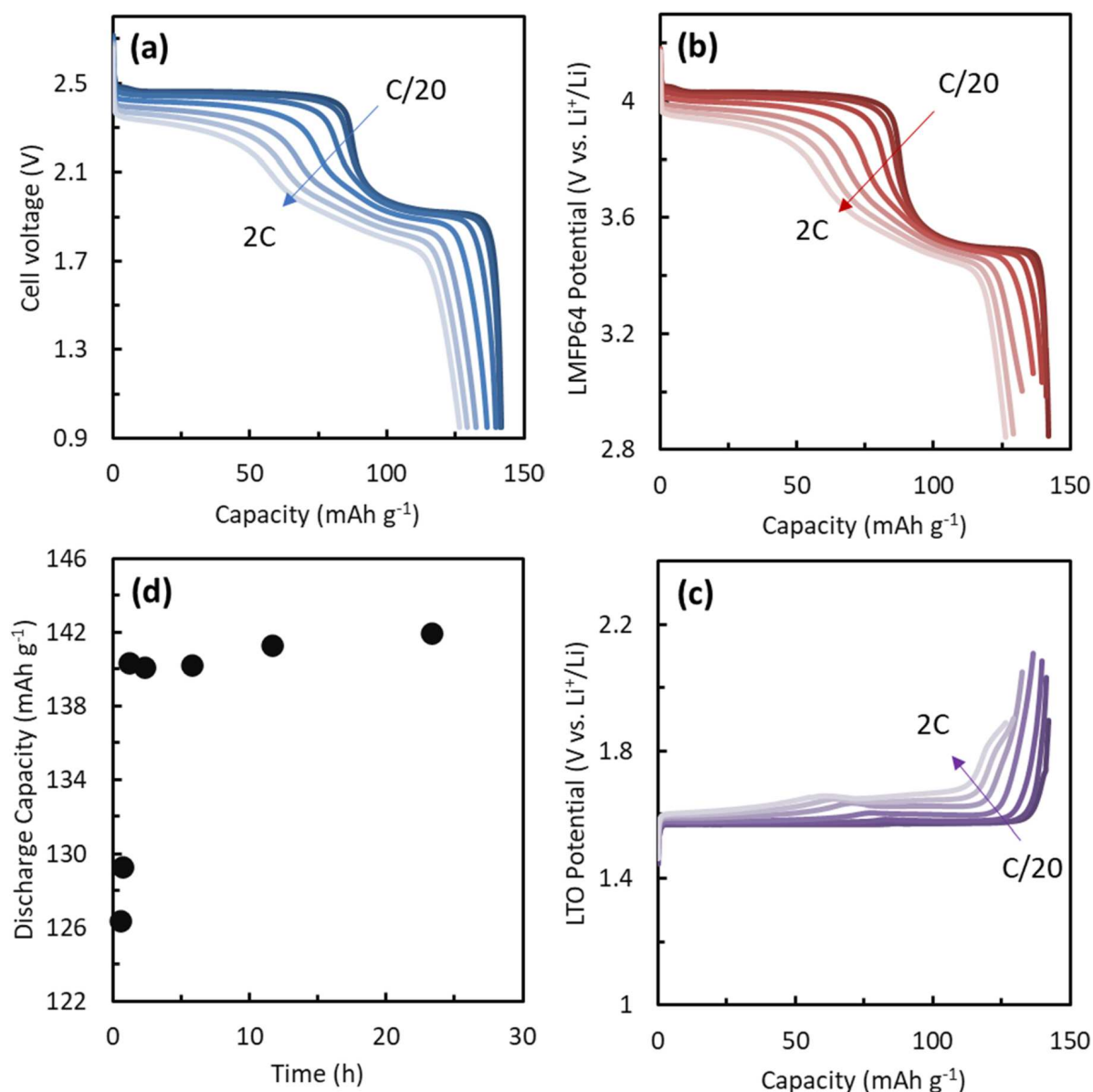


Figure 5. (a) Cell voltage, (b) LMFP64 potential, and (c) LTO potential profiles from a 3-electrode cell discharged at rates from C/20 to 2 C; arrows indicate the direction of increasing rate. (d) Discharge capacity vs discharge time plotted to determine the 1 C rate. In all plots, g in refers to grams of LMFP64 in the cathode.

data (Fig. 12) show that the carbon, phosphorus, and fluorine concentrations, averaged across various LTO particle surfaces, increased from 38%, 2%, and 1.3% to 43.3%, 3.4%, and 8.7% respectively, indicating the presence of electrolyte residue and electrolyte reaction/decomposition products. The titanium content, which arises from the LTO, decreased from 17.8% to 11.2%, indicating surface coverage of the particles. The oxygen content, which can arise from both LTO and the electrolyte-solvent, also decreased from 17.8% to 11.2%. The O/Ti, F/Ti, P/Ti, and C/Ti ratios increase from about 2.3, 0.07, 0.11, 2.13 to about 2.99, 0.78, 0.3, 3.87, respectively, suggesting that the LTO particle surfaces are covered by both organic (solvent-derived) and inorganic (salt-derived) products.

ICP/MS: These measurements were conducted to quantify the Mn content on the LTO electrodes. The results (Fig. 13) show that the Mn content on the LTO anodes increases on cycling/aging: the effect of high-temperature exposure is far greater than the effect of cycling. The increased Mn content is due to the dissolution of Mn from the LMFP64 cathode, which migrates through the electrolyte and deposits at the anode.

Data from coin (2-electrode) cells cycled at 30 °C.—Initial and long-term aging performance of cathode-overhang cells.—For the cathode-overhang coin cells, the 1st cycle charge and discharge capacities, measured at C/10 rate, were ~152 and 145 mAh g⁻¹ respectively, which yields a coulombic efficiency (CE) of 95.4%. The capacities increased somewhat on cycling, possibly indicating increased “wetting” of the electrodes by the electrolyte: the discharge capacity and CE values reached ~147 mAh g⁻¹ and 99.7% respectively after the first 5 C/10 cycles. ASI measurements across the charge-discharge segments were collected on some of the cells. Representative data are shown in Fig. 14; the ASI trends observed in these data mirror those observed in the three-electrode cell data.

Representative discharge capacity vs cycle number data obtained during long-term cycling are included in Fig. 15a. The capacities measured at C/25 rate are greater than the C/2 capacities, which is a consequence of the cell impedance reflected in the latter data. Both values increase gradually for the 1st 200 cycles, then decrease on continued cycling. Capacity retention values determined from the C/25 data (Fig. 15b) and from the C/2 data (Fig. 15c) are about 80%

