A bio-inspired approach to increase device-level energy density

by

Alan Ransil

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Submitted to the Department of Materials Science and Engineering on April 13, 2018, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

Battery research has historically focused on improving the properties of the active materials that directly store energy. This research has resulted in active materials with higher specific capacity, increased the voltage of batteries in order to store more energy per electron, and lead to the development of electrolytes and binders compatible with high-performance active materials. However, Lithium-Ion Batteries (LIB) are nearing the limits of energy density achievable using a traditional battery design. Structural batteries are a fundamentally distinct route to optimize device performance, aiming to replace structural materials such as metals, plastics, and composites with multifunctional energy-storing materials. By increasing the device mass fraction that is devoted to energy storage, this strategy could more than double the battery life of electronic devices without requiring improved active materials. In this thesis, I show that rigid, load-bearing electrodes suitable for structural batteries can be fabricated using a novel silicate binder. This binder can be used to distribute load both within layers and throughout the battery by adhering adjacent battery layers. This innovation turns the entire battery stack into a novel monolithic engineering ceramic referred to as a Structural Ceramic Battery (SCB). Unlike previously published binders, this material does not soften with the introduction of electrolyte, it promotes charge transport within the electrode, and it is compatible with a range of active materials employed in batteries today. This thesis furthermore outlines versatile manufacturing methods making it possible to produce SCBs with a wide variety of shapes and form factors amenable to large-scale production. It is envisioned that this SCB architecture will be
used to improve the energy density of both ground-based and flying electric vehicles, and
that as improved active material chemistries are discovered they will be dropped in to this
architecture in order to promote future increases in vehicle-level energy density.

Thesis Supervisor: Angela M Belcher

Title: Professor of Biological Engineering and of Materials Science and Engineering
Acknowledgements

"I may be wrong and you may be right,
and by an effort, we may get nearer to the truth."

- Karl Popper, *The Open Society and its Enemies*, 1945

I showed up in Angie's office in 2012 wanting to work on new battery architectures, and she was willing to spend years mentoring me and helping me grow as an engineer. Angie's research group is a unique place where it feels like anything is possible. Her ability and desire to foster a culture of unbounded creativity allow us all to envision and work towards genuinely new solutions to consequential problems. Working as a graduate student in her lab has been an immense privilege, and want to thank her for tremendous insight and mentorship over the course of my degree.

Professors Yang Shao-Horn and Niels Holten-Andersen have likewise helped me a huge amount during my PhD. Their perspectives on solving electrochemical and mechanical problems have repeatedly given me unexpected ideas, challenged me to solve problems in new ways, and shown me flaws in my thinking to help me strengthen my work.

I'm grateful to the whole Belcher group for helping me with tasks as mundane as finding the alconox to ones as esoteric as applying Popperian epistemology to puzzling experimental results. Throughout my PhD Jackie has worked alongside me, sharing her genius solutions to phage-based problems I was struggling with that she had already solved. Dahyun (now Professor Oh) taught me how to amplify phage, how to make biotemplated battery materials, designed many of the protocols I used during my PhD, and would help me better understand what my batteries were doing. Maryam would always give me insight about my results and what to try next. Geran has frequently helped me troubleshoot problems I was having in lab. Nimrod would help me brainstorm new ideas and come up with solutions to experimental issues. It is amazing how much Jifa knows about getting experiments to work, and he would always help me with my synthesis woes. Shuya has a wealth of electrochemical knowledge, and has helped me improve my experimental setup immensely. Uyanga has come up with brilliant solutions to short phage problems. Briana likewise invented new phage constructs that made progress in our DARPA program possible. Nir would help me work through why my batteries were behaving the way they were and figure out what to do to fix them. Thank-you to Griffin for being our group's safety EHS representative; you make it look easy but I'm sure it's not. Col. Burpo came up with the protocol for biotemplated nanofoams that I spent much of my time working on and alerted
me to the tremendous gains that structural batteries could make possible. Ngozie has an amazing knack for knowing what avenue of research to explore (even when I doubted it - I'm still amazed about the phosphides). And thank you to Peter Jansen for keeping me from taking myself too seriously.

The undergraduates I've worked with have not only helped me get science done faster but given their own insights that have helped shape my work. Thank you to Saleem, Fauziah, Akshay, Sam and Isaiah.

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A great number of people have helped me better contextualize materials research in terms of its impact, and better understand how to bring materials out of the lab. Thank you to Changqiong Zhu, Rupak Chakraborty and Wenhao Sun for working with me to bring materials into the 'real world.' Kieran Strobel has shown me how to solve problems in Aerospace and I hope to continue working with him to realize the potential of SCBs. Stephen Steiner has shown me how much you can do with a deep determination to bring materials to market. Mark Edwards has supported both me and Stevie immensely. Francis O’Sullivan has continually helped me to better understand the economics of energy markets, what problems are important to solve, and why. Carlos Solares has mentored me in the business of making materials. Also thank you to Karen, Leon, Amy and Cory at the Deshpande center for not just funding part of my research but supporting us as we move towards a structural battery that can enable new vehicle designs.

Many of my former mentors taught me lessons that were often remembered during my PhD. Among these are Yet-Ming Chiang, Billy Woodford, Michael McGehee, Richard Cushman, Carol Stanton, Jack Coakley and Diane Munroe.

It would feel strange not to mention some of the people who have had a huge intellectual effect on me, but who I've never met and won't appear in the citations below. In this category I’d like to acknowledge Karl Popper, Steve Grand, David Deutsch, Naomi Oreskes, Dan Ariely, James Baldwin, Philip Pullman, Thomas Piketty, Vannevar Bush, Robert Reich, Arlie Russell Hochschild, Timothy Snyder, and Eddie Izzard.

I grew up in an environment that felt a lot like Angie’s lab, in that creativity was encouraged and I was able to learn and build anything as long as I cleaned it up afterwards. As a result, I was able to study chemistry (burning things, water electrolysis, acid and base reactions, crystal growth), physics (building motors from scratch, a bed of nails, Ruben’s tube, the magic of siphons), biology (lizards, frogs, earthworms, dissecting squid, gardening), filmmaking, and history (historically themed dinner parties) throughout my childhood. Thank you Mom, especially for the time you homeschooled me. Thank you Dad for never answering questions with “because.” Thank you Bryan for putting up with me and being my partner in crime.
Finally, I want to thank Chelsea. We got engaged six months after I started in the Belcher group, and were married in 2014. It’s striking how many of the things we dreamed of then, like getting a dog together, are real parts of our life now. I of course want to thank Chelsea for supporting, being there for, and helping me on the winding and difficult road that is graduate school. What I want to thank her more for is having faith in me throughout. And most of all, I want to thank Chelsea for sharing her life with me, pushing me to be better, and valuing growth over validation. I am so lucky to have found you.
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1. Introduction: the case for structural energy storage

The dominant design paradigm in most engineering is to use modular components. These can be optimized for a single use, can be easily repaired or modified without requiring an overhaul of the entire design, and because of the restricted interactions between modular components they lead to devices which fail non-chaotically. By contrast, in the natural world we frequently find that living systems are composed of multifunctional components.

In this section, I will discuss multifunctional materials in the context of natural systems, suggest why we find them in natural compared to rationally designed systems, and outline where we might profitably expect multifunctional materials to improve the properties of devices. I will then discuss the benefits of applying a structural energy storage paradigm specifically to cars and aerial vehicles.

1.1. Multifunctional materials in nature

Multifunctional materials are those which are not designed to fulfill only one role, but have multiple distinct roles in the system to which they belong. These materials are extremely common in the natural world, in which many of the materials that make up living systems play multiple distinct roles. Figure 1 gives several examples. One notable design parameter is that energy storage tends to be highly distributed in living systems, with carbohydrates being found throughout their tissues. Structural materials frequently fulfill multiple roles, such as storage and distribution of energy in the case of wood and production of blood
and immune cells in the case of bone. In addition, many of the tissues which fulfill distinct roles such as thermally insulating blubber and actuating muscle can be broken down in order to provide energy. To highlight how alien this concept is in the context of rationally designed materials, such a design choice might be akin to a car engine burning itself in order to keep going once it runs out of gas. The engine wouldn’t suddenly break down once this begins, but would simply shrink and become less powerful until either there is no engine left or until you reverse the process by refueling.

Figure 1: Examples of multifunctional materials in living systems. (a) wood provides structure to trees, as well as storing and distributing sap and nutrients. (b) Marine mammal blubber functions as both energy storage and thermal insulation. (c) muscles serve as actuators, distributed short term energy storage, and can act as long term energy storage which may converted via catabolism. (d) bones are multifunctional materials that both provide structure and produce blood cells.

It should also be mentioned that these multifunctional biological materials frequently achieve their functionality due to a complex multiscale composite architecture. Wood and bone, for example, are cellular materials with cells containing sap and marrow respectively that are vital for the emergence of their multifunctional behaviors. The veins permeating
fatty tissue are necessary for their growth and their conversion into fuel for the rest of the body. Multifunctionality is also built in at many length scales: muscle fibers have their own complex protein structure and the chemical composition of fat and muscle is the basis for their ability to store energy. Similarly, complex multiscale architectures will be important in the rational design of multifunctional materials and their chemical composition will be pivotal.

1.1.1. Where should we expect to find multifunctional materials?

Why are rationally designed structures frequently composed of modular, single-function components and when should we expect a design process to result in multifunctional architectures \textit{a priori}? Under what circumstances should we employ multifunctionality in our designs? This subsection and the following subsection will hazard answers to these questions.

Figure 2 is a schematic of an evolutionary process to design a system. In this schematic, the behavior of the whole system (in blue brackets) emerges from the attributes of individual components and the interactions these components. According to this design strategy, attributes of the system are varied randomly and choice is made based on the emergent behavior of the entire system. During each design cycle (which may be, for example, the life cycle of an organism or one round of bio-panning in phage display), the system receives either a passing grade or a failing grade from the environment. If the system survived, its attributes are then randomly mutated and another round of selection occurs.
Figure 2: Evolutionary design of an organism, where the organism itself is enclosed in blue brackets. While the organism may be composed of many components and these components may each have a large number of relevant attributes, the evolutionary test is done on the emergent system level. We should thus expect multifunctionality rather than modularity.

Because the testing in this paradigm is done on the level of emergent system behavior, we should expect groups of components and their attributes to contribute to a functioning system. We should not necessarily expect the components to have well-defined individual roles. This is of course observed in biology outside of biomaterials. Individual genes, for example, frequently exhibit pleiotropic effects. This means that their mutations affect many attributes of an organism rather than one single attribute.

Rational design processes also test devices at the emergent system level, but they
exhibit another design stage as shown in figure 3. Here is shown a design paradigm in which the “field test” or physical experiment is analogous to an evolutionary test. This is a test done of the actual system in the real world. But the system is also tested during the design process in the head (and frequently in the computer) of whoever is designing it. This ‘Thought Experiment’ process, shown in green, represents that design stage.

Figure 3: Rational design, in which a thought experiment performed using mental or computational models is incorporated. This design step acts on the level of individual components and attributes, and can thus optimize individual components. Furthermore, because mental and computational models may become less accurate as the number of interactions grows, limiting interactions between components may reduce discrepancy between the model and real-world behavior. It is suggested that these two effects drive the use of modular architectures in rational design.

From looking at the diagram in figure 3, it should be apparent that the rational design
process is able to act on the level of individual system components and their attributes. This is in contrast with the evolutionary process, which tests only the overall emergent system behavior. The actual internal workings of the system are a black box from the point of view of environmental evolutionary tests, and failing an evolutionary test (i.e., the organism dying) doesn’t result in any actionable information as to which component attributes to change or how to change them. By contrast, thought experiments do use models incorporating individual system components. When a design fails a thought experiment, this does provide actionable information as to what attributes to vary. Rational design is thus able to optimize components and attributes directly, which we would expect to lead to modularity. Indeed, a rationally designed system may be able to find performance maxima by optimizing modular device components that evolutionary systems would take much longer to find by simple brute force search.

Hypothesis 1: Rational design is able to optimize individual device components in a way that evolution cannot achieve efficiently, because individual components and their attributes are directly exposed to mental models.

A second hypothesis as to why rationally designed systems lead to modularity has to do with the interactions between components. The thought process stage can be done quickly and cheaply compared to experiments in the real world. However, it has limitations. It relies on mental and computational models of the system in place of the real-world behavior of the system itself. Because every relevant interaction between system components must
be incorporated into the model, the model may become less accurate from the system's real
behavior as the number of interactions is increased. Assuming that every component is able
to interact with every other component, the number of interactions between $N$ components
will be $\binom{N}{2}$ ("$N$ choose 2"), or:

$$\text{Interactions} = \frac{N!}{2(N - 2)!}$$

Because of the potentially large number of components, attributes and interactions,
the system-level behavior may be difficult to model accurately. It may even diverge chaot-
ically from real-world behavior with respect to changing individual attributes. One ap-
proach to avoid this is to limit the number of interactions between components: to prevent
components from interacting more than is necessary. This would favor meeting design
requirements, to the extent that this is possible, through the properties of individual com-
ponents instead of by many-component interacting assemblies. This describes a modular
architecture.

_Hypothesis 2: Rational design minimizes interaction between components in order to
improve the agreement of mental and computational models with real system behavior._

It should be noted that this link between modularity and chaotic system behavior would
be expected to drive the use of modular components in evolutionarily designed systems as
well. Modular design has been extensively documented in evolutionary biology, and there
continues to be disagreement about its origin [34, 172, 188].
1.1.2. When should we employ multifunctional materials?

The previous subsection outlines the benefits that can be gleaned from a modular design approach. Are there benefits to a multifunctional approach, and in what situations should we expect these benefits?

Returning to the models for evolutionary and rational design paradigms shown in figures 2 and 3, we can think of each system component as exhibiting a set of attributes. In a purely modular case, where each system component has one function, we might imagine a utility function in which total device performance is the sum of the utilities of each component:

\[ Utility = \sum_{i=1}^{N} M_i (B_i + C_i) \]

In this sum, \( M_i, B_i \) and \( C_i \) are the Mass, Benefit, and Cost of component \( i \) respectively. They may have the same units in a simple utility function, or they may have different units (making Utility multidimensional) depending on the analysis. In any case, Mass, i.e. a measure of how much of component \( i \) is present in the design, scales both \( B_i \) and \( C_i \). In this model, as we choose components with different attributes those attributes will affect both \( B_i \) and \( C_i \).

The crucial element here is that available materials impose design tradeoffs on the values of \( B_i \) and \( C_i \). In a modular design, we might just pick the material with the best combination of \( B_i \) and \( C_i \) to fulfill the role that component \( i \) plays in the design. This
strategy would fail when available materials are insufficient to meet the design criteria: when \( B_i \) is too low or \( C_i \) is too high. In this case, one route available would be to use multifunctional materials. If material \( i-1 \) can confer a benefit that effectively increases \( B_i \) without increasing \( C_{i-1} \) or \( C_i \), then a multifunctional design would be optimal.

For example, a battery is a component of a device conferring both stored energy \( B_{\text{Battery}} \) and weight \( C_{\text{Battery}} \). If you are an engineer aiming to design an Unmanned Aerial Vehicle (UAV) capable of flying for two hours on a single charge, there may be no modular design able to fulfill this design criterion along with whatever other criteria (for example, wingspan) you are aiming to hit even if you choose the best battery currently on the market. A multifunctional design, in which some of the structure stores energy, may circumvent this limitation.

Thus, **multifunctional materials would be expected to optimize performance when the optimal materials choice is insufficient to meet design criteria within the constraints of a modular design.**

When we believe that we are approaching fundamental limitations on the performance of materials used in devices and exceeding those limitations would in theory enable better performance, this should spur the development of multifunctional options. Physical and chemical limits on the energy density of metal ion batteries fall into this category.
1.2. The limits of electrochemical energy storage for vehicles

The energy density of batteries has increased steadily since lithium ion batteries (LIBs) were commercialized in 1991. However, there are good reasons to believe that intercalation batteries will reach the physical limits of their energy density. Energy density is voltage times capacity:

\[ \int_{SOC} Vdq \]

in which \( V \) is the battery cell voltage, \( q \) is specific capacity (for example in Ah/kg) and the integral is taken over the entire state of charge (SOC) range, ie. from fully charged to fully discharged. Battery capacity is expected to be limited because both \( V \) and \( q \) are likely to show diminishing returns with future improvements in intercalation battery performance.

Starting with improvements in \( V \), the lowest possible voltage for a LIB negative electrode is that of metallic Li. This is already the subject of extensive research and some recent product announcements. Table 1 shows the standard reduction potentials of some candidate working ions. In order to increase the voltage of a battery, this reaction should have an extremely positive or negative value. As shown, Li exhibits the lowest reduction potential of feasible redox couples. Elements with highly positive reduction potentials could in principle be used as well, in which case the elemental electrode would be positive. For example, F could theoretically be used to make batteries with a voltage comparable to Li
or Na but presents severe safety challenges. There are relatively few candidate working ions at these positive potentials, and they would not in any case be likely to allow substantially higher voltage systems than Li.

<table>
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<tr>
<td>(Li^+ + e^- \rightleftharpoons Li)</td>
<td>-3.04 V</td>
</tr>
<tr>
<td>(K^+ + e^- \rightleftharpoons K)</td>
<td>-2.93 V</td>
</tr>
<tr>
<td>(Ca_2^+ + 2e^- \rightleftharpoons Ca)</td>
<td>-2.87 V</td>
</tr>
<tr>
<td>(Na^+ + e^- \rightleftharpoons Na)</td>
<td>-2.71 V</td>
</tr>
<tr>
<td>(Mg_2^+ + 2e^- \rightleftharpoons Mg)</td>
<td>-2.37 V</td>
</tr>
<tr>
<td>(Al_3^+ + 3e^- \rightleftharpoons Al)</td>
<td>-1.66 V</td>
</tr>
<tr>
<td>(Zn^+ + e^- \rightleftharpoons Zn)</td>
<td>-0.762 V</td>
</tr>
<tr>
<td>(Cl_2 + 2e^- \rightleftharpoons 2Cl^-)</td>
<td>+1.36 V</td>
</tr>
<tr>
<td>(F_2 + 2e^- \rightleftharpoons 2F^-)</td>
<td>+2.87 V</td>
</tr>
</tbody>
</table>

Table 1: Standard reduction potentials of some candidate working ions against a standard hydrogen electrode. Li has the lowest reduction potential of any practical system. On the opposite end, fluorine-based systems pose extreme safety challenges.

On the positive electrode side, stability limitations of bulk materials limit the voltage of batteries. The standard reduction potential of lithium peroxide in aprotic solvent, \(Li_2O_2 \rightleftharpoons 2Li + O_2\), is 2.96V vs. Li metal [15]. While some oxygen-containing transition metal compounds are more stable, many release oxygen at voltages above 4.5V (vs. Li
metal). This is observed, for example, in high voltage 'oxygen loss' layered oxides \cite{61} and other high voltage electrode materials such as pyrophosphates \cite{154}, and poses a thermodynamic limitation on increasing the voltage of LIBs.

A third limitation on LIB voltage comes from electrolytes. Commonly used aprotic electrolytes are not stable even across the voltage range used in batteries today, with stable cycling being the result of a passivating solid electrolyte interphase rather than thermodynamic stability. \cite{23, 104, 187, 194} Increasing this stability window through more stable liquid electrolytes, solid electrolytes and passivating coatings may result in improvements in voltage and therefore energy density. However, this seems unlikely to result in large improvements (ie. a doubling) in energy density without some genuinely new strategies.

On the capacity side, several strategies have been identified that could result in capacity improvements such as using metal-air batteries, sulfur-based chemistry, and multivalent working ions. A review of these efforts is beyond the scope of this thesis. These efforts do have the potential to at least double the capacity of batteries compared to today’s state of the art. They are limited, however, by the mass of the anion-working ion complex used. In developing SCBs, we have aimed to build an architecture that is compatible with these chemistries so that they can be integrated into a structural design as improvements are realized.

Overall, there are a set of theoretical limitations on improvements in battery energy density imposed by thermodynamic stability and the choice of materials. This situation—in which performance of many devices is limited by battery energy density and that energy
density is fundamentally limited by the choice of single-function materials – motivates the development of multifunctional materials.

1.3. Structural batteries in ground vehicles

An illustration of the potential of structural batteries to improve vehicle performance comes from an analysis of electric cars. As shown in figure 4, the theoretical energy density of the active materials used in Tesla’s batteries is 533 Wh/kg, taking the capacity and voltage of the NCA/graphite redox couple. This corresponds to the energy density of an ‘ideal’ battery made only with the active materials involved in the LiNi0.8Co0.15Al0.05O2 + C6 ⇌ Ni0.8Co0.15Al0.05O2 + LiC6 reaction. Packaging these materials into a battery requires the addition of ‘inactive’ materials such as current collectors, separator, electrolyte and cell casing required for battery operation but not directly involved in storing energy. These materials lower the energy density at the cell level to about 230 Wh/kg [84, 109]. The battery pack, composed of thousands of cells, a cooling system and a battery management system, has an energy density of about 160 Wh/kg. [104, 185] Meanwhile the vehicle-level energy density, taking the battery pack capacity divided by the curb mass of the unloaded vehicle, is about 40 Wh/kg.
Figure 4: Progressive reduction in the energy density of the energy-storing components of a Tesla model S. Battery active materials refer to the NCA/graphite redox couple used in the battery. Battery Cell is based on Panasonic 18650. Battery pack is based on an 85 kWh Tesla Model S pack. Model S vehicle is based on the energy in the 85 kWh pack divided by total vehicle mass. Each packaging step introduces more inactive material which is not involved in energy storage. Using structural battery, energy storage materials may replace some of the inactive components and increase the overall vehicle energy density.

This demonstrates that there is in principle scope to replace components of the automobile with energy storing material, in order to increase vehicle-level energy density using a structural battery. Figure 5 analyzes the feasibility at a subsystem level, showing that in principle about 36% of the vehicle mass might be replaced. It should be noted that the battery pack shown in these pie charts has an energy density of about 160 Wh/kg.
whereas the structural battery may have an energy density closer to the cell level of about 230 Wh/kg. Furthermore, because the structural battery will have a high surface area, it is envisioned to not require heavy cooling systems as cells in battery packs do. This could increase the range of the vehicle by a factor of two to three, without requiring advances in active materials level energy density.

![Figure 5: Mass breakdown of a Model S in order to evaluate the feasibility of replacing components of the vehicle with structural battery. (a) Subsystem mass fractions of Model S components, from [5]. (b) Mass fraction that might be replaced in principle.](image)

1.4. Structural batteries in airborne vehicles

Structural batteries have a substantial potential to impact airborne vehicles. Following [159], the equation for the endurance of an electric-motor propelled winged aircraft is:
Here, $t_e$ is endurance (i.e., flight time), $E_B$ is the energy contained in the battery system (multiplied by the round-trip efficiency, which will be ignored for this analysis), $M$ is the total system mass, $\rho$ is the density of air, $S$ is the wing area, $C_L$ and $C_D$ are the lift and drag coefficients, and $\eta_p$ is the propeller efficiency. If we modify this vehicle by including a structural battery but maintain its aerodynamic shape, we can take $E_B(x)$ and $M(x)$ to be functions of the amount of multifunctional material included. Differentiating these, we get:

$$\frac{dt_e}{dx} = \left[ \frac{dE_B}{dx} M^{3/2} - \frac{3}{2} \frac{dE_B}{dx} M^{-5/2} \frac{dM}{dx} \right] \cdot \left( \frac{\rho S C_L^2}{2 C_D^2} \right)^{1/2} \cdot \eta_p$$

Making a finite design change $\Delta x$, we can normalize the change in endurance $\Delta t_e$ by the initial endurance to get:

$$\frac{\Delta t_e}{t_e} = \frac{\Delta E_B}{E} - \frac{3 \Delta M}{2 M}$$

Equations 1 and 2 quantify how design decisions on battery mass and weight affect flight time. In particular, we can break the total vehicle mass down into battery mass and the mass of non-energy-storing systems.
\[ M_{Total} = M_0 + M_{Batt} \]

In which case, battery energy is the product of battery mass and the specific energy \( C_{sp} \):

\[ E_B = C_{sp} \cdot M_{Batt} \]

This makes it simple to calculate the dependence of endurance on battery mass. Two cases for this are shown in figure 6. In figure 6a, endurance is shown as a function of the ratio of battery mass to \( M_0 \). Interestingly, endurance shows a maximum at \( M_{Batt}/M_0 = 0.5 \). Thus, increasing the battery mass fraction beyond 33% of total vehicle mass lowers endurance. This follows from equation 2, which shows that fractional increases in mass fraction are more heavily weighted (by \( 3/2 \)) than fractional increases in stored energy. However, using a multifunctional material to replace structural mass with energy storing mass increases endurance. This is shown in figure 6b, which assumes that total vehicle mass remains constant and the mass fraction devoted to battery simply increases (at constant \( C_{sp} \)). Following equation 1, the endurance increases linearly.
Figure 6: Effect of structural battery addition on UAV endurance for winged vehicles. (a) At constant specific energy, endurance decreases when the ratio of battery mass to non-energy-storing mass exceeds one half. (b) At constant total vehicle mass, replacing structural mass with multifunctional energy storing material increases range. (c) An analysis of the effect of structural battery design on a Raven UAV, from [136], for different fractions of total mass replaced by structural battery.

Work has been done in the literature applying these principles to UAV design [136, 159–161]. Figure 6 shows the result of an analysis on the Raven UAV, a popular military vehicle manufactured by Aerovironment. [136]. They estimate that it should be possible to increase endurance in this UAV design by more than a factor of two (ie. 100% increase).
2. Strategies for structural energy storage

In the existing literature, several strategies exist for taking advantage of a structural energy storage architecture. Published work spans approaches involving no modification to the battery architecture at all but simply transferring load to off-the-shelf architectures, to transferring load to current collectors, to modifying actual battery electrodes to bear load. Extensive work has been done on the use of carbon fiber as an anode for structural batteries and as an electrode for structural capacitors. In addition, much has been published on modifying polymers in order to serve as binders in structural batteries. This section will provide an overview of all these strategies, then introduce the Structural Ceramic Battery (SCB) design and highlight its benefits.

2.1. Transferring load to conventional batteries

Mechanical and Aerospace engineers have long shown interest in the structural battery concept. A strategy they have used to achieve structural energy storage is to simply design vehicles to transfer load to off-the-shelf batteries. Research in this area doesn’t require re-design of the actual battery electrodes or impose any electrochemical trade-offs.

Aerospace engineers have historically shown particular interest in this approach, due to the high cost of launching satellites into space and the resulting benefit of any technology that could be used to lower their mass. One example was developed at the University of Southampton, focusing on spacecraft sandwich panels. [39, 131] As shown in figure 7
(a), lithium polymer batteries were purchased and built into panels. A similar design was demonstrated at the National University of Defense Technology using foam core sandwich panels with similar lithium polymer cells. [179]

More recent work has shown that batteries might be used to absorb mechanical energy in the case of an electric car crash, by connecting the cells in a ‘butterfly’ arrangement designed to function as a crumple zone as shown in figure 7 (b-c) [173]. The goal of this architecture is to transfer load to cells and joints between them so that a crash can occur without rupturing the cells. If successful, this architecture will lower the mass of structural materials required in a vehicle crumple zone. A similar strategy incorporated batteries into a vehicle crumple zone by placing sacrificial tubes between the cells. [103] This was considered a multifunctional, energy-absorbing battery pack.