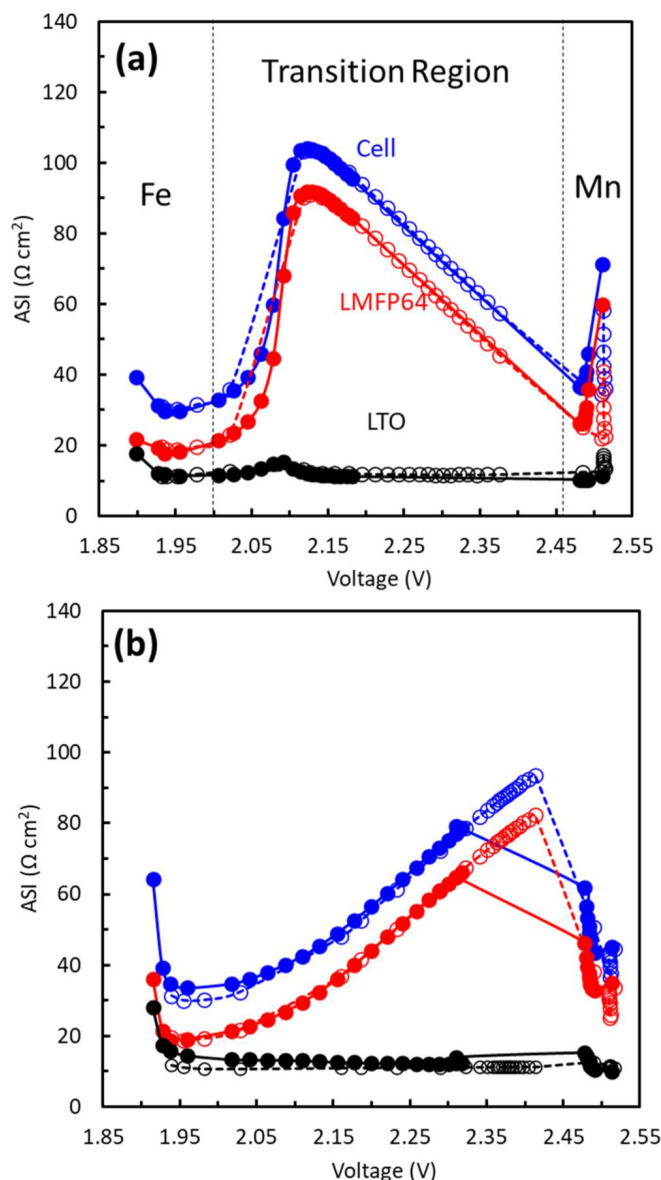


Figure 6. Area specific impedance (ASI) as a function of cell voltage during a 30 °C test. The cell (blue), LMFP64 (red) and LTO (black) data were collected using (a) 3 C, 10-s charge and (b) 3 C, 10-s discharge pulses during the cell charge segment (open circles, dashed line) and discharge segment (filled circles, solid line). The symbols indicate location of the data points; the lines are simply to guide the eye. Note that the LMFP64 is delithiated during the charge pulses and lithiated during the discharge pulses. The top panel shows locations of the Fe-redox, Mn-redox and transition regions. The Transition Region designation is based on the data in Fig. 4, which shows that this region is between cell voltages of 2.0 and 2.45 V.

and 66% respectively after 900+ cycles. The difference between these data reflects impedance growth (Fig. 15d) in the cells, which is about 15 $\Omega \text{ cm}^2$ and mostly uniform across the cell voltage spread.

Comparing data from cathode-overhang and anode-overhang cells.—Representative plots comparing data from the cathode-overhang and anode-overhang cells after 300+ cycles are shown in Fig. 16. The discharge capacity vs cycle number data (Fig. 16a) show that the cathode-overhang cells have a lower capacity fade (<1%) than the anode-overhang cells (9.5%), determined using the C/25 values, after 300+ cycles. Voltage profiles for the anode-overhang cell (Fig. 16b) indicate a contraction of the Fe plateau for cycle 307 compared to that of cycle 7. The Mn plateau length remains the same, suggesting that the LTO potential profile shifts relative to that of the LMFP64 potential profile; more on these shifts (or slippage) below. The cathode-overhang cell (Fig. 16c) also shows a contraction of the Fe plateau but the Mn plateau length is greater for cycle

307 than cycle 7. These data suggest that Li^+ ions from the LMFP64 electrode overhang contribute to the capacity during cycling. Impedance profiles (Fig. S5) are similar, showing small uniform increases across the discharge segment in both cell types.

Electrochemistry of harvested electrodes from the coin cells.—LMFP64 and LTO electrodes harvested from cells after 900 cycles at 30 °C were reassembled into half-cells and cycled at C/100 (Fig. S6). The harvested LMFP64 electrodes had capacity comparable to pristine samples (Fig. S6a), indicating no lithium site loss. Harvested LTO electrodes also exhibited negligible capacity loss, suggesting minimal active material degradation or loss during cycling (Fig. S6a).

Discussion

The electrochemical performance of LMFP64/LTO full cells, as well as the behavior of individual electrodes characterized in both

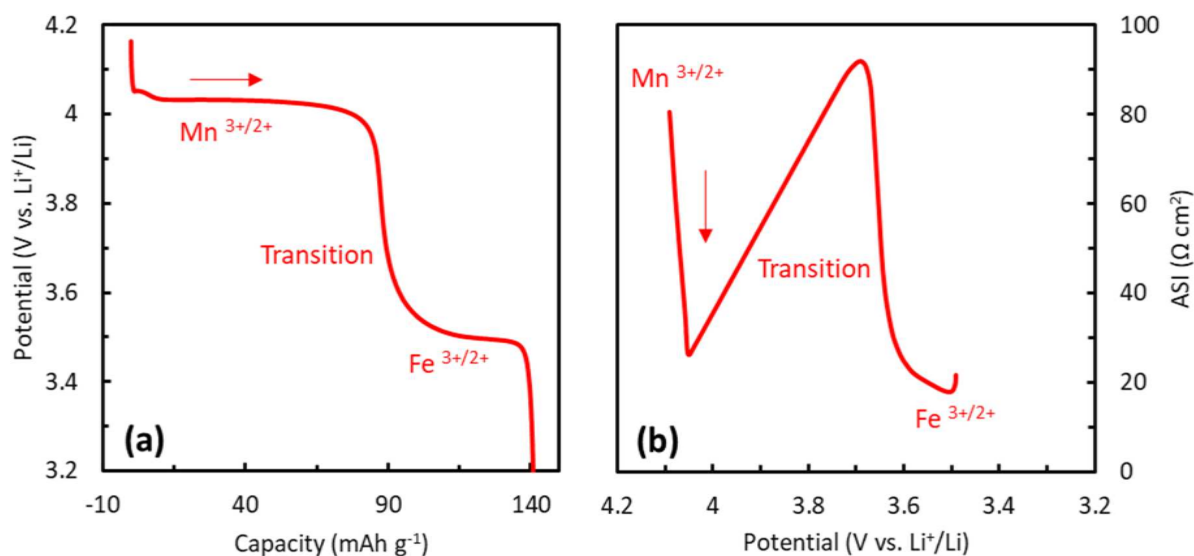


Figure 7. Data from the LMFP64 electrode from the three-electrode cell. (a) Capacity vs LMFP64 potential and (b) ASI data (using charge pulses) vs LMFP64 potential during cell discharge. The arrow indicates the direction of electrode delithiation.

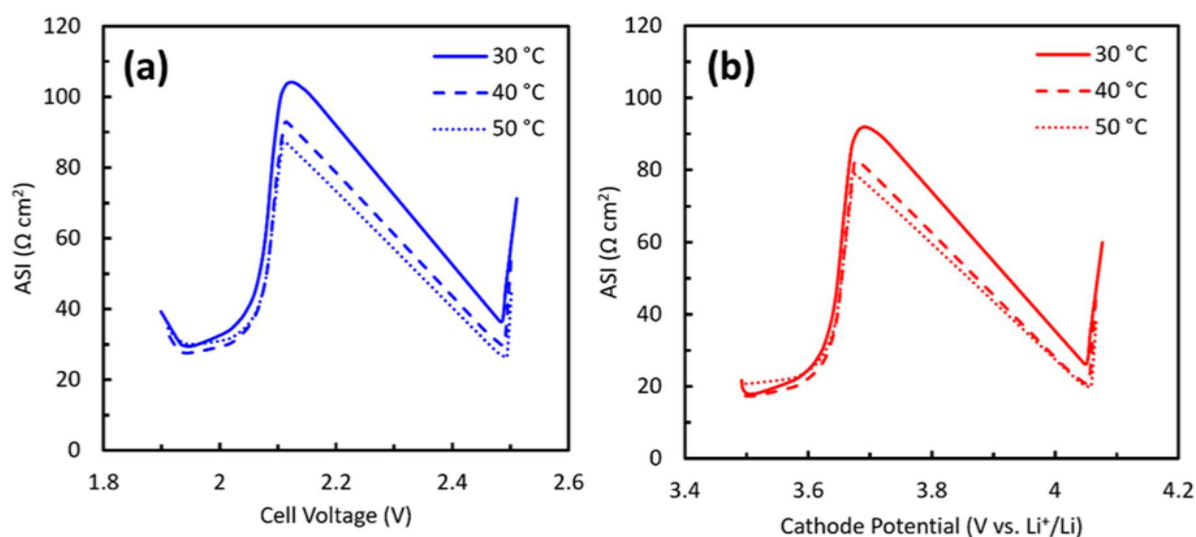


Figure 8. Charge-pulse cell ASI of a 3-electrode cell taken over the course of discharge for the (a) full cell and (b) cathode at temperatures of 30, 40 and 50 °C.

half-cell and three-electrode configurations, highlights the benefits and limitations of combining a high-voltage olivine cathode with a zero-strain, low-potential LTO anode. We will now discuss the main observations from our experiments and their consequences of cell performance and long-term stability.