Figure 7: Strategies for using conventional batteries as structural elements. (a) Spacecraft sandwich panels were developed to transfer load to off-the-shelf batteries as detailed in [39, 131]. (b-c) Batteries were connected in a 'butterfly' architecture in order to safely absorb mechanical energy in a vehicle crumple zone. The structure is shown in both the initial configuration (b) and after absorbing load (c). Scale bars are 2cm. [173]. (d) A prototype of the Wasp UAV employing custom-shaped Lipo cells as structural wing skins. [160, 161]
This strategy has also been applied to Unmanned Aerial Vehicles (UAVs). Prototypes of the Wasp UAV employed shaped cells using a PVDF-HFP binder developed by Bellcore as shown in figure 7 (d) [160]. Publications noted that the costs associated with custom cell designs were a significant barrier to adoption of this strategy [161]. Clearly, any technology aiming to make structural batteries commonly used will require facile production methods in order to lower the unit costs associated with custom runs. It should be noted that the Wasp is now a production UAV manufactured by Aerovironment, and that the production version does not feature a structural battery design. My conversations with an engineer at Aerovironment pointed to the complication and cost of manufacturing outweighing the benefit in this case. Improvements in the performance of structural batteries and their manufacture may change the cost-benefit calculus in the future.

Other work showed that thin film batteries could be embedded directly into carbon fiber reinforced plastic sheets [112]. These cells were able to withstand the processing conditions necessary to produce full composites and cycled normally when the composite was subjected to 450 MPa tensile load.

It should be noted that this strategy, to transfer load to off-the-shelf batteries, is not on the face of it unlikely to provide significant performance improvements. Batteries that are not optimized as structural elements should not be expected to bear much load, or to be efficiently integrated into vehicles. The theoretical performance improvement of a structural battery strategy derives from electrode components bearing structure, and to the extent that batteries are not optimized to transfer load to electrodes they will not achieve
their full potential. The Wasp project, for example, projected only a 26% performance improvement [168] by transferring load to an off-the-shelf battery, far short of the projected improvements discussed above.

2.2. Transferring load to current collectors

A recent structural battery strategy, explored as part of the ARPA-E RANGE program, is to transfer mechanical load to the current collectors of a battery. [143, 195] This strategy lies mid-way between a true structural battery in which electrodes are re-designed to bear load, and an off-the-shelf battery used for structure as discussed above.

The design, shown in figure 8, includes a conventional battery stack fabricated in a metal panel. Current collectors of 9 µm thick copper (negative) and 15 µm thick aluminum (positive) foil were coated with conventional NMC and graphite electrodes made using PVDF binder. These were mechanically attached to the battery casing so that external loads would be transferred to these foils. The stack was laminated together with Celgard separator, and the entire battery panel was sealed using epoxy. After fabrication and drying, the battery was filled with electrolyte and the filling port was plugged.
Figure 8: A design for transferring external load to the current collectors of a battery. \[143, 195\] (a) The basic design, showing parallel battery layers with current collectors mechanically bonded to a metal casing. (b) This battery was loaded in the plane of the current collectors during testing. (c) A cross-section showing the layers of battery material in this prototype. (d) The finished prototype forms a panel that might be integrated as a load-bearing element of vehicle structure.

This design achieved an energy density of 102 Wh/kg and a bending stiffness of 1995 N/mm. [195] Three-point bending results were not significantly affected by the addition of electrolyte, and performance of these tests did not substantially affect electrochemical properties.

This design exhibits some substantial benefits. It is clearly compatible with a wide range of battery chemistries, is conceptually simple, and achieves respectable energy den-
sity and mechanical properties (though less than half the energy density of state-of-the-art battery cells). However, there are some theoretical and practical drawbacks to this work. Firstly, because load is being transferred to the current collectors and not the electrodes, the structural performance of this design will be limited by the current collector volume fraction. This inherently poses a trade-off between electrochemical and mechanical performance. Secondly, the cell may only be loaded in the transverse direction as shown in figure 8b. In directions perpendicular to the plane of the current collectors, they will not effectively increase the rigidity of the battery. The third concern is the manufacturability of these cells in arbitrary shapes. It is envisioned that during the design process, engineers will require cells of many shapes to be produced in order to evaluate structural battery enabled vehicle prototypes. It is not obvious that this battery design could be easily manufactured to accommodate arbitrary shapes, particularly curved shapes such as those required for UAV wings or automotive panels.

2.3. Carbon fiber electrodes

As graphitic carbon fiber (CF) is a high-performance structural material and graphite is commonly used as a Lithium Ion Battery (LIB) negative electrode, it is natural to investigate CF as a multifunctional LIB active material. Much of the work done to date on structural LIBs has employed this strategy.

Extensive work has been done evaluating the fundamental electrochemical and mechanical properties of various CFs for structural battery applications. As shown in figure 9a,
the reversible capacity of carbon fiber in a LIB half-cell is typically about 100-150 mAh/g depending on the variety of carbon fiber used. [76, 145] This is in contrast with a theoretical capacity of 372 mAh/g, or about 34% of theoretical. This capacity is plotted against specific strength in figure 9b.

The electrochemical origin of the relatively low specific capacity of graphite fiber is an interesting area of debate. One potential origin is lithium diffusion into and out of the fibers limiting electrochemical utilization. As shown in figure 9c, the diameter of individual carbon fibers is under 10μm. This is below the average particle diameter of graphitic mesoporous carbon microbeads used in batteries, with a median value of 17μm. [21]. However, as in-plane lithium diffusivity in highly oriented graphite is four orders of magnitude higher than diffusivity perpendicular to the graphitic planes [113], orientation of graphite sheets parallel to the axis of CF may play a role in preventing full graphite utilization. As the tensile strength of graphite is also anisotropic, and higher in the plane of the graphite sheets [90], the orientation of graphite along a carbon fiber imposes a trade-off between mechanical strength and electrochemical charge transport. Studies measuring the diffusivity of Li⁺ in CF have indeed shown a variation of about four orders of magnitude from $10^{-6}$ cm²/s to $10^{-10}$ cm²/s, [76, 152, 165, 167] suggesting that varying degrees of orientation play a substantial role in determining diffusivity.

A second origin for the poor electrochemical utilization of CF may be the area-specific loading of these materials. A 3K weave T300 tow, among the highest performing CF samples electrochemically evaluated, has a weight of 5.75 oz/yd² [18] or 19 mg/cm². This
is a high active material loading, corresponding to an area specific capacity of 2.9 mAh/cm² at a nominal capacity of 150 mAh/g. This corresponds closely to the area specific capacity of commercial electrodes, [47] with a maximal area specific capacity dictated by lithium ion diffusivity through battery electrode and separator layers. If this weave could achieve higher active material utilization at low rates, therefore, it would not be able to achieve higher than 150 mAh/g at typical cycling rates. Thinner carbon fiber weave with a lower loading may thus be better optimized for structural battery performance. It should be noted that in the case of carbon fiber used as a structural element, the fiber is coated in a non-lithium-conducting epoxy. This layer was not present in the half cells evaluated in figure 9, and add an additional barrier to the practical use of CF as a multifunctional negative electrode active material. Development of lithium conductive adhesives will be discussed in the following section.

![Graph and image](image)

Figure 9: Evaluation of carbon fiber (CF) used as a negative electrode in LIBs evaluated in [45]. (a) Cycling data of various CFs in a half cell, cycled at 1.7μA/cm². The material achieves about 34% of the 372 mAh/g theoretical capacity. (b) Specific capacity of various CFs plotted against specific strength. (c) A scanning electron micrograph of an individual carbon fiber shows that the fiber diameter is under 10μm.
Several published projects have used carbon fiber negative intercalation electrodes in structural LIBs. Some of the earliest structural battery work, done at the Army Research Lab, used this architecture. To date, the highest performing packaged structural battery cell uses such an architecture as well, achieving 116 Wh/kg and 35 GPa stiffness with a carbon fiber negative electrode, a lithium iron phosphate positive electrode, and a gel electrolyte. It should be noted that while energy density is given, more extensive electrochemical data are not.

Another interesting tactic that uses a CF weave is to electrodeposit a separator directly onto the CF tow. This has been demonstrated and even used to make an interpenetrating battery by subsequently adding positive electrode slurry. This is a novel approach that may be built upon in the future development of structural LIBs.

Overall, the performance of CF as a structural battery material is excellent from a structural point of view but mediocre electrochemically. This is partially due to the low (under 45%) electrochemical utilization of graphite in carbon fiber under reasonable cycling conditions. In addition, it should be noted that a structural battery design relying on a single active material will not be able to make substantial electrochemical performance improvements as batteries improve. A structural battery architecture is desired which is able to accommodate new active materials as they become available, improving in specific energy along with the state of the art.
2.4. Structural polymer-based binders

A major focus in structural energy storage work has been to produce a polymeric binder material that is able to contribute to battery structure while promoting ion transport. These two requirements are somewhat at odds.

One of the factors putting ion transport and structural integrity at odds is the relationship between ionic mobility and configurational entropy of the polymer. The addition of plasticizers has been well established in the literature to increase ionic conductivity. \cite{7,94,118,148} While this makes intuitive sense, as plasticizers increase the configurational entropy and mobility of polymer chains and would thus be expected to increase the mobility of Li$^+$ ions, plasticizers also have the effect of softening the polymer they are added to. This decrease in softness results in a polymer less able to bear load. One potential method for breaking this trade-off between mechanical stiffness and ionic conductivity is to employ a ‘solid plasticizer’, or solid particles which act to stabilize the amorphous phase of the polymer electrolyte, \cite{24,30,137} and ‘nano-fillers’, or solid particles that act to simply increase the stiffness of the polymer by forming a composite and improve conductivity through favorable ionic surface interactions. \cite{69,70,114,169} This strategy has been considered for structural energy storage applications, but it was noted that the resulting tensile strength of these composite structures remains low. \cite{140}

Extensive work has been performed at Imperial College London using epoxy-based resins in conjunction with ionic liquids to enable carbon fiber based structural superca-
The original motivation of this work was to use an established structural binder for carbon fiber, and modify the material in order to better conduct Li$^+$ ions. It should be noted that common organic electrolyte solvents soften epoxy, so that ionic liquid electrolytes are preferred as the ion conducting phase.

Figure 10: Synthesis and evaluation of bicontinuous epoxy-ionic liquid electrolytes. (a) This class of materials is formed by mixing epoxy and an ionic liquid, with following phase separation during curing. [141] (b) The resulting microstructures exhibit intricate multiscale morphologies, as shown using SEM micrographs. [142] (c) As is common in multifunctional materials, a trade-off is observed between materials properties. In this case, a trade-off is noted between stiffness and ionic conductivity. [141]

Figure 10 demonstrates the synthesis, morphology, and characterization of these bicontinuous electrolytes. As shown, the epoxy and the conducting phase are mixed together and then phase separate in order to form a bicontinuous network as the epoxy cures. It was shown that by controlling the degree of miscibility through composition, the morphology can be controlled. [142] In general, increasing amounts of epoxy will lead to stiffer composites with better mechanical properties. By contrast, higher volume fractions of the ionic liquid electrolyte will improve ionic conductivity. This trade-off has been quantified in
figure 10c. As shown, the best composite in this system exhibits about 10x lower Young’s modulus than the pure epoxy and 10x lower ionic conductivity than the pure ionic liquid.

Figure 11: A polymer-based structural battery. (a) The architecture of this battery, including an LCO positive electrode and a graphite negative electrode. Poly(ethylene oxide) is used as a polymer gel electrolyte, PVDF as a binder, and carbon fibers are used as structural members. (b) The discharge capacity of this structural LCO electrode compared to a conventional electrode. (c) A tensile test comparing the mechanical properties of the structural electrode to a conventional electrode.

The highest-performing ‘true’ structural battery (meaning that load is transferred to electrodes) for which we have tensile strength data uses a polymer electrolyte. The performance of this battery is shown in figure 11. In this design, PVDF is used as a binder and PEO is used in addition as a polymer gel electrolyte. The increased strength compared to a conventional electrode comes from using high molecular weight PVDF, and improving the electrode strength by the use of carbon fiber additives.

As shown in figure 11b, the discharge capacity of the structural battery electrode is only about 60% that of the conventional electrode. This may be due to lower electronic conductivity. The increase in electrode ultimate tensile strength (UTS), shown in figure 11c, is significant compared to the non-structural electrode. However, for many structural
applications further improvements beyond 12 MPa UTS will be necessary. Additionally, structural data is only given for a single electrode measured dry. As the PVDF binder is expected to soften with the addition of electrolyte, the actual UTS in operation may be lower. The energy density of this cell is given as 35 Wh/kg, or about 14% that of state-of-the-art commercial cells today.

2.5. Freestanding electrodes

There is a significant body of work regarding battery electrodes with enhanced mechanical properties. While relatively few papers advertise the ability of a design to bear load as part of the structure of a device, many characterize electrodes as ‘freestanding,’ ‘flexible,’ or ‘multifunctional’ because of the intrinsic properties of these electrode designs. [17] This section does not attempt to present a full review of flexible battery designs, but highlights some research judged to be particularly applicable to load-bearing battery architectures.

Several fabrication methods exist for producing carbon nanotube fabrics or papers. [51, 57, 115] These materials tend to be electronically conductive and strong due to the intrinsic properties of the CNTs that compose them. One of the major families of freestanding battery electrode architectures involves coating these structural carbons with active materials, frequently producing electrodes with an excellent combination of mechanical and electrochemical properties. [170] This has been used to produce anodes based on silicon, [35, 38, 126, 180, 182, 190], tin and titania structures, [89, 193] cobalt oxide, [202] as well as lithium iron phosphate cathodes. [127] An example of this architecture from the
Yushin group involving CVD silicon coating of carbon nanotube cloth is given in figure 12 a-b. Methods have also been developed for coating carbon substrates with active material precursors and subsequent transformation to produce freestanding electrodes. [17] It should be noted that mechanical test results, when available in this body of literature, are predominantly performed on individual electrodes rather than full batteries.

A second family of freestanding electrodes comes from extending the traditional electrode architecture, in which active material and conductive additive are interspersed. This concept has been applied to produce freestanding binder-free electrodes using LiNi₀.₅Mn₁.₅O₄ and both carbon nanofibers [36] and multi-walled carbon nanotubes [36] fabricated using vacuum filtration. This is a compelling approach because the lack of binder material could in principle allow high capacity electrodes for energy dense cells. However, the structural performance of these electrodes does not appear to have been tested. Another example was fabricated by using a traditional slurry-based process and a sodium carboxymethylcellulose (CMC) binder in order to produce freestanding SnO₂ anodes. [77] When CNTs were used as a conductive additive to replace super-P, the UTS of these electrodes, measured dry with no electrolyte, increased from 13 MPa to 33 MPa, as shown in figure 12c.
Figure 12: Freestanding electrode architectures. (a) A carbon fiber fabric coated with silicon using a CVD process. [35] (b) Tensile test results from the electrode architecture shown in (a) demonstrate excellent mechanical properties, with a UTS exceeding 150 MPa. (c) Mechanical test results on freestanding electrodes using a CMC binder show a UTS improvement by more than a factor of two when conductive Super-P binder is replaced by Carbon Nanotubes. [77]

A third important family of freestanding electrode materials which are potentially applicable to structural applications are fiber-based battery architectures. One variation of this strategy involves spinning or twisting carbon nanotubes into a yarn followed by subsequent CVD coating with silicon as shown in figure 13a-b. [86, 150] This yarn is then able to be woven into fabric which can be used as an anode and is able to bear load. Alternative architectures involve wires containing positive and negative intercalation electrodes that
are wound in the same structure as demonstrated in figure 13c. [127,183,197] This strategy has been shown to produce electrodes able to undergo 600% tensile strain. [197] Additionally, fiber architectures have been extended beyond traditional intercalation batteries to a range of chemistries. These include flexible sulfur electrodes, [91] and metal-air batteries based on lithium, zinc and aluminum. [188,189,198] An example of a fiber-based lithium air battery is given in 13d-e. Such architectures could in principle result in very long battery life structural components of devices.

Figure 13: Battery architectures based on fiber morphologies. (a-b) A coaxial yarn design based on spun CNTs that are subsequently CVD coated using silicon. These fibers can be woven and show excellent mechanical properties. [150] (c) A schematic showing two fibers, blue representing the negative electrode and red representing the positive electrode, wound in parallel into a full cell. [197] (d-e) A coaxial lithium-air battery. This cell could stably undergo 100 cycles when limited to 500 mAh/g capacity, and could be woven into a cloth. Mechanical properties were not measured. [198]
Overall, work on freestanding electrodes has produced a broad array of potential architectures. Use of these designs to produce flexible batteries has frequently been explored, but their use to bear load - requiring a rigid architecture - is uncommon. In addition, mechanical tests have generally been performed on individual electrodes rather than on full cells. In order to enable structural batteries, rigid versions of these architectures must be developed and the development of robust packaging solutions will be necessary.

2.6. Structural ceramic batteries (SCBs): a new design

This work introduces an alternative strategy for the production of structural batteries. The proposed architecture, the structural ceramic battery (SCB), is shown in figure 14. This architecture uses a rigid ceramic binder in both electrode layers as well as the separator, which serves several purposes.

Firstly, a conventional battery employs composite electrodes with no binder adhering one battery layer to the next (figure 14a). If this were to be used as a structural battery, it would be vulnerable to delamination between the layers. Figure 14b shows a schematic of the layers of this battery, while figure 14c shows this delamination in the perpendicular direction and figure 14d shows it in the shear direction. By contrast, use of the ceramic binder both within and between battery layers as shown in figure 14d counters these failure modes.

The second use of this ceramic binder is to make the electrodes themselves rigid. While
this is difficult to achieve with polymers such as typical PVDF binder that soften when exposed to electrolyte, ceramic binders can be chosen that maintain their stiffness. (figure 23 below).

Figure 14: Comparison between conventional batteries and the Structural Ceramic Battery (SCB) Architecture. (a) A conventional battery [15] features electrode and separator layers made of composite materials that are both non-load-bearing and not laminated together. (b) A schematic of an electrode stack, using the same colors as shown in a. (c) Failure of a conventional battery stack under a normal tensile force via delamination between layers. (d) Failure of a conventional stack upon applied shear force. (e) The SCB architecture contains a ceramic binder that permeates all three electrode layers, allowing adhesion between them and resulting in a monolithic engineering ceramic stack.

Thus, this work is devoted to the evaluation of a ceramic silicate binder for use in batteries, rigid SCB architectures based on this binder, and manufacturing methods for producing these SCBs.
3. Methods

3.1. Nanoindentation

To measure the Young's modulus of silicate films, an as-received 26.5wt% solution of sodium silicate waterglass (Sigma Aldrich) was diluted by mixing 100 µl of waterglass with 1 ml of milli-Q deionized water (DI). 100 µl of this dilute solution was cast onto a glass microscope slide. These slides were heated in air to 90°C for 2 hours to completely dry the film, then to a final treatment temperature for an additional two hours. All ramp times were 30 minutes.

The Young's modulus was measured using a Triboscan Nanoindenter using a diamond Berkovich tip. A 7x7 point grid was indented for each sample (49 points). Displacement control mode was used with a peak displacement of 100 nm and a trapezoidal load function. Indentation was performed for 10s of loading, with a 3s hold before 10s unloading. The initial, elastic, part of the unloading curve was fit for the analysis.

Oliver Pharr analysis was used in order to result in a reduced modulus value $E_r$. This was related to the Young's modulus of the sample by:

$$\frac{1}{E_r} = \left(\frac{1 - \nu^2}{E}\right)_{\text{Tip}} + \left(\frac{1 - \nu^2}{E}\right)_{\text{Sample}}$$

Values of the Poisson ratio $\nu$ and Young's modulus for the diamond tip are known to be 0.07 and 1140 GPa, respectively. For the silicate sample, a Poisson ratio value of 0.18
was used from [124].

3.2. Electrode fabrication

Electrodes were made based on a standard approach. A typical slurry was made using the components shown in table 2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Material</td>
<td>0.33 g</td>
</tr>
<tr>
<td>Super P</td>
<td>0.041 g</td>
</tr>
<tr>
<td>Silicate Waterglass</td>
<td>0.142 g</td>
</tr>
<tr>
<td>DI Water</td>
<td>0.473 g</td>
</tr>
</tbody>
</table>

Table 2: Typical composition of an electrode slurry, used for both positive and negative electrodes.

Active materials were commercial battery powders obtained from MTI. Super P was treated with 30% diluted bleach (sodium hypochlorite) solution under sonication for 30 minutes in order to better suspend it in aqueous solution, following [10]. Waterglass was a 26.5% sodium silicate solution in water, used as obtained from Sigma Aldrich. Solids were first ground in a mortar for 10 minutes. Liquids were mixed in a vial then added to the solids. Slurry was cast onto substrate, typically either a battery spacer for electrochemical experiments or a glass slide for fracture toughness tests, of the required thickness. Relative
amounts of components were adjusted as described in the text. Reinforcements such as carbon nanofiber were added to the solids and ground. Required amounts of organic temporary binder such as sodium carboxymethylcellulose and glycerol were added to the liquids and dissolved.

Generally, samples were dried in air and subsequently heat treated. Heat treatments consisted first of a ramp to 90 °C and a two hour hold at this temperature to dry the electrode. Subsequently, the electrodes were heated to a higher treatment temperature and held for two hours. All ramps were 30 minutes.

3.3. Fracture toughness measurements

Fracture toughness measurements were done on films of 40 μm thickness, prepared as described above, following the procedure outlined in [5]. A CSM instruments Micro Scratch Tester was used with a 200 μm AG-297 Rockwell diamond indenter. Scratches were performed along the sample, and the horizontal force in the direction of the scratch was measured. Using linear elastic fracture mechanics, the fracture toughness can be calculated from the energy release rate of a crack to be:

\[ K_C = \frac{F_T}{\sqrt{2pA}} \]

Where \( K_C \) is the fracture toughness, \( F_T \) is the horizontal force, \( p \) is the perimeter of the indenter tip, and \( A \) is the area of the crack tip. The denominator \( \sqrt{2pA} \) is a
function of the indentation depth $d$ known for a given tip geometry.

Using this framework, loading conditions were found under which the force converged to a nearly constant value of $\frac{Fr}{\sqrt{2\phi A}}$ at high depths. The resulting values are plotted against $d/R$, where $R$ is the tip radius. For low depths near the beginning of the scratch tests, plastic deformation results in a high and decreasing value of $\frac{Fr}{\sqrt{2\phi A}}$. $K_C$ is found by averaging over the latter part of this curve.

3.4. Rate capability and cycle life measurements

Coin cells were made using CR2023 casings prepared in an Argon glovebox maintained at $[O_2]$ and $[H_2O]$ below 0.1 ppm. For half cell tests, cells were typically fabricated on a stainless steel spacer. Deposition of a 50 μm thick film from the slurry outlined above followed by drying and heat treatment resulted in an approximately 15 μm thick electrode. The spacer with electrode adhered to it was placed on a spring in the coin cell casing. 25 μl of 1M LiPF$_6$ in 1:1 v:v EC:DMC electrolyte (Sigma) and two pieces of Celgard 3501 separator were placed on top. A 9/16” diameter Li foil was punched out and flattened with a stainless steel bar, and placed on top of the separator. The cell was crimped then removed from the glovebox.

Rate tests were done using Biologic VSP and VMP3 battery testers. Three forming cycles were done at the C/20 rate based on the theoretical capacity of the active materials. The nominal capacity of the cells was taken to be the final lithiation (for positive electrodes) or delithiation (for negative electrodes) capacity of the cell. Subsequent tests were done
based on this nominal rate. One rate test cycle typically consisted of C/10 charge (positive electrodes) or discharge (negative electrodes) followed by a test half cycle at a rate that varied. Three test cycles were done at each rate under investigation.

Cycle life tests consisted of three forming cycles as described above, followed by charge and discharge at a symmetric rate using a Lanhe battery cycler. Rate was based on nominal capacity.

3.5. Transmission electron microscopy

For TEM tests, electrodes were made as described above on glass slides. Ethanol was added to the electrode surface and the sample was scraped with metal tweezers in order to suspend electrode particles in the liquid. 2 μm of suspension was placed on a carbon-coated Cu TEM grid (Electron Microscopy Sciences).

Imaging on an JEOL 2100 FEG microscope was done using parallel illumination beam and 100um diameter condenser aperture.

The microscope was operated at 200 kV and with a magnification in the ranges of 20,000 to 800,000 for assessing particle shape and size and atomic arrangement. All images were recorded on a Gatan 2kx2k UltraScan CCD camera. STEM imaging was done by HAADF (high-angle annular dark field) detector with 0.5nm probe size and 12cm camera length. EDX (Energy Dispersive Spectroscopy) was measured in STEM mode using X-Max80mm2 SSD detector and analyzed using the Inca software.
3.6. X-Ray Diffraction

XRD was done using both powder samples and electrode films cast on a glass substrate. Powder samples were made by adhering powder to a glass slide with vaseline. Electrodes were prepared as described above, and not heat treated prior to investigation. A Rigaku SmartLab was used. The instrument has a Cu K-α generator set to 45 kV and 200 mA. Samples were imaged using a parallel beam geometry with a soller slit of 2.5”, open PSA, a Ni filter, and a D/teX Ultra linear position sensitive detector. Samples were analyzed using a 2 theta/omega scan with a step size of 0.01, speed 7, and automatic attenuation.

In-situ measurements were taken using a furnace attachment. An argon flow of about 200 cc/min was used to simulate electrode sintering conditions used elsewhere. 10 minute ramps were used between temperature set points. Each temperature scan took approximately 70 minutes.

3.7. Scanning electron microscopy

For scanning electron microscopy, samples were mounted using conducting carbon tape onto aluminum sample holders. Nonconducting samples were then sputter-coated with 8nm of gold to prevent charging. Imaging was done using a JEOL 6010 LA microscope with a tungsten filament. The beam voltage was set to 20 kV and samples were investigated in secondary electron imaging (SEI) mode.
3.8. Electrochemical impedance spectroscopy

EIS was performed with Biologic VMP3 and VSP instruments. CR2023 coin cells were made using the configuration shown in figure 42a with 50 μl of 1M LiPF₆ in 1:1 v:v EC:DMC electrolyte (Sigma). Galvanic mode was used, applying a constant current of 0.4 mA and an oscillating signal of 100μA. The frequency was varied from 0.5 MHz to 1 Hz. 10 points per decade were sampled.

3.9. Tensile Tests

Dogbone-shaped structural battery layups were made as described in the text. These samples were tested using a Zwick BTC-EXMARCO.001 Mechanical Tester (Roell). A 10 N load cell was used with an accuracy of 0.1N. The machine was controlled using Test Xpert III software, based on the ASTM E8 standard. Grip-to-grip separation at test start was 6 cm, with a strain rate of 5 mm/min and a pre-load of 0.5N. Sample thickness was measured using calipers.
4. Evaluating the properties of inorganic polymer binders

Slurry-processed inorganic materials have been used for millennia as engineering materials, most notably in cement structures. Ancient cements comprising largely alkali-activated aluminosilicates date back at least to the Roman empire. [46, S2, 120]

Water-soluble silicates have been used as binders in a wide variety of industries, which will be described below. These materials are formed by the reaction between a hydroxide and silica at high temperature followed by dissolution in water, resulting in a viscous solution. When dried, this produces a clear coating able to form durable ionic bonds with many materials.