Voltage hysteresis: A key observation (Fig. 4) is the presence of voltage hysteresis in the LMFP64 electrode, which is more pronounced in the Mn-redox region than in the Fe-redox region. Notably, this hysteresis persists even at very low current densities ($<C/100$), suggesting that it arises from intrinsic thermodynamic properties of the material rather than kinetic limitations. Malik et al.²⁰ offered a theoretical explanation for this phenomenon based on first-principles calculations. They proposed that hysteresis in LMFP stems from differences in the local atomic environments encountered during lithiation and delithiation. In the fully delithiated state, lithium vacancies are typically surrounded by oxidized transition metal ions (Mn^{3+} or Fe^{3+}), as is the case in pure MnPO_4 . Lithiation of MnPO_4 leads to the formation of LiMnPO_4 , where lithium ions are coordinated primarily by reduced Mn^{2+} , resulting in a relatively stable phase. In contrast, lithiation of mixed-metal

compositions such as LMFP64 leads to intermediate states where lithium ions are surrounded by both Mn^{2+} and Fe^{3+} . These mixed local environments are energetically less favorable, particularly because of repulsive $\text{Li}^+ - \text{Fe}^{3+}$ interactions, which raise the system's energy. Consequently, the average voltage during lithiation is reduced on the Mn plateau, contributing to the observed hysteresis between charge and discharge.

On the Fe-redox side, a complementary effect occurs. During delithiation, Fe^{2+} is oxidized to Fe^{3+} , and lithium is extracted from a relatively ordered environment where Li^+ is initially coordinated with Fe^{2+} . However, in the mixed-metal LMFP system, delithiation on the Fe plateau can result in local environments where residual Mn^{2+} remains near lithium sites. These configurations can again produce unfavorable interactions, this time between Fe^{3+} and Mn^{2+} , which increase the energy of the delithiated state compared to the pure FePO_4 phase. This asymmetry in the energy landscape between lithiation and delithiation, across both Mn and Fe redox transitions, contributes to the overall voltage hysteresis seen in the data (Fig. 4).

Rate Effects and Impedance Characteristics: At higher C-rates the lengths of the Mn-redox and Fe-redox plateaus become smaller

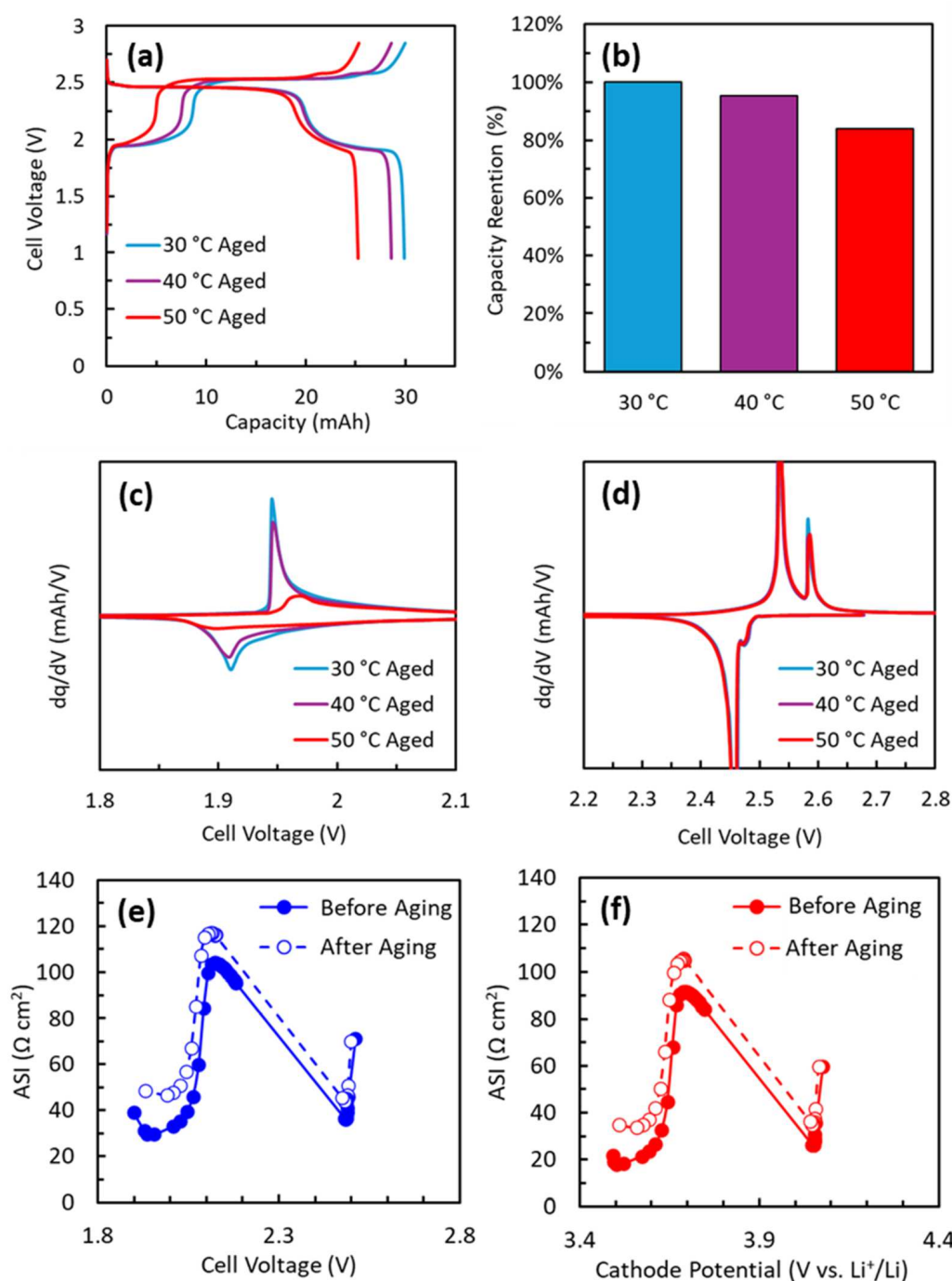


Figure 9. (a) C/10 voltage profile; (b) capacity; differential capacity plot of the (c) Fe and (d) Mn regions for the 3-electrode LMFP/LTO cell after being exposed to temperatures of 30 °C (blue), 40 °C (purple), and 50 °C (red); and ASI of the (e) cell and (f) cathode before and after temperature aging. All data were obtained at 30 °C.

and the width of the intermediate “transition region” broadens for the LMFP64 cathode (Fig. 5). This trend suggests increasing deviation from equilibrium two-phase behavior at higher current densities. In two-phase systems like LMFP, lithium insertion or extraction typically proceeds via a moving phase boundary between lithiated and delithiated domains. At slow rates, this phase boundary has time to propagate uniformly, producing flat voltage plateaus associated with distinct redox couples. However, under high-rate conditions, the kinetics of boundary motion become sluggish relative to the imposed current, causing the system to pass through a spectrum of non-equilibrium states. This results in shorter apparent plateaus and a broadened voltage region between the two redox couples.