Since the 1970s, the term ‘Geopolymer’ has been used to refer to aluminosilicate materials processed by gellation from basic solution. These have been promoted by the geopolymer institute, [60] an industry group advocating their use as structural and building materials. A significant body of academic literature has been published on the processing and work on geopolymer composites will therefore be discussed as well.

Finally, in this section a comparison will be presented between conventional organic polymer binder and inorganic silicate binders for use in SCBs.

4.1. Alkali silicates

The basic design principle of a Structural Ceramic Battery (SCB) is to use an inorganic binder that accommodates diverse active material types and structural reinforcements,
distributes load, and sufficiently promotes ion transfer. Alkali silicates suit many of these requirements as they are easy to process, compatible with a range of active materials, stiff and retain their mechanical properties when exposed to electrolyte solvent, and are somewhat lithium ion conductive.

4.1.1. Alkali silicate properties and synthesis

Sodium silicates, the best-studied alkali-silicate system, are composed of compositions Na₂O-SiO₂ as shown in figure 15. This binary system contains a network former SiO₂, and a network modifier Na₂O. While pure SiO₂ glasses have a high degree of connectivity between SiO₂ tetrahedra, addition of Na₂O increases the incidence of non-bridging oxygens. This affects both the crystallography and the mechanical properties of the silicate, increasing thermal expansion and lowering the hardness with increasing Na₂O content.

In addition, increasing Na₂O content tends to result in compounds that are less stable with regards to air and moisture, forming carbonates and various hydrates. At the other end of the spectrum, SiO₂-rich compositions form many metastable compounds that decompose very slowly into equilibrium phases. Furthermore, these systems tend to form several polymorphs at a given composition. These properties present challenges in the study of sodium silicate compounds as results are often highly dependent on processing conditions.
Sodium Metasilicate
\[ \text{Na}_2\text{Si}_3\text{O}_7 \]
Sodium Trisilicate: Neosilicate (Water glass, metastable)

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Na(_2)O</th>
<th>x(SiO(_2))</th>
<th>SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>0.0</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>1200</td>
<td>1.11</td>
<td>1.18</td>
<td>1.02</td>
</tr>
<tr>
<td>1400</td>
<td>1.22</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>1600</td>
<td>1.40</td>
<td>1.22</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Higher ionic conductivity
Easier processability
Lower Air stability (Forms Na\(_2\)CO\(_3\))

The binder primarily used in this work is sodium trisilicate 'waterglass', with a 1:3 molar ratio of Na\(_2\)O:SiO\(_2\). This material was selected as a promising binder because of its extensive use in many industries (see below) and ease of processing. The material is produced as a viscous aqueous solution at about 26.5wt% solids. It can easily be applied to surfaces and dried in ambient, which produces a sodium silicate hydrate film. The dry film is clear and amorphous. Figure 16 shows TGA and XRD data derived from heating these films. As shown, the amorphous hydrate loses water as it is heated. About 90% of the water is lost below 300°C, above which temperature it begins to crystallize into β-
sodium disilicate, or $\beta$-$\text{Na}_2\text{Si}_2\text{O}_5$ (known as natrosilite when found as a mineral). Based on the stoichiometry of this crystalline phase compared to that of the waterglass film, there remains amorphous silicate when this occurs. At higher temperatures above 500°C, the formation of cristabolite silica $\text{SiO}_2$ is observed. It should be noted that the materials project lists seven polymorphs of sodium disilicate and over 250 polymorphs of silica [67], underscoring the structural diversity of this materials system.

Figure 16: Processing of sodium trisilicate waterglass dried from solution. TGA (a) and XRD (b) data from dried waterglass films, from [49]. Waterglass loses about 22% of its mass during heating, with a stable weight above about 500°C. In situ XRD data shows that the amorphous solid is stable up to 300°C and that $\beta$-$\text{Na}_2\text{Si}_2\text{O}_5$ (*) begins to form between 300°C-400°C while cristobalite $\text{SiO}_2$ (#) forms at 550°C. The structures of $\beta$-$\text{Na}_2\text{Si}_2\text{O}_5$ (c, mp-3193) and cristobalite $\text{SiO}_2$ (d, mp-6945) are shown, from the Materials Project [67].
Additionally, the charge transport properties of alkali silicates have been extensively investigated. Transport of Li\(^+\), Na\(^+\), K\(^+\), and H\(^+\) through SiO\(_2\) \cite{f3,14} in particular has been studied in depth, as cation currents from contamination proved a significant barrier to the initial commercialization of microelectronics. \cite{27,62} It is worth a brief summary of these results in the context of the development of a silicate-based binder coating, as migration through SiO\(_2\) represents the Li-poor end of the silicate spectrum.

Li\(^+\) diffuses through interstitials in the SiO\(_2\) structure, \cite{49,168} with a diffusivity of 1.3 \times 10^{-13} \text{ cm}^2/\text{s} at room temperature (calculated from mobility data measured via Isothermal Transient Ionic Current, ITIC tests \cite{1,49}). Early studies of cation motion in SiO\(_2\) demonstrated very low diffusivities in the range of 10^{-18} \text{ cm}^2/\text{s}, \cite{2,144,168}, and it was later shown that this was the result of deep trap states unaccounted for when initial data were interpreted. \cite{61,63,80,111} ‘Slow’ and ‘fast’ diffusive modes have been observed, likely corresponding to the depth of potential energy wells which Li\(^+\) ions hop between. \cite{63,80} The depth and concentration of ion traps - relative to the concentration of ions themselves - thereby seem to play significant roles in Li\(^+\) diffusion. Further evidence for this relation between trapping and diffusivity is found in experiments exhibiting cations (thought to be Li\(^+\)) with mobilities 11 orders of magnitude higher than that expected by initial studies, in X-ray assisted detrapping experiments. \cite{1} Greew and Verwey account for Li\(^+\) detrapping via an emission frequency fit to experimental data, \cite{48,49} but it seems likely that the 15 keV ion implantation process used to dope their samples would result in extra trap states in proportion to doping concentration which may interfere with subsequent ion motion, and
therefore that a gentler doping procedure may result in ions hopping between shallower potential wells with a correspondingly higher mobility.

Even the corrected diffusivity value of $10^{-13}$ cm$^2$/s through pure SiO$_2$ would thus be too low to promote battery cycling, unless the silica coating on the electrode were limited to a few tens of nanometers. However, very high doping levels or the use of alkali-rich lithium-silicate compounds may result in a preponderance of fast-diffusing ions due to the filling and effective passivation of deeper traps.

Evaluation of lithium silicates as electrolytes for LIBs has shown that microscale thickness silicate films are sufficiently conductive to function as Li$^+$ conductive materials. The metasilicate Li$_2$SiO$_3$ was deposited using Pulsed Laser Deposition (PLD) and its conductivity was measured at different film thicknesses on different substrates. [40, 41] These measurements were done at elevated temperature, and a conductivity of $2 \times 10^{-5}$ S/cm was found at 500°C with the amorphous film conductivity being about a factor of 30 higher than the polycrystalline film. In the context of the mobility studies on Si$_2$ described above, this low conductivity in the polycrystalline silicate may be due to the presence of trap states at grain boundaries. In addition, the conductivity showed a dependence on film thickness and on substrate (see figure 17a) which suggests that transport through these 150 nm thick films is highly influenced by its interface with the substrate. Conductivity measurements conducted on PLD-deposited Li$_4$SiO$_4$ and Li$_2$SiO$_3$ films near room temperature [102] showed about an order of magnitude higher conductivity for Li$_2$SiO$_3$ than would be expected from extrapolating the curves given in [10, 11] (see figure 17b). This is
to be expected when extrapolating curves over several orders of magnitude, and so these results are taken to be roughly in agreement. The latter study [102] used amorphous PLD deposited films, but used a Pt-coated substrate in contrast with the resistive substrates used in the former. [10, 11]

Silica and silicates have also been used as thin film coatings to improve the rate capability of LIBs. There exists an extensive literature on coating active materials with ceramic thin films such as Al$_2$O$_3$ [17,71-73] and SiO$_2$. [85,105] in order to improve rate capability and cyclability. A review of this subject is beyond the scope of this thesis, but it should be mentioned that such coatings are know to improve the interfacial properties of active materials and result in accelerated charge transfer kinetics. For example, LiCoO$_2$ was coated with 2-3 nm thick lithium metasilicate via a sol-gel process. [133] This was shown to improve the rate capability of a solid state battery fabricated using these powders (figure 17c).
Figure 17: Evaluation of lithium silicates as ionically conducting materials. (a) The ionic conductivity of PLD-deposited Li$_2$SiO$_3$ at elevated temperatures and on varying substrates, from [11]. (b) Ionic conductivity of PLD-deposited Li$_4$SiO$_4$, Li$_{2.2}$V$_{0.54}$Si$_{0.46}$O$_{3.4}$ and Li$_2$SiO$_3$ near room temperature, from [102]. (c) Discharge curves from LiCoO$_2$ cells in which SiO$_2$ and Li$_2$SiO$_3$ coatings have been applied to lower interfacial resistance, from [41].

Additionally, it was shown that Li$_4$SiO$_4$ and Li$_2$SiO$_3$ films can be used as solid electrolytes in thin-film solid state LIBs. These batteries were deposited on a Pt and Cr-coated SiO$_2$ substrate. The LiCoO$_2$ positive electrode and subsequently the electrolyte film were both deposited via PLD. A Li metal film was then thermally evaporated and used as a front contact. The batteries were cycled using cyclic voltammetry (CV), with results shown in figure 18. The Li$_2$SiO$_3$-based battery was shown to have lower rate capability than the Li$_4$SiO$_4$-based device, as shown in figure 18b in which both are cycled at the same sweep rate. This difference in rate capability was attributed to the 10x difference in ionic conductivity measured between the two electrolyte materials (figure 17b). Both showed good stability over 10 CV cycles.
Figure 18: Use of lithium silicates as solid electrolytes in PLD-deposited solid-state thin film batteries, from [102]. (a) Cyclic voltammetry (CV) curve of cell using 3.0μm thick Li₄SiO₄ electrolyte 0.5 mV/s. (b) Cycling data comparing cell characterized in (a) to cells made using LVSO and Li₂SiO₃ solid electrolytes. Both lithium silicate cells were measured using CV, sweeping at 0.5 mV/s.

It should be noted that PLD is a technique well-suited for producing planar thin films. In addition, it requires the use of vacuum equipment and is relatively wasteful of active materials. For these reasons, alternative deposition methods will likely be required to result in practical structural batteries, which require thick battery stacks and cost-effective production methods. The majority of the work presented in this thesis has been done using sodium trisilicate, favoring an industrially produced and easily processable material. It should be noted that the conductivities of Li silicates allow significant scope to improve the transport properties of the electrodes presented.

4.1.2. Uses of alkali silicates in industry

Sodium trisilicate waterglass was investigated as a binder because it is a well-studied member of the silicates with a well-known propensity to form ionic bonds that makes it a durable binder in a wide range of industries.

A survey of the products they are used in is shown in figure 19. These products are advertised for their durability. For example, conductive paste (figure 19a, [110]) using sodium silicate as a binder is advertised to cure and become stronger as it is heated up
to 2000°C. This makes it useful for preparing samples for electron microscopy that require heat treatment. It is used in refractory and construction materials, for example to bind refractory insulation such as perlite-based blocks (figure 19b).

Silicates are used as a sealant for cement surfaces (figure 19c, f) and as a major constituent of portland cement, the most common cement used in construction. Its composition is given in Table 3 below.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime (CaO)</td>
<td>60 to 67%</td>
</tr>
<tr>
<td>Silica (SiO₂)</td>
<td>17 to 25%</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>3 to 8%</td>
</tr>
<tr>
<td>Iron oxide (Fe₂O₃)</td>
<td>0.5 to 6%</td>
</tr>
<tr>
<td>Magnesia (MgO)</td>
<td>0.1 to 4%</td>
</tr>
<tr>
<td>Sulphur trioxide (SO₃)</td>
<td>1 to 3%</td>
</tr>
<tr>
<td>Soda and/or Potash (Na₂O+K₂O)</td>
<td>0.5 to 1.3%</td>
</tr>
</tbody>
</table>

Table 3: The mineral composition of modern portland cement, from [19]. As shown, SiO₂ is the second most common component after CaO.

While numerous reactions occur during cement curing, one of the primary reactions is the Pozzolanic reaction of calcium hydroxide with silicic acid [95]:

$$\text{Ca(OH)}_2 + \text{H}_4\text{SiO}_4 \rightarrow \text{Ca}_2^+ + \text{H}_2\text{SiO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaH}_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$$

Silicate hydrates are thus one of the primary structural components of concrete.
In addition to portland cement, silicates are also used as 'cementless' mortars as binders for building materials based on fly ash and slag. [93, 108, 191] In this application, silicates should perhaps be seen as the aluminum-poor end of the spectrum of geopolymer materials (see below).

Potassium silicate was discovered by Adolf Wilhelm Keim in the 19th century to be an effective binder for inorganic pigments, resulting in an extremely durable mineral paint product. [31, 107, 130] An example of the durability of these paint compositions is shown in figure 19d. This mural was commissioned in 1881 and painted by Christian Schmidt over 130 years ago using Keim brand mineral paint. The building it is on, the city hall of the town of Schwyz in the Swiss Alps, is exposed to extreme alpine conditions. It has has retained its vibrancy despite the harsh climate due to the chemical stability of the paint’s inorganic composition, being touched up only twice since the initial application. [97] An additional example of waterglass being employed for its durability is its use to preserve eggs (figure 19e). As written in a cookbook from the 19th century, “Putting eggs down in a solution of water glass is without doubt the most satisfactory method of storing them in the home.” [123] The sodium silicate waterglass is used to bond with the calcium carbonate eggshell, sealing its pores. This is chemically and morphologically similar to the use of silicate as a cement sealant. Finally, silicate is used as an adhesive for cardboard.
Figure 19: Uses of water soluble alkali silicates. Sodium silicate is used as a binder in conductive paste (a), [110] able to withstand heating to 2000°C. It is used as a binder in refractory insulating materials (b) and building materials. [65, 108, 191] It is used as an accelerant and sealer for cement (c, f). The vibrant mural (d) on the Schwyz Rathaus in the Swiss Alps is one of the earliest examples of modern potassium silicate mineral paint being used, painted about 130 years ago. [97]. Sodium silicate waterglass has also been used as a sealant for egg shells, which preserves them (e). [123]

Fundamentally, the three properties of sodium silicate that make it useful in these industries are its ability to form ionic bonds with many materials, the stability of those bonds, and the stability of the silicate material itself. As battery active materials are primarily ionic compounds in addition to carbon-based materials, we expected them to form strong bonds in order to produce stable electrodes analogous to the cases mentioned above. This was the motivation for the development of SCBs.
4.2. Geopolymer binders

The term ‘Geopolymer’ applies to aluminosilicate binders with varied composition. Thus, the silicate binders discussed above can be considered as geopolymers at the silicon-rich end of the composition spectrum. While solutions of these polymers are prepared at high pH and this is necessary for activation and subsequent setting of the material, these compounds are distinct from alkali-activated cements as their setting does not rely on calcium. [3, 20, 84, 156]

A simplified reaction mechanism for geopolymer activation is shown in figure 20a. This is a multi-stage process involving the dissolution and subsequent gelation of aluminate and silicate species. Typically, this process is begun by the activation of a kaolinite aluminosilicate, nominally Al₂Si₂O₅(OH)₄ (figure 20b-c) by the addition of a silicate waterglass solution. The alkaline conditions predominant in the solution cause the dissolution of kaolinite and saturation of aluminate and silicate in the aqueous phase. As shown in figure 20a, gelation of these inorganic species and the following reorganization and growth of the resulting solids produces a porous structure. The ratio of aluminum to silicon affects the kinetics of this complex curing process, the ultimate pore morphology, and the compressive strength of the resulting material with an optimal ratio that depends on additional factors such as heat treatment temperature and pH. [20, 54, 55, 73]
Figure 20: Chemistry of geopolymer binders. (a) The setting process for geopolymer binders is complex, and is driven by the dissolution and subsequent gelation of aluminate and silicate species. [25] (b) Kaolinite clay is a naturally occurring mineral that can serve as a source of both aluminate and silicate in geopolymers. [90] (c) Al₂Si₂O₅(OH)₄, the main component of Kaolinite, forms a layered structure with alternating planes of Al and Si. [18]

4.2.1. Uses of geopolymer binders in research and industry

The primary use of geopolymers has been as a concrete alternative to ordinary portland cement (OPC). Composites with fly ash are able to achieve compressive strength com-
parable to OPC, \cite{151,155} with improved fire performance in some cases \cite{16,201}. The pore structure of the composite heavily influences the properties of the material following heating, likely by affecting the escape of moisture \cite{78}. Geopolymer coatings have been applied to steel \cite{15,157} and balsa wood composites \cite{12,13} in order to confer improved fire retardant properties and used to produce fire resistant interior wall panels. \cite{92} In addition, the chemistry of the geopolymer is compatible with organic additives such as melamine, acrylic, and polyvinyl acetate. These can be added directly to the geopolymer in order to produce composites \cite{132,196}, improving the strength of the resin by organically reinforcing the geopolymer \cite{21a}.

Reduction of CO$_2$ emissions compared to OPC is an often-cited benefit of geopolymer formulations \cite{88}. The basis of this claim is that while OPC is produced by the release of carbon dioxide following the reaction \( \text{CaCO}_3 \xrightarrow{\text{Heat}} \text{CO}_2 + \text{CaO} \), geopolymer chemistry has no comparable CO$_2$ release step. Some studies have shown a significant reduction in emissions compared with portland cement \cite{98} though the variation is wide and depends on the specifics of the supply chain (figure 21b). A more conservative study found only a 9\% reduction, \cite{164} alleging that other work had failed to properly account for energy expended during mining of raw materials to produce the sodium silicate activator.

In addition, the properties of foamed geopolymer have been studied. This can be used to form lightweight, somewhat thermally insulating concrete \cite{6,128,129,199,200} as shown in figure 21c. In order to produce more highly thermally insulating materials, it is also used as a binder for porous composites \cite{59,166}
One of the main geopolymer applications relevant for the production of SCBs is their use as binders for carbon fiber and glass fiber. While conventional organic polymers used in these composites are highly flammable, geopolymer binders are able to produce composites that show highly improved fire resistance as shown in figure 22a [25,93]. Silicates, similarly, have been used as a glass fiber binder. [146]

The use of geopolymers as binders for carbon fiber and glass fiber weaves could produce composites with comparable flexural strength to those made with organic polymer binder, [44] though results depended on the weave used.

In addition, work has been done evaluating the reinforcement of geopolymers with non-aligned carbon fiber additives. Addition of carbon fibers (3.5 v%) to potassium silicate...
aluminate results in strengthening and toughening \[^{[58]}\] of the composite. It was found that flexural strength measured by a three-point bending test exhibits a maximum at 4.5 v% fiber reinforcement, increasing the strength drastically from 16.8 MPa to 96.6 MPa (figure 22b).

One study examined the failure of carbon fiber reinforced geopolymer composite \textit{in situ} using an environmental SEM as shown in figure 22c. \[^{[87]}\] Three regimes were observed. At low loading, the beam behaves elastically. At intermediate loading, microcracks formed along the beam edge under tension. The formation of these microcracks results in decreased elastic modulus that was visible in the stress-strain curve, though the beam continued to behave elastically in this regime. With increased loading, one microcrack undergoes catastrophic failure. This relieves stress on the remaining microcracks as the beam fails.

A notable gap in the literature seems to be the study of the surface properties of the carbon fiber reinforcements. While this has been extensively studied in conventional epoxy composites, the literature on carbon-reinforced geopolymers does not seem to have investigated the effect of pretreatment (ie. surface oxidation) of the reinforcement.
4.3. **The mechanical properties of silicate binders**

In order to employ silicate binders in lithium ion battery electrodes, it was first necessary to evaluate the mechanical properties of the binder, measure the effect of electrolyte on those properties, and determine the effect of various electrode formulations on fracture toughness. These results show that the mechanical properties of sodium trisilicate make it a suitable binder for rigid electrodes, as it is stiff and does not soften appreciably in the presence of electrolyte solvent. By contrast, the poly(vinylidene fluoride) binder commonly used is a softer material that softens further when exposed to electrolyte. Porous electrodes made using sodium trisilicate increase in fracture toughness as additional binder is added.

4.3.1. **Young’s Modulus Comparison**

The goal of an SCB is to produce electrodes capable of bearing load. To this end, electrodes must be rigid composites held together by a stiff binder in order to resist deformation. To determine the suitability of silicate as an electrode binder for SCBs, the Young’s Modulus $E$ was measured using nanoindentation. For a material in uniaxial compression or tension, $E$ is proportional to stiffness $k$: 74
\[ E = \frac{Lk}{A} \]

In which \( k \) is the slope of the stress-strain curve in the linear elastic region, \( L \) is the length of the specimen and \( A \) is the cross-sectional area. Thus, \( E \) is an intrinsic materials property proportional to the force necessary to deform a specimen of the given material, with samples of higher-\( E \) material exhibiting increased stiffness.

\( E \) was measured using nanoindentation, and results are shown in figure 23. The stiffness was first measured as a function of heat treatment temperature (figure 23b). The modulus for the sample heated at 290°C showed high variation, possibly due to nonuniformities induced by drying. As expected, \( E \) increased during heating to 400°C. The bulk of structural water is removed below 400°C (figure 16a) and crystallization begins near this temperature. \( E \) did not change significantly at 500°C. These modulus values fall within the expected range for heat treated sodium silicate. [124]
Figure 23: Sodium silicate is a stiff material that does not soften in response to electrolyte solvent, establishing its suitability as a binder for rigid electrodes. (a) The hysitron nanindenter used to measure binder stiffness. The sample was kept in the small dish shown, which was filled with electrolyte solvent for the relevant tests. (b) Trisilicate young’s modulus as a function of heat treatment temperature. While the modulus increases during heating to 400°C, variations are modest in relative terms compared to organic polymers. (c) Measurement of the effect of electrolyte solvent on binders. The silicate is unaffected, while PVDF becomes more than an order of magnitude softer. PVDF data from [79].

Next, it was necessary to determine the effect of electrolyte on the proposed binder. For this test, electrolyte solvent consisting of a 1:1 v:v mixture of ethylene carbonate and dimethyl carbonate was used. The most common binder used in commercial batteries, poly(vinylidene fluoride) (PVDF), was used as a benchmark for comparison. In figure 23c, the measured silicate data is plotted along with corresponding PVDF nanoindentation data from [79]. It is shown that the silicate exhibits more than a fifty times increase in modulus compared to PVDF. Furthermore, the silicate does not soften appreciably in the presence of electrolyte solvent. PVDF, by contrast, undergoes a decrease in $E$ by a further factor of fifty.

4.3.2. Fracture toughness measurements

To evaluate the use of silicate as an electrode binder, LiFePO$_4$ (LFP) electrodes were made with various compositions as shown in table 4, based on a standard slurry method (figure 24a). This slurry was doctor bladed as a 100 µm thick layer onto a glass substrate, dried, and heat treated to 500°C. During drying and sintering, the samples decreased in thickness
by about 45\% (figure 24b).

<table>
<thead>
<tr>
<th>Component</th>
<th>MTI Electrode</th>
<th>SCB Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO_4 (LFP)</td>
<td>93.5 wt%</td>
<td>80-96 wt%</td>
</tr>
<tr>
<td>Super P</td>
<td>4 wt%</td>
<td>2-10 wt%</td>
</tr>
<tr>
<td>Binder</td>
<td>2.25 wt%</td>
<td>2-10 wt%</td>
</tr>
</tbody>
</table>

Table 4: Electrodes were tested over a range of conductive additive and binder compositions. Shown is the range tested, in comparison with the composition recommended by MTI from [22].

The fracture toughness $K_{IC}$ of the samples was measured. $K_{IC}$ is a measurement of a material's resistance to brittle fracture, and is thus a figure of merit in the evaluation of structural materials. It was hypothesized that increased silicate content would improve $K_{IC}$ of the material, while increased conductive carbon content would lower $K_{IC}$.

Figure 24: Silicate electrodes were fabricated based on conventional slurry techniques, and evaluated. (a) A typical aqueous slurry using conductive carbon, sodium trisilicate, and LFP. (b) A profile of the electrode surface. Films used for nanoindentation were about 55 $\mu$m thick.
A scratch test was used to measure $K_{IC}$ of these samples. The results are presented in figure 25. In these graphs, the mass fraction silicate binder and conductive Super-P carbon are shown. The remaining unspecified mass fraction is entirely LFP active material. As shown in figure 25a, increasing the amount of Super-P conductive carbon at 5 wt% silicate monotonically lowers $K_{IC}$. This makes intuitive sense, as Super-P is a high surface area carbon with little structural integrity that is not expected to exhibit strong interactions with the active material. Thus, as its mass fraction increases the electrode becomes weaker. Another intuitive trend is shown in figure 25c. This demonstrates that when the mass fraction of binder and conductive carbon are equal, increasing them monotonically increases $K_{IC}$. As increasing Super-P content by itself weakens the electrode, this trend demonstrates that the silicate binder increases electrode toughness. Thus, silicate functions effectively as a binder material.
Figure 25: $K_{IC}$ is generally decreased with Super-P content and increased with silicate content, though increase with silicate is not monotonic. (a) Increasing the mass fraction of Super-P conductive carbon at constant silicate content decreases $K_{IC}$. (b) As silicate content is increased, $K_{IC}$ shows a minimum at an intermediate value. Increased silicate ultimately results in higher $K_{IC}$ for high silicate loading. (c) When the mass fractions of Super-P and silicate are equal, increasing the amount of binder monotonically increases $K_{IC}$.

The trend shown in figure 25b is somewhat less intuitive. This shows that increasing the silicate binder mass fraction at a constant 10wt% Super-P does not monotonically increase $K_{IC}$ as might be expected. Instead, high silicate contents lead to high $K_{IC}$ while an intermediate 5 wt% silicate results in a $K_{IC}$ minimum. Some clues as to the origin of this are to be gleaned from TEM data (presented below). Micrographs show that silicate migrates to the carbon and to the interface between the carbon and the LFP. It is possible
that at low silicate loading, the silicate is effective at bonding the LFP active material to the conductive carbon. Thus, fracture occurs when weak but elastic Super-P connections between electrodes break. As the silicate content increases to an intermediate level, it seems that the silicate covers the Super-P sufficiently to prevent its elastic deformation but does not form strong bonds between active materials in of itself. This results in low \( K_{IC} \). At higher silicate loading, the silicate is clearly effective at bonding LFP particles to each other as shown by the trends in 25b, c.
5. Development of silicate-based electrodes

5.1. Previous use of silica as electrode binders

There is a body of literature covering the use of silica as a binder for carbon electrodes. These electrodes are chemically similar to SCB electrodes in that they use a silica-based binder. However, they are produced via sol-gel synthesis. Thus, the silica made from them is pure (rather than a soluble silicate), they require organosilicon precursors, and the deposition involves a complex set of chemical and morphological changes characteristic of sol-gels. At the same time, they will be briefly mentioned here because they provide the closest electrochemical analogue to SCBs in the existing literature.