These findings are consistent with rate-dependent phase transformation behavior reported in operando diffraction studies of LMFP materials, such as by Ravnsbæk et al.²¹ here, the authors demonstrated that modifying the transformation strain in LMFP olivines can improve high-rate performance by facilitating more facile phase boundary movement. As strain accumulates during rapid cycling, it may energetically penalize two-phase separation and favor solid-solution-like behavior, manifesting as a broad transition region between the Mn and Fe redox processes. In our LMFP64 electrode, this effect may be amplified by internal microstructural heterogeneities or surface reaction layers that impede fast lithium transport. The resulting “smearing” of the redox transitions reflects the material’s

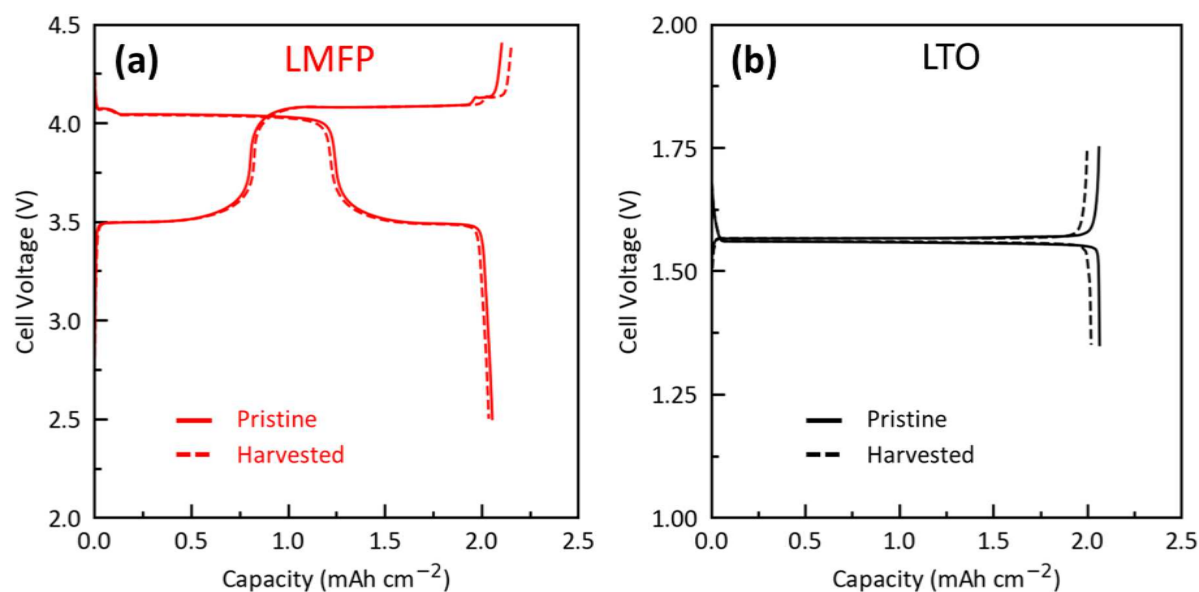


Figure 10. C/100 voltage profiles of (a) LMFP and (b) LTO half cells made from pristine (solid line) and harvested (dashed line) electrodes.

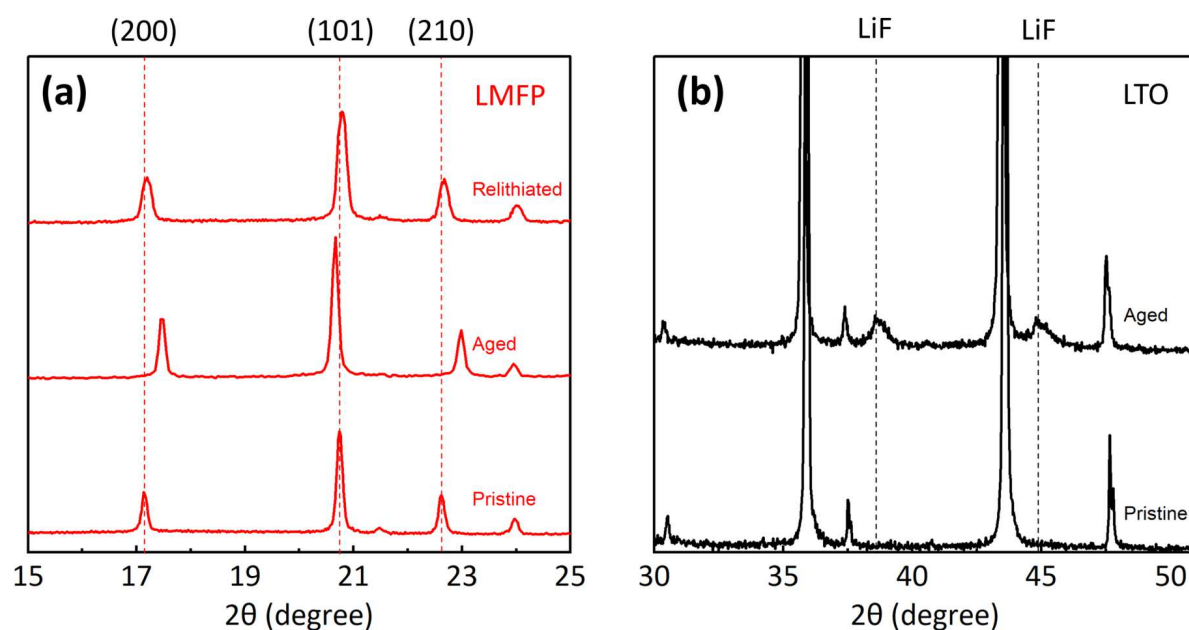


Figure 11. XRD patterns of (a) LMFP cathode and (b) LTO anode before and after aging.

intrinsic limitations in maintaining distinct two-phase boundaries under kinetic constraints.

The LMFP64 ASI data shows the highest impedance in the transition region between the Mn-redox and Fe-redox. Additionally, ASI in the Mn-redox plateau > ASI in the Fe-redox plateau. The latter is in accordance with first-principles calculations by Johannes et al.,²² which reveal that LiMnPO_4 has a significantly higher hole polaron migration barrier than LiFePO_4 , due to the more localized nature of Mn^{3+} -O bonding near the valence band maximum. This electronic effect leads to intrinsically slower lithium diffusion in Mn-rich regions, consistent with the experimentally observed sluggish kinetics on the Mn-redox plateau in our data (Fig. 7).

The mechanisms governing the ASI increase in the transition region between the Mn and Fe redox regimes are not fully understood. This increase has been reported previously¹² with the authors noting a spike increase in the charge-transfer resistance and a

decrease in contact (ohmic) resistance during LMFP delithiation. Other studies have reported peaks in the Li^+ ion diffusion plots in this transition region.^{23–25} We observe that the region between the $\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox involves coexistence of multiple phases. Solid-solid interfaces and phase boundary movement impose high Li^+ migration barriers, which could impact impedance.^{20,26} Furthermore, theoretical studies indicate that Li-vacancy activation energies and electronic conductivity degrade in mixed-metal-valence regions, elevating the ASI relative to the pure Fe or pure Mn plateaus.²² Note that we also observe a pronounced asymmetry between ASI profiles measured during charge and discharge pulses (Fig. 6, S3) in the transition region. This asymmetry reflects the path-dependent kinetics of lithium (de)intercalation and is likely exacerbated by differences in local cation environments and migration barriers associated with Fe and Mn redox couples. As a result, the material exhibits different impedance responses depending on

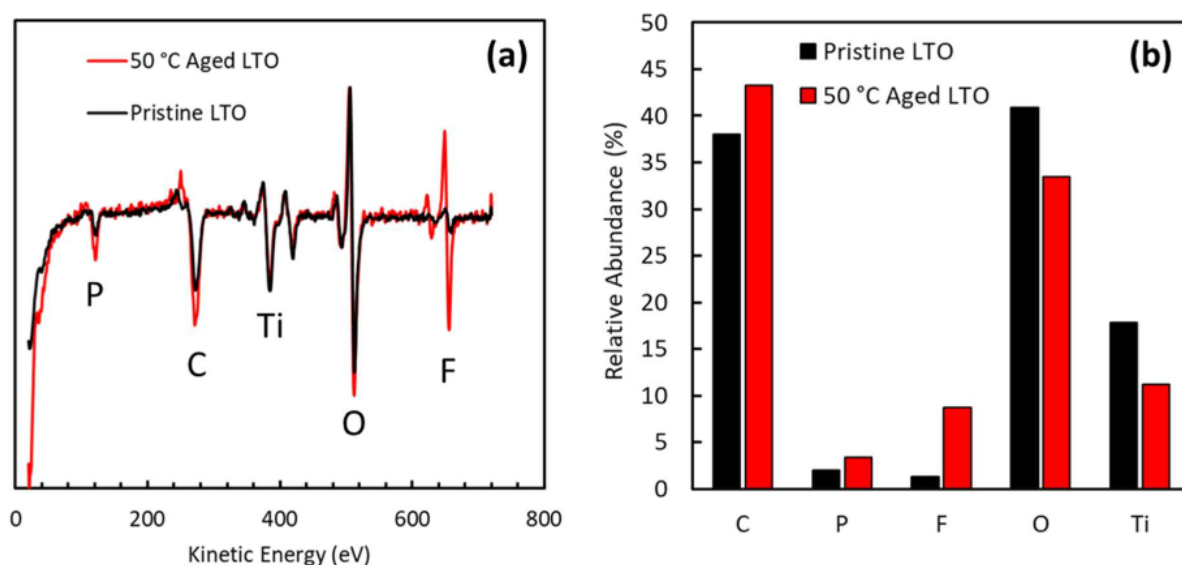


Figure 12. (a) Differential Auger spectra of pristine LTO electrode (black) and temperature aged LTO electrode (red). (b) Relative element concentration at the surface of LTO particles from pristine (black) and temperature-aged (red) electrodes.

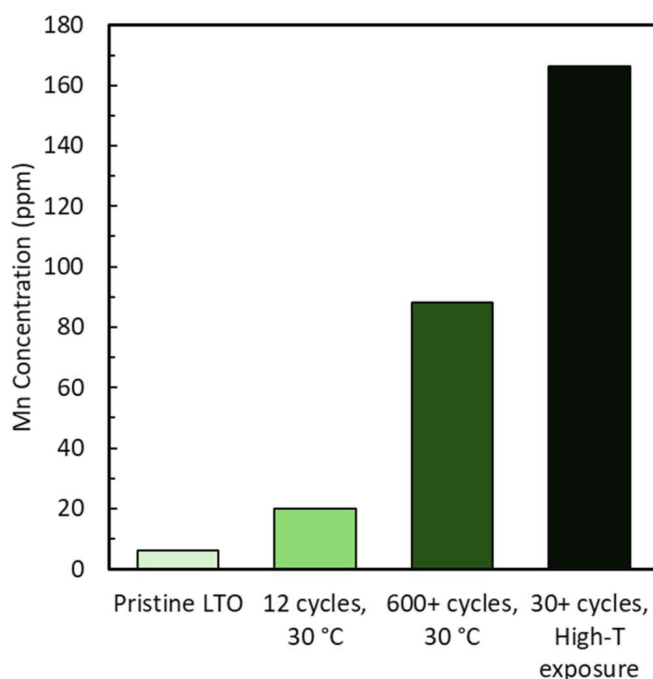


Figure 13. Mn concentration at the surface of LTO particles as determined from ICP-MS measurements. The measurement accuracy is $\pm 10\%$ of the reported value. For the pristine LTO electrode, the small amounts of Mn could be from the carbon additives added to improve electronic conductivity. For the aged (harvested) electrodes, the Mn content reflects the amount dissolved from the LMFP64 cathode and deposited from the electrolyte during the experiments.

whether lithium is being inserted or removed, especially during the short timescales relevant to pulse measurements.

The LTO anode, on the other hand, shows mostly uniform impedance except at the extremes of the charge and discharge segments (Fig. 6). The data confirm the high-rate capability of the LTO and its minor contributions to overall cell polarization, especially at moderate rates. This is a known advantage of LTO, whose zero-strain insertion process and high conductivity yield stable electrochemical signatures.^{27,28}

Temperature Effects on Capacity and Impedance: The cell impedance is lower at higher temperatures (Fig. 8) due to enhanced ionic conductivity of the electrolyte and accelerated charge transfer kinetics at both LMFP and LTO interfaces. The ASI decrease

indicates that the Li^+ migration barriers are lower at the higher temperatures: evidently, the migration barriers in the Mn-redox and transition regions are more affected by temperature than those in the Fe-redox region.

However, while the impedance drop improves rate capability, the capacity fade remains non-negligible. This suggests that capacity degradation is not purely governed by ohmic or kinetic limitations, but also involves chemical or interfacial degradation processes. In particular, the LTO anode, though stable against Li plating, is known to undergo side reactions at elevated temperatures that consume cyclable lithium. AES analysis of our aged LTO samples revealed increased concentrations of carbon, fluorine, and phosphorus at the surface, indicative of decomposition products from electrolyte