Carbon ceramic electrodes were introduced in 1994 [163] as an alternative to carbon paste electrodes employing an organic binder. They were shown to be highly stable compared to carbon paste electrodes [90, 106, 116, 163] and have been proven a remarkably versatile electrode design that can be chemically modified for numerous applications. They have been used for ion detection [98, 138, 178], for sensing biomolecules [122, 134, 135], as a fuel cell electrode [52, 53, 121] and for various other reactions of interest such as hydrogen evolution [4, 5, 119].

We are aware of exactly two papers in which a carbon ceramic electrode was used as a lithium intercalation battery electrode both from the Aurbach group in the late 1990's. [12, 117] The electrochemical performance of these tests was not particularly promising (figure
26a), showing significantly worse cycling stability than PVDF-based graphite electrodes. This was attributed to the formation of non-passivating SEI on the electrode surface, (figure 26b-c) more so than was observed in the PVDF-based electrodes. It was speculated that the SiO$_2$ binder morphology and interaction with graphite promotes the formation of this SEI. Interestingly, we observe much improved cycling stability using a silicate-based binder. Extending the logic of Aurbach et al., it is possible that the morphology of the sol-gel derived electrode does not effectively coat the graphite surface whereas the silicate does an improved job of passivation.

![Figure 26](image_url)

Figure 26: Two papers use SiO$_2$-based sol-gel binders for lithium intercalation batteries. (a) The cycling data for these electrodes is worse than comparable data for conventional PVDF-based electrodes. (b-c) Formation of SEI on the graphite surface in carbon ceramic electrodes. The pristine electrode (a) is covered by a thick insulating layer after one electrochemical cycle in an ethylene carbonate/dimethyl carbonate electrolyte. 

There are additionally a few examples of silicate being used as a binder in non-intercalation batteries. Sodium silicate was used as a binder in zinc air battery negative electrodes, resulting in improved electrode conductivity and higher conversion.
efficiency compared to electrodes made using polycarbonate binders. Silicates have been used as binders in thermal batteries. Lithium silicate is also cited as being used as a passivating layer on electrode surfaces resulting in reduced self-discharge for intercalation batteries, but no data was presented for this formulation.

5.2. **Silicate electrode processing and rate capability**

As demonstrated above, sodium silicate can be used as a mechanically robust adhesive for electrode components. In order to determine its use as a binder we investigated the electrochemical performance of composite electrodes. Silicate was employed to replace PVDF in electrodes based on aqueous slurries, and we used half cells to investigate performance as a function of composition and heat treatment. LiFePO$_4$ was chosen for the majority of these studies, as it is a well-studied and highly electrochemically reversible compound with a 3.5V voltage plateau within the electrochemical stability window of common organic electrolytes.

5.2.1. **Silicate electrode composition and processing**

In order to carry out electrochemical tests, performance was first investigated as a function of heat treatment. Silicate-LiFePO$_4$ LFP (s-LFP) and silicate-Graphite (s-Graphite) electrodes were made using the composition shown in table 5.
Table 5: Electrode compositions used for heat treatment tests.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Material (LFP or MCMBs)</td>
<td>85 wt%</td>
</tr>
<tr>
<td>Super P</td>
<td>10 wt%</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>5 wt%</td>
</tr>
</tbody>
</table>

These electrodes were heated to 90°C and held for two hours, then heated to a higher treatment temperature and held at this temperature for two hours. Figure 27 shows discharge data of half cells made using electrodes processed at various treatment temperatures.

LFP shows a strong effect of heat treatment as evidenced in figure 27a, demonstrating an increase in capacity with heat treatment up to 500°C. At the low 290°C treatment temperature, the voltage curve shows a long tail. This indicates that a significant fraction of the active material is not electrochemically accessible at the C/10 rate. As the treatment temperature is increased, the electrode evidently undergoes a transformation resulting in substantially improved capacity. Four potential reasons for this could be that (1) the silicate reacts with the LFP to change its bulk chemistry and heat treatment reverses this reaction, that (2) silicate and LFP react in order to produce a non-lithium-conducting layer that is removed by heat treatment, that (3) electrical pathways are improved by the heat treatment, or that (4) the silicate itself becomes more lithium conductive during heat treatment. The effect of this heat treatment is further investigated below via electrochemical
cycling and transmission electron microscopy.

As shown in figure 27b, heat treatment temperature has little effect on graphite electrodes made using a silicate binder. This was expected, as graphite is intrinsically electrically conductive, chemically inert in the presence of silica as shown in [117], and highly lithium conductive.

![Figure 27: Voltage curves showing the effect of heat treatment on electrode performance. (a) s-LFP half cells charged at C/10 and discharged as shown at C/10. (b) s-Graphite half cells lithiated at C/10 and delithiated as shown at 2C. Both datasets correspond to discharge of a full cell.](image)

Figure 28 shows data from the same cells as presented in figure 27, with performance at increased rates displayed as a Ragone plot. It is seen that cells heat treated at lower temperature not only show worse performance at low rates (as demonstrated in figure 27) but also demonstrate much worse rate capability (i.e., a dropoff in capacity as rates are increased). This suggests that the effect of heat treatment on rate is likely due to variation
in charge transport rather than any reaction affecting the chemistry of the LFP bulk.

Figure 28: Ragone plot demonstrating rate of s-LFP electrodes shown in figure 27, examining the effect of heat treatment. Electrodes heated at higher temperatures show substantially improved rate capability.

The composition of s-LFP electrodes using a silicate binder was varied as shown above in table 4, using as a starting point the compositions tested for fracture toughness and the ratios used in [22]. Rate capability tests were performed on half cells as described in the methods. This resulted in discharge curves at various C-rates as shown in figure 29.
Figure 29: Representative voltage curves showing the effect of electrode composition on s-LFP rate capability. Examples of low (a) and high (b) binder content are demonstrated, in which the binder content equals the Super P conductive carbon content.

Capacity at the 5C rate was plotted as a function of composition, and presented in figure 30. This current was chosen to be an intermediate cycling rate expected to be strongly affected by differences in charge transport. Figure 30a shows the effect of silicate content on 5C rate. As demonstrated by the strongly sloped trend line, increasing silicate content decreases capacity at the 5C rate irrespective of Super P content. By contrast, as shown in figure 30b, these data do not show a strong overall dependence of 5C capacity on Super P mass fraction. A linear regression performed on the data in figure 30b yields a slope of -1.6, or 20% of the slope of the data in figure 30a. This indicates that silicate content affects rate and that Super P content does not substantially affect rate, under these conditions.
Figure 30: Capacities of electrodes at 5C rate. (a) Silicate has a strong effect on rate capability, with 10wt% silicate exhibiting a relatively low capacity at 5C. (b) Super P has very little effect on rate capability under these conditions. The trend line shown in (a) is for the dataset as a whole, and is labeled with its slope m in units of mAh/g/m%.

An interpretation of the data in figure 30b is that the effect of Super P on rate depends on the silicate content. At low (2%) silicate content, there appears to be little effect of Super P on rate. At high (10%) silicate content, even large amounts of Super P do not lead to high 5C rate capability. For intermediate (5%) silicate concentration, increasing the amount of Super P appears to lead to higher 5C capacity.

These rate capability results elucidate the mechanism behind improvement of C/10 capacity with heat treatment shown in figures 27 and 28. As Super P content does not seem to substantially affect rate under these conditions, we can conclude that electrical pathways are likely not responsible for the improvement in rate observed with increasing heat treatment temperature. By contrast, the fact that silicate content greatly affects
rate suggests that we should look to chemical mechanisms impeding Li$^+$ transport for the origins of this effect.

5.2.2. Comparison to conventional electrodes

In [9], the structural battery electrode presented showed only 60% of the capacity of a conventional electrode (figure 11b). In order to compare between batteries made using the silicate binder and conventional PVDF electrodes, batteries were constructed using the two compositions and rates were compared. The conventional cell was made using the optimized composition from MTI described in table 4 while the silicate cell was made using the composition shown in table 5 and heated to 500°C. Figure 31 shows the results of this comparison.
Figure 31: A comparison of the rate capabilities of electrodes made using the silicate binder to an electrode made using conventional PVDF binder. The conventional half cell was made using standard procedures outlined by MTI. The loading of the silicate electrode was 1.6 mg/LFP/cm², and the loading of the conventional electrode was 1.07 mg/LFP/cm². Unlike the case of previous structural electrode designs (figure 11b), no rate penalty is incurred by using the silicate binder.

As shown, the silicate electrode shows comparable performance to the conventional PVDF electrode. It should be noted that the loading of the silicate electrode is about 49.5% higher than that of the conventional electrode, and its rate capability remains excellent despite this. We thus should not expect a substantial penalty in active material capacity or rate as a result of using a silicate binder.

5.3. Silicate-based electrode structure

In order to determine the origins of the rate behavior observed in s-LFP electrodes, they were investigated via transmission electron microscopy (TEM). Samples of s-LFP made as described in the methods were examined. Electrodes with no heat treatment were compared to electrodes heated to 500°C so that the effect of heat treatment could be observed.

TEM micrographs revealed that the s-LFP electrodes exhibited crystalline LFP regardless of heat treatment, as demonstrated by the lattice fringes observed (figure 32). Furthermore, the electrodes were coated with a 5-25nm thick carbon layer deposited on the LFP as received. This layer is expected to be both lithium and electron conducting, and to thus promote charge transport kinetics. This is consistent with the rate behavior
observed in figure 30b, in that only a small amount of carbon is needed to promote electrical conductivity. Increasing the amount of carbon would thus not be expected to improve rate capability.

Elemental mapping provides further clues as to how the rate behavior of the electrodes is affected by composition. As shown in figure 33, iron and phosphorous are co-localized as expected in LiFePO$_4$. Carbon is ubiquitous in the electrode, both coating the active material surface and forming conductive interconnects between active particles. Silicate, meanwhile, is largely localized in the conductive carbon and at the interfaces between this carbon and the active material (see figure 34). At this composition, it does not primarily coat the active LFP. This is consistent with the rate dependence on composition observed in figure 30. As silicate has an affinity for the conductive carbon, when the silicate content
is small it does not influence rate because it mainly coats conductive carbon in-between active particles. In this location it does not have a substantial effect on ion transport into and out of the particles themselves. When the silicate content is high compared to the Super P carbon, it may coat the active materials and block ion transport.
Figure 33: Elemental mapping of s-LFP electrodes. (a) electrode with no heat treatment, (b) electrode treated at 500°C. Both electrodes show localization of silicate primarily in the conductive carbon rather than on the active surface.

Figure 34 shows a high-resolution elemental map of a s-LFP electrode heated to 500°C, focusing on the interface between the LFP and the conductive carbon. As demonstrated in the overlay, silicate is substantially co-localized at the interface between the conductive carbon and the active LFP. This further demonstrates that the silicate acts as a binder, acting to adhere electrode components in order to contribute to electrode mechanical stability.

Figure 34: High-magnification elemental mapping of a sample heat treated at 500°C. Here, it is shown that the silicate is localized in the conductive carbon and particularly at the interface between Super P and LFP. This supports the idea that silicate acts as a binder material joining the active and conductive electrode components.

During TEM investigations of the s-LFP electrodes heated to 500°C, it appeared that crystalline silicate was not present. This is surprising, as $\beta$-Na$_2$Si$_2$O$_5$ is known to form when waterglass is heated above 400°C (fig. 16b). The lack of crystalline silica was confirmed
with XRD (figure 35 below). It is possible that the amorphous silicate is stabilized at high temperatures by either interactions with conductive carbon, or by ion exchange with the LFP.

Evidence of ion exchange was observed from elemental mapping in TEM as shown in table 6. The amount of detectable sodium decreases with heat treatment by more than a factor of three. A likely explanation for this is that sodium is exchanged with lithium in the iron phosphate. As sodium is light and difficult to detect using EDX, sodium in the LFP particles may not be observed. Because the primary source of sodium in the electrode is the silicate, ion exchange of lithium for sodium may appear to remove sodium from the system. This is consistent with the fact that crystalline $\beta$-Na$_2$Si$_2$O$_5$ was not observed, as ion exchange would be expected to stabilize the amorphous silicate.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Na/Si Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.8 +/- 0.6</td>
</tr>
<tr>
<td>500°C</td>
<td>0.54 +/- 0.16</td>
</tr>
</tbody>
</table>

Table 6: Atomic ratio of sodium to silicon measured from elemental mapping in TEM. Detectable sodium decreases with heat treatment, suggesting ion exchange with the LFP.

5.4. Compatibility of silicate with electrode materials

The compatibility between silicate and electrode materials was evaluated in order to better design durable and cyclable SCBs. First, X-ray diffraction (XRD) was used in order to
provide further evidence of electrode structure and its evolution with heat treatment. LFP powder was first measured as-received. As expected, this material was a highly crystalline olivine with the space group Pnma (figure 35).

A silicate electrode with the composition shown in table 5 was investigated during in situ heating in an argon atmosphere. This heat treatment regime was meant to simulate the electrode sintering process. As shown in figure 35, the bulk LFP remained stable with heating and crystalline sodium silicate was not observed until 700°C. At this temperature, one peak appears at 21.1°2θ likely corresponding to β-Na₂Si₂O₅. The lack of crystalline impurities observed at 500°C is consistent with TEM observations (above).
Figure 35: X-Ray diffractogram of silicate electrode with LFP active material. Known peaks of Pnma LiFePO$_4$ are indicated with dotted lines. The silicate electrode prepared at room temperature does not appear to exhibit crystalline impurities. As the electrode is heated \textit{in situ} in an argon environment it remains chemically stable up to 700 °C, where an impurity appears. Peaks were observed to shift with heating due to thermal expansion.