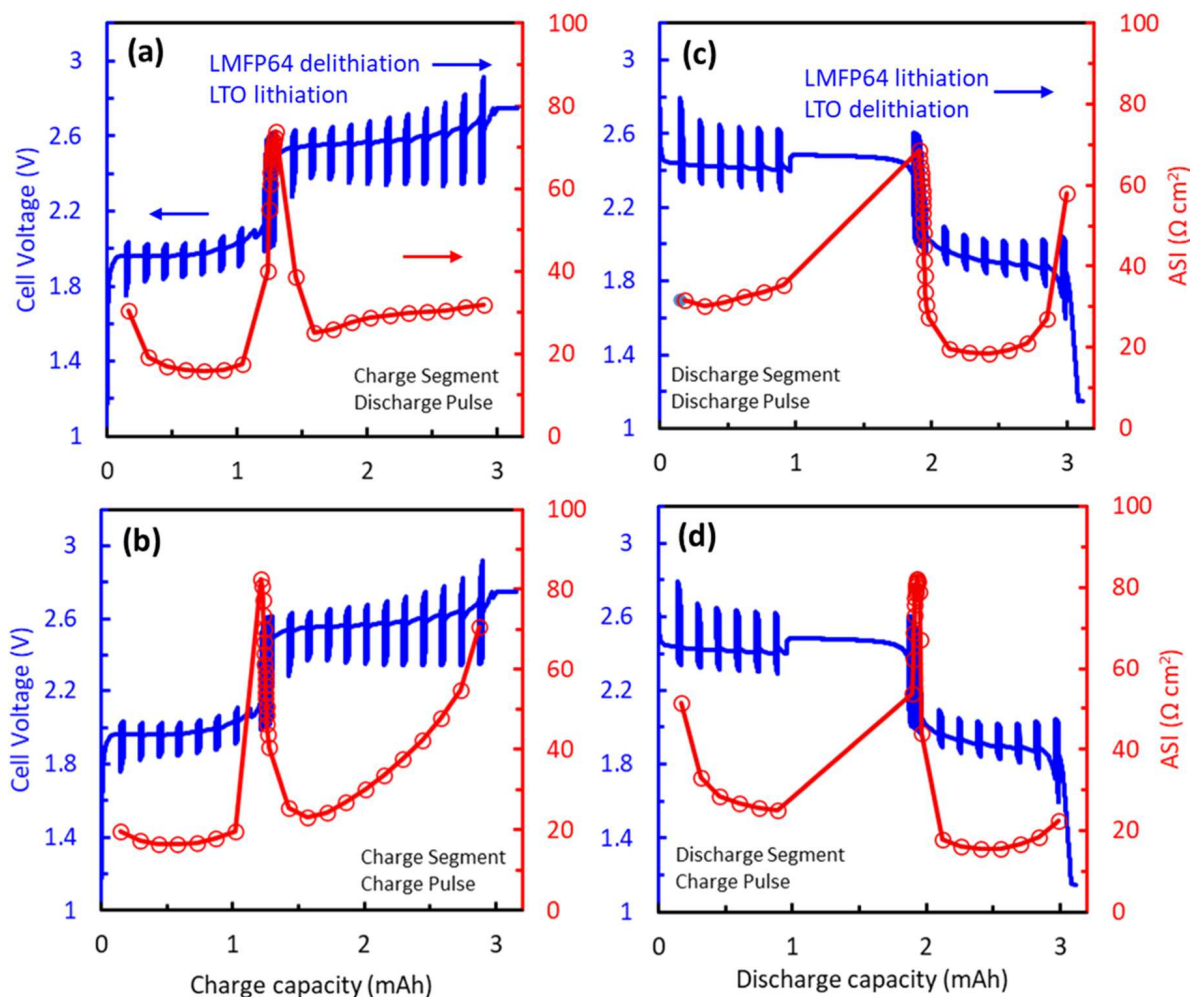


Figure 14. Cell voltage (left axes, blue) and ASI (right axes, red) plotted as a function of cell capacity during the charge (a), (b) and discharge (c), (d) segments of the cycle. The ASI data were acquired using 3 C, 10-s discharge (a), (c) and charge (b), (d) current pulses. The symbols indicate locations of the data acquisition; lines in the plots are only intended to guide the eye. The data were acquired on cathode-overhang coin cells at 30 °C. Observe the sharp impedance increase observed in the LFP ↔ LMP transition region.

breakdown, including LiF and phosphate species, features consistent with prior reports on LTO aging.^{29–31} These products could hinder lithium transport and/or isolate active particles, causing the small loss in capacity observed for the harvested LTO electrodes from the temperature-aged cell (Fig. 10b).

Computational studies support the likelihood of parasitic side reactions at the LTO-electrolyte interface. Periodic DFT calculations have demonstrated that surface-exposed Ti sites on LTO can catalyze electrolyte decomposition, particularly in the presence of trace water, resulting in EC dehydrogenation, PF_6^- breakdown, and gas generation (e.g., CO_2 , H_2).³² Such reactions could promote early-stage SEI nucleation and lead to irreversible Li trapping, which could be accelerated by transition metal elements such as Mn observed in our ICP-MS data.³³ The main effect of this Li consumption is the potential slippage between electrodes, as differential degradation alters the open circuit potential of each electrode (see schematic in Fig. S7).³¹ This slippage explains the decrease in the Fe-redox plateau width, and the corresponding differential capacity peak, seen in Figs. 9a, 9c.

Our data also show a small cell impedance increase (Fig. 9e) after the high-temperature exposure, which arises at the LMFP64 electrode (Fig. 9f). This increase could result from resistive surface films, stemming from high-temperature electrolyte oxidation, that impede Li^+ transport. Another reason for the increase is partial cation disordering and lattice distortion at the LMFP64 particle

surfaces. The XRD data (Fig. 11a, S4a) show that the bulk LMFP64 structure is unaffected. However, transition metal (Fe, Mn) dissolution,³⁴ which likely happens from the particle surface, could induce structural changes and lower Li^+ diffusivity at localized regions. This effect could be exacerbated by residual Mn^{3+} , a Jahn-Teller ion, which is known to distort and induce strain in the crystal lattice.

Effect of Overhang and Long-Term Cycling: In the coin cell tests we observed a pronounced dependence of capacity retention and voltage behavior on the electrode overhang. Cells with cathode overhang exhibit a more symmetric voltage profile and slower capacity fade than cells with the anode overhang (Fig. 16). After 300 cycles, the cathode-overhang cells show <1% capacity fade, compared to ~9.5% in anode-overhang cells.

To isolate the effect of overhang type, we plot the capacity-voltage data as hysteresis plots and compute the charge and discharge endpoint slippage for the cathode overhang and anode overhang configurations (Fig. 17 and insets). Note that the charge endpoint slippage (CES) is measured from the end of the first charge to the end of the n th charge after formation; the discharge endpoint slippage (DES) is measured from the end of the first discharge after formation to the end of the n th discharge. The difference between the DES and CES is reflected as capacity loss ($\text{DES} > \text{CES}$) or capacity gain ($\text{DES} < \text{CES}$) in the cells.

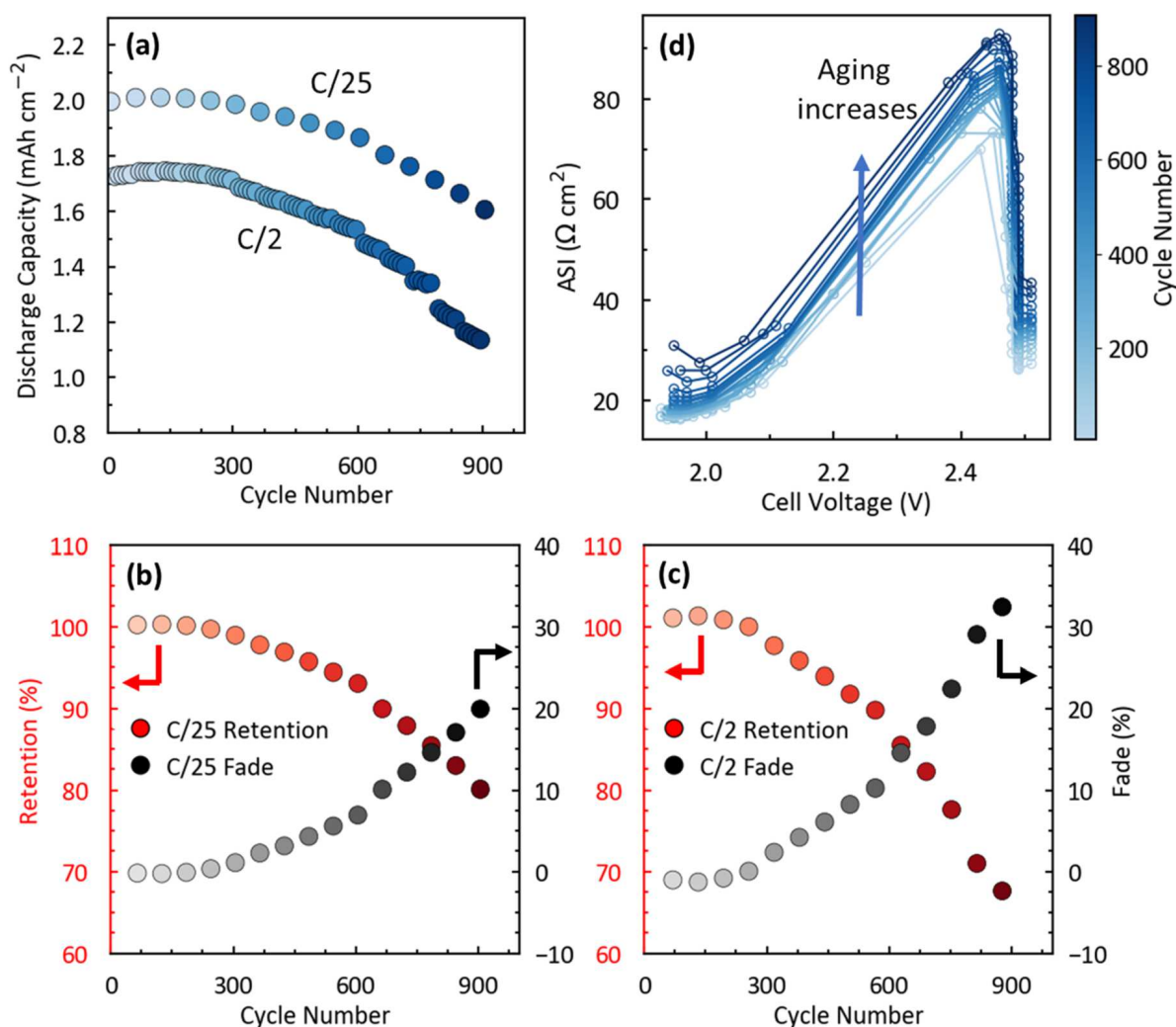


Figure 15. (a) Discharge capacity vs cycle number for a cell with cathode overhang. Discharge capacity retention (reds) and fade (greys) determined from the (b) C/25 data and (c) C/2 data. (d) ASI vs cell voltage plots determined from the HPPC cycle during cell discharge using 3 C, 10-s discharge current pulses. The arrows in the plots indicate the direction of increased aging.

For both overhang configurations, the endpoint slippages increase with cycle number. For the cathode overhang cell, the values are similar to ~ 250 cycles and then the DES becomes slightly greater: after 300+ cycles, the CES and DES values are ~ 0.21 and 0.22 mAh cm^{-2} respectively. For this cell, the Mn plateau width increases and the Fe plateau width decreases (Fig. 16c), as noted earlier. For the anode overhang cell, the CES is smaller than the DES for all cycle numbers: after 300+ cycles, the CES and DES values are ~ 0.09 and 0.28 mAh cm^{-2} respectively. For this cell, the Mn plateau width remains the same, while the Fe plateau width decreases (Fig. 16b) with cycle number.

The DES arises from electrolyte reduction reactions at the LTO electrode,^{31,35} which decreases Li^+ inventory of the cell. The CES is typically attributed to electrolyte oxidation reactions that occur at the cathode. For the cathode overhang cells up to ~ 250 cycles DES < CES, a capacity gain! As the upper cutoff (cycling) voltages for the anode overhang and cathode overhang cells are the same, the magnitude of electrolyte oxidations should be similar. Therefore, the capacity gain must come from the lithium inventory available in the overhang of the cathode overhang cells. This contribution appears to diminish after ~ 250 cycles, as the CES and DES begin to diverge. This deviation is evident in Fig. 18, which shows slippage data from a cell that experienced 900+ cycles. Here, the CES and

DES values match till ~ 250 cycles, after which the former gradually tapers off while latter continues almost linearly. The effects are reflected in the discharge capacity plots (Figs. 15a–15c), which show relative stable values till ~ 250 cycles, after which the capacities begin to fade.

These results reflect the importance of Li inventory balance. In the absence of cathode overhang, any irreversible Li loss (e.g., through parasitic reactions at the LTO surface) cannot be compensated by excess lithium stored in the overhang region. As a result, the cell experiences a gradual Li-deficiency, shifting the operating voltage window away from the optimal redox regions of both electrodes. The effect is especially detrimental in LMFP-based cells because the redox features of LMFP are sharply defined due to its two-phase reaction mechanism. Any slippage away from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ or $\text{Mn}^{2+}/\text{Mn}^{3+}$ plateau reduces the accessible capacity significantly. The superior performance of LMFP-overhang configurations demonstrates that a controlled excess of lithium in the positive electrode can offset Li^+ losses. For large-format LMFP/LTO cells, optimizing electrode overhang dimensions, alignment tolerances, and lithium stoichiometry offers a straightforward means to mitigate capacity fade and impedance growth. Combined with stable SEI-forming electrolytes, these strategies provide practical pathways to preserve capacity retention during long-term cycle and calendar aging.

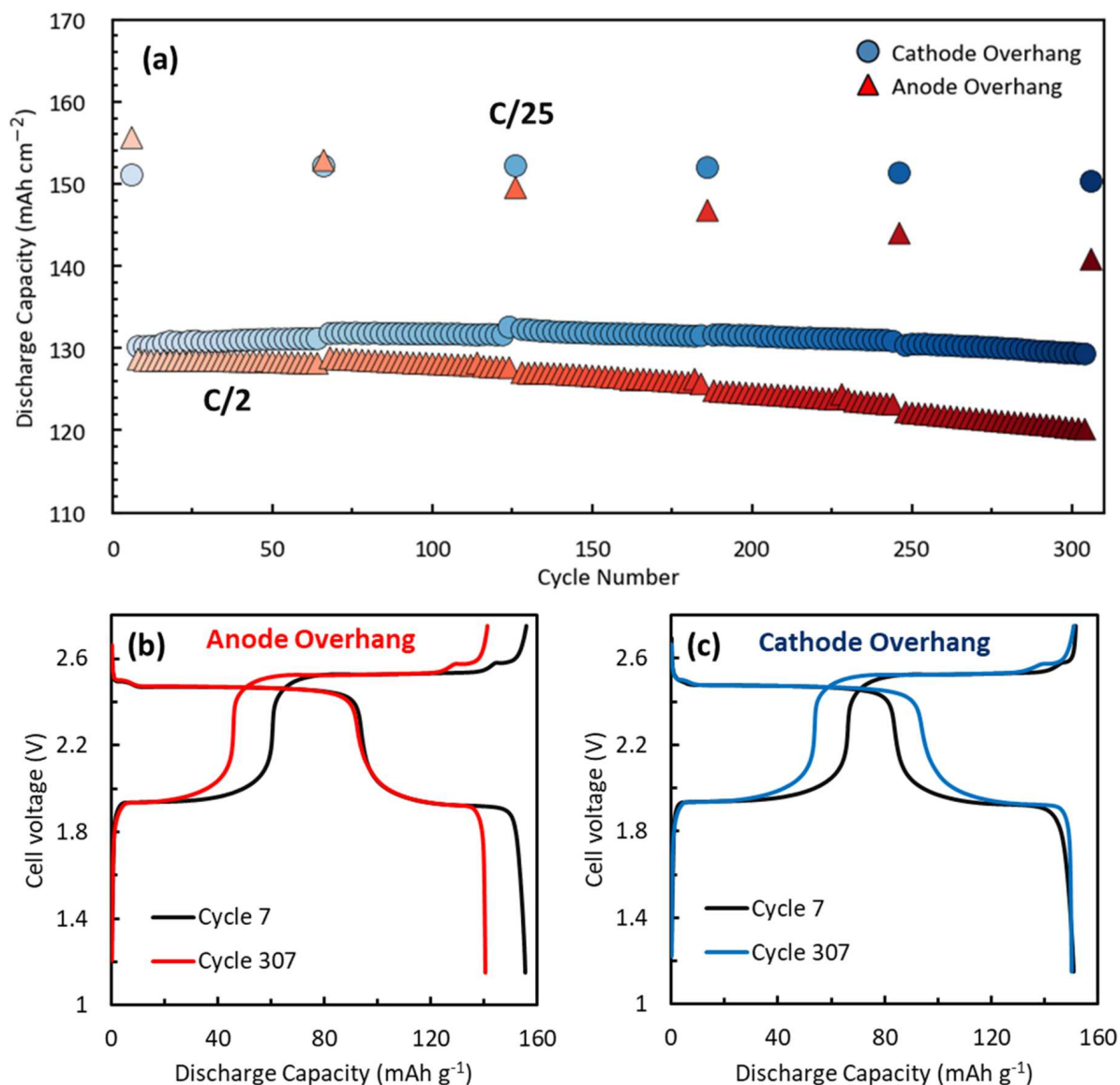


Figure 16. (a) Discharge capacity vs cycle number for a cell with cathode overhang (blues) and anode overhang (reds). Capacity-voltage profiles (C/25 rate) for the (b) anode overhang and (c) cathode overhang cells at cycle 7 (black) and cycle 307 (red and blue for anode and cathode overhangs, respectively). All data were collected at 30 °C.

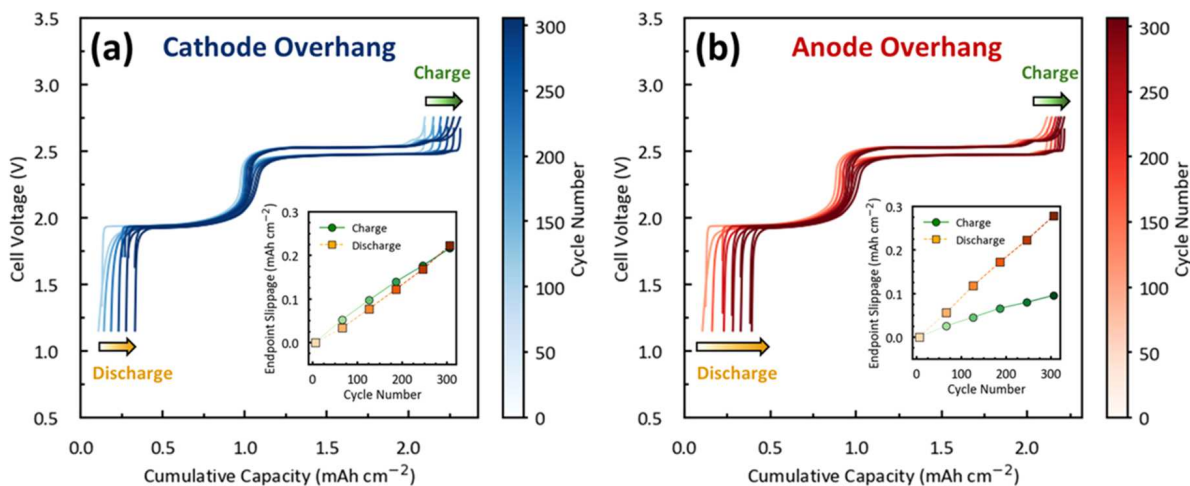


Figure 17. Capacity-voltage hysteresis plots at C/25 rate for LMFP64/LTO cells with (a) cathode overhang and (b) anode overhang during 300+ cycles at 30 °C. Insets show magnitudes of charge and discharge endpoint slippage for each configuration.

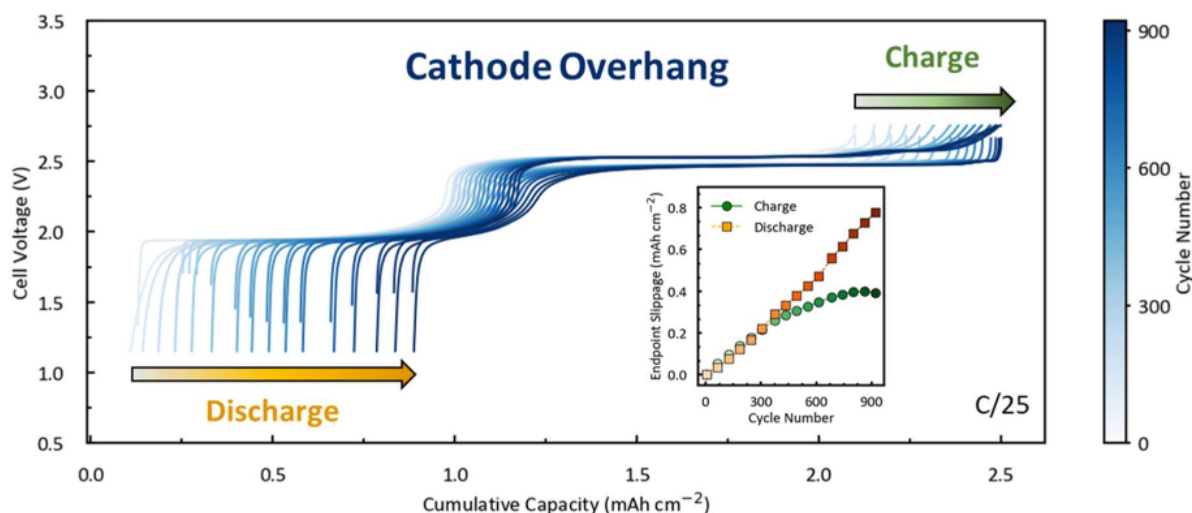


Figure 18. Capacity-voltage hysteresis plots at C/25 rate for LMFP64/LTO cells with cathode overhang, during 900+ cycles at 30 °C. Inset shows the change in charge and discharge endpoint slippage with cycle number.

Conclusions

This study systematically investigates the electrochemical behavior, impedance characteristics, and long-term stability of lithium manganese iron phosphate ($\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$, LMFP64) cathodes paired with lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) anodes in lithium-ion cells. Using a combination of half-cell, three-electrode, and coin-cell configurations, along with post-cycling physicochemical analyses, the work provides fundamental insights into the intrinsic redox processes, kinetic limitations, temperature effects, and degradation mechanisms relevant to this cobalt- and nickel-free, high-voltage battery chemistry. The findings highlight critical factors affecting performance and lifetime, offering guidance for optimizing LMFP-based systems for electric vehicle applications.

1. **Electrochemical Characteristics:** LMFP64 cathodes deliver initial capacities near 150 mAh g^{-1} with clearly defined $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox plateaus, and excellent rate capability, retaining over 90% capacity at 1 C versus low-rate cycling.
2. **Voltage Hysteresis Origin:** Pronounced hysteresis in the Mn-redox plateau is linked to thermodynamically distinct local environments and unfavorable $\text{Li}^+-\text{Fe}^{3+}$ and $\text{Fe}^{3+}-\text{Mn}^{2+}$ interactions in the mixed-metal LMFP lattice, persisting even at very low cycling rates.
3. **Impedance Dynamics:** The LMFP64 electrode dominates cell impedance, which varies strongly with state of charge. Highest impedance is observed in the Mn-to-Fe redox transition region, caused by coexistence of multiple phases and elevated lithium-ion migration barriers. Increased temperature reduces impedance, particularly in Mn-redox and transition regions, improving kinetics.
4. **Rate-Dependent Phase Behavior:** At high C-rates, shortened redox plateaus and broadened intermediate voltage regions indicate non-equilibrium phase transformations. This kinetic limitation is compounded by microstructural heterogeneities and surface reaction layers, leading to smeared redox features.
5. **Thermal Aging and Degradation Mechanisms:** Capacity fade under elevated temperature cycling primarily results from parasitic side reactions at the LTO anode interface, consuming cyclable lithium and producing surface films containing electrolyte decomposition products.
6. **Electrode Overhang Effects:** Cathode-overhang cells demonstrate superior capacity retention (<1% fade after 300 cycles) compared to anode-overhang cells (~9.5% fade). The excess lithium inventory available in the cathode overhang compensates for the irreversible lithium loss to the anode SEI that occurs during cycling.

7. **Structural and Surface Stability:** Postmortem XRD confirms the bulk crystal structure of LMFP64 remains intact after long-term cycling and thermal aging, although surface lattice distortions and cation disordering may increase impedance. LTO anodes maintain structural integrity but accumulate surface films that marginally reduce capacity.

Together, these results establish a comprehensive understanding of the interplay between redox chemistry, impedance evolution, and degradation phenomena in LMFP64/LTO lithium-ion cells. This knowledge is critical for guiding material and cell design improvements aimed at delivering batteries with high voltage, power, and durability for electric vehicle and other energy storage applications.

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