Furthermore, the fact that the XRD pattern exhibited by s-LFP electrodes is extremely stable is additional evidence against silicate undergoing a reaction with bulk LFP that would influence rate capability as discussed above. If the rate behavior as a function of heat treatment shown in figures 27 and 28 were caused by such a reaction, this would be likely to influence the XRD pattern. For example, the formation of a crystalline reaction product would appear as an impurity that is removed with heat treatment. Alternatively, the degradation of bulk LFP may lower the intensity of the LFP peaks and increase their relative width by the Scherr effect. Thus, it appears likely that the effect of heat treatment on rate is the result of changes in the silicate and the conductive carbon rather than in the olivine LFP.

The compatibility of silicate with electrode materials was furthermore evaluated by electrochemical cycling stability tests. Results of these tests are shown in figure 36. Both of these electrodes exhibit the compositions shown in table 5 and were heat treated to 500 °C. The s-LFP shows high stability over 750 cycles at the 1C rate. Meanwhile, s-graphite shows no degradation over 300 cycles at C/5 following a rate test (350 cycles total). These promising results show that the silicate binder appears intrinsically compatible with LFP.
and graphite active materials.

Figure 36: Long-term cycling stability of electrodes made using sodium trisilicate binder, measured in half cells. (a) The LFP electrode shows little degradation after 750 cycles at 1C rate. (b) The graphite cell shows no degradation after 350 cycles at the C/5 rate.
6. Fabrication of Structural Ceramic Batteries

The previous sections established that silicate is an effective adhesive between battery active materials and conductive additives, showed that they are electrochemically compatible, and produced a series of design criteria relating composition and heat treatment of silicate-based electrodes to electrochemical performance. This section will further modify the composition of these electrodes to produce structural batteries, and demonstrate a robust fabrication process.

6.1. Addition of a temporary binder to electrodes

Following the process outlined above for electrode fabrication, aqueous slurries are prepared and coated onto a substrate. For the previous tests, slurries were cast onto a substrate which was used as a current collector in the ultimate battery. In order to make energy dense SCBs and to make them easier to fabricate and ultimately to manufacture, it is desirable to remove these electrodes from their substrates and handle them as freestanding films. However, the electrodes as deposited in previous sections were not sufficiently mechanically robust. The addition of organic polymers was thus investigated in order to increase their durability before sintering.

Two organic polymers were chosen, poly(vinyl alcohol) (PVA) and sodium carboxymethylcellulose (CMC) for investigation as binders in these freestanding films. These polymers were chosen because both are water soluble and frequently used in films in order to prevent
film cracking and to improve robustness. Furthermore, they can be used as temporary binders during the electrode fabrication process as they will decompose during heat treatment and lose 65% of their initial mass [33] in order to leave the rigid silicate binder.

Tests were done to evaluate what loading of silicate, CMC, and PVA are necessary to produce crack-free films. Slurries were made using a 1:1.4 ratio of solids to water in the solution. The slurries consisted of lithium iron phosphate, water, and enough polymer to result in the desired mass fraction in the dry film. These films were cast 1050 μm thick onto a paper substrate. This thickness was chosen because it results in approximately 470 μm thick dry films, substantially thicker than any battery electrode that would be expected to exhibit good kinetics. Thus, linear elastic fracture mechanics would predict that a composition immune to film cracking at this thickness will be strong enough to resist cracking at any reasonable battery electrode thickness. Results are shown in figure 44.
These results show that addition of significant amounts of binder can be used to produce crack-free electrode films. CMC and PVA are both able to result in crack-free films at 20wt%, while more silicate (between 20-50wt%) is required if only inorganic polymer is used.

The films can be made not only freestanding but flexible with the addition of a plasticizer to increase the elasticity of the CMC. This is shown in figure 38, in which addition of glycerol causes the strain at failure to increase by a factor of eight. Additionally, glycerol is a small molecule (figure 38c) with a boiling point of 290°C. Thus, it is expected to
entirely evaporate during heat treatment as the CMC is pyrolized. The residual binder required as shown in figure 44 can therefore be effectively reduced, resulting in a material post-sintering that has a very low organics content.

\[ R = H \text{ or } \text{CH}_2\text{CO}_2\text{H} \]

Figure 38: The chemistry of binders used, and the mechanical properties of CMC with plasticizer. (a) Sodium trisilicate, the permanent binder used in this system. (b) Sodium carboxymethyl cellulose, the temporary organic binder used to prevent thick films from cracking during drying. (c) Glycerol, the small molecule added as a plasticizer to CMC in order to make mechanically flexible electrode sheets. (d) Mechanical properties of various CMC film compositions, showing that the addition of glycerol can substantially increase the elasticity of these films, from [20].

### 6.2. Reinforcing SCB electrodes

Linear carbon-based structures on several length scales can be used to reinforce structural materials. These are surveyed in table 7. They span dimensions from thin single-walled nanotubes to the graphitic carbon fiber used in industrial composites.
The use of multi-walled carbon nanotubes (MWCNTs), carbon nanofiber (CNF) and chopped carbon fiber (CCF) materials as both structural support and as conductive additive was explored, initially without CMC so that the effect of reinforcement could be easily evaluated. It was found that addition of 10 wt% CCF to replace Super-P resulted in immense film cracking. MWCNTs produced electrodes that were brittle upon being removed from their substrates. Films reinforced with CNF exhibited improved mechanical performance.

Table 7: Dimensions of typical carbon-based materials used to reinforce composites span orders of magnitude in both length and width. Given are typical values for materials that are easily obtained from commercial sources. Materials with extreme dimensions have been reported, but are beyond the scope of this work.

<table>
<thead>
<tr>
<th>Reinforcement</th>
<th>Width</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-Walled Carbon Nanotubes</td>
<td>0.45-3 nm</td>
<td>Up to 2 μm</td>
</tr>
<tr>
<td>Multi-Walled Carbon Nanotubes</td>
<td>5-100 nm</td>
<td>1-10 μm</td>
</tr>
<tr>
<td>Carbon Nanofiber</td>
<td>70-200 nm</td>
<td>50-200 μm</td>
</tr>
<tr>
<td>Carbon Fiber</td>
<td>5-10 μm</td>
<td>mm - meters</td>
</tr>
</tbody>
</table>
The electrochemical performance of electrodes derived from flexible sheets was tested in order to determine whether the temporary CMC binder is electrochemically compatible with the previously investigated electrode chemistry, and to what degree structural CNF is able to replace Super-P as a conductive additive.

As shown in figure 40, electrodes made using flexible sheets are able to achieve comparable capacity to the SCBs made without CMC or CNF evaluated in previous sections. It is concluded that CNF and CMC carbonized at 500°C do not have deleterious effects on electrochemical performance. However, Fig. 40a shows that Super-P is required in order to achieve high LFP capacity while Fig. 40b shows that no Super-P is required in graphite electrodes. This is attributed to the electronic conductivity of the active materi-
als. Graphite, being electrically conductive, is able to achieve excellent electronic transport throughout the electrode with only minimal conductive additive. As LFP is relatively electrically insulating, it requires high surface area Super-P in order for all the active material to participate in cell cycling.

Figure 40: Electrochemical performance of half cells made using electrodes derived from flexible sheets. (a) Discharge comparison of LFP cell made using the SCB chemistry described above with no CMC or CNF, compared to cells made using CMC. As shown, the performance of the flexible sheet derived electrode is comparable to the conventional SCB. However, Super-P is required in order to achieve this performance. (b) Graphite cells derived from flexible sheets outperform conventional electrode chemistry, likely due to participation of graphitic CNF. Super-P is not necessary in order to achieve excellent electrode capacity. All electrodes were heat treated at 500°C. Capacities are normalized by LFP and Graphite content.
6.3. Separator development

As shown in figure 14, the SCB design employs a ceramic binder throughout layers of the battery stack including both electrodes and the separator. In order to achieve this, it was necessary to design a separator paste using the silicate binder. The SCB electrode composition described above was used as a starting point for the binder paste, with 0.5 \( \mu m \) diameter SiO\(_2\) particles replacing active material particles.

The effect of silicate content on rate capability was expected to be substantially different in the separator compared to the electrodes. This is because Li\(^+\) needs only to pass through the separator during cycling, not to intercalate in and out of separator particles. We believe that slow Li\(^+\) transport kinetics through the silicate into and out of the active material substantially limit silicate content in the electrodes, whereas only pore blocking is expected to limit silicate content in the separator.

Thus, we fabricated separators with varying silicate content. The base composition for a 10wt% silicate separator is described in table 8. The silicate loading was varied, maintaining a constant mass fraction of SiO\(_2\), CMC, and glycerol in the wet slurry. Slurries were coated onto a glass fiber tow and dried. Similar to the electrodes, this resulted in a flexible film. These films were heated to 500\(^\circ\)C in argon in order to sinter the separator and simulate the heat treatment process that an SCB undergoes during processing.
Table 8: Example composition of separator paste at various processing steps. The wet slurry was coated onto a glass fiber tow and dried. The tow was subsequently heated to 500°C to result in the final composition. Pastes were made varying the silicate, SiO₂ and water content in order to result in different silicate compositions as described in the text. All composition values in this table are given in wt%.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wet Slurry</th>
<th>Dry Film</th>
<th>Sintered Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicate</td>
<td>2.7%</td>
<td>7.4%</td>
<td>10%</td>
</tr>
<tr>
<td>SiO₂ Particles</td>
<td>22%</td>
<td>61%</td>
<td>85%</td>
</tr>
<tr>
<td>CMC</td>
<td>3.9%</td>
<td>11%</td>
<td>5%</td>
</tr>
<tr>
<td>Glycerol</td>
<td>7.8%</td>
<td>21%</td>
<td>0%</td>
</tr>
<tr>
<td>Water</td>
<td>82%</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Morphologies of samples with varied silicate composition are shown in figure 41. As the silicate composition is varied, samples up to 10 wt% silicate show very little aggregation of SiO₂ particles. The morphology of these samples is largely a porous film of individual particles. At 10wt%, there begins to be some aggregation as shown by the arrows in figure 41. The 19wt% sample is composed of 10-20μm aggregates of SiO₂, while the 43wt% silicate sample is a uniform film of silica with particles embedded in it.
Figure 41: Effect of separator paste composition on morphology. The sample at 10 wt% silicate exhibits the composition described in table 8. This sample shows some aggregation of particles as highlighted by the arrows. All scale bars are 5 μm.

The resistance of these films was tested using electrochemical impedance spectroscopy (EIS). Cells were made using the configuration shown in figure 42a and measured as described in the methods, following [100, 102]. The solution resistance $R_s$ was taken to be the high-frequency intercept of the Nyquist impedance plot with the real axis, as shown in figure 42b. $R_s$ was measured for experimental samples as well as control samples containing no sample. The resistance corresponding to transport through the separator and other device components was controlled for by calculating the effective resistance corresponding to transport through separator samples, taken to be:
\[ R_{\text{Eff}} = R_{S, \text{Sample}} - R_{S, \text{Control}} \]

This \( R_{\text{Eff}} \) is shown in figure 42c.

Figure 42: The separator composition was measured using electrochemical impedance spectroscopy (EIS). (a) Separator samples made as described in the text were loaded into CR2023 coin cells in the configuration shown. (b) Control and test samples were tested using EIS, and the high-frequency intercept with the real axis was taken to be \( R_s \). (c) \( R_{\text{Eff}} \) corresponding to \( \text{Li}^+ \) ion transport through the sample was calculated and plotted as a function of separator composition.

As shown in figure 42c, \( R_{\text{Eff}} \) is approximately constant for compositions under 10wt% silicate and increases approximately linearly from 10wt% to 43wt%. This is highly compatible with the separator morphology shown in figure 41. As shown in scanning electron micrographs, sample morphology changes very little with the addition of silicate under 10wt%. The morphology in this case corresponds mainly to 0.5µm diameter SiO₂ particles with very little apparent volume fraction devoted to silicate filler. At 10wt% we begin to observe aggregates of particles with a substantial volume fraction devoted to silicate.
These electrochemical results suggest that at high volume fractions silicate, electrolyte is displaced and/or the tortuosity of the separator increases. The result is to increase the ionic resistance of the separator.

6.4. SCB fabrication

In the above sections, we have therefore developed the components of an SCB corresponding to both electrodes and the separator. The following step is to combine all of these components into a full SCB.

SCBs were initially made on glass substrates, obviating the need for CMC and CNF as the electrodes were not designed to be freestanding. This configuration is shown in the inset of figure 43a. Two glass substrates were coated with current collector paste purchased from ted pella, using a carbon current collector for the positive electrode and a nickel paste for the negative electrode. SCB electrodes were coated onto these substrates, heat treated, and layered with glass fiber and a separator paste. This whole battery stack was packaged and cycled.
Figure 43: Large-format SCB fabricated on rigid substrates. (a) Discharge curve of the LFP/Graphite cell at C/10. The cell reaches an adequate capacity based on the mass of its limiting graphite electrode. The inset shows a schematic of this battery configuration. (b) A photograph of the packaged SCB cell.

The resulting battery was initially charged at C/10 to 4V, and shows an excellent capacity when discharged at C/10. In this cell, the negative electrode limited capacity and its mass was therefore used to normalize capacity. The loading of components in this configuration are shown in table 9. As shown, the graphite represents an area specific capacity of 1.3 mAh/cm² which is in the range needed for commercial cells. This cell has room for further optimization, but represents a proof of concept of the feasibility of the SCB approach.
<table>
<thead>
<tr>
<th>Component</th>
<th>Loading (mg/cm²)</th>
<th>Fraction Loading</th>
<th>Total Area Specific Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Current Collector</td>
<td>4.4</td>
<td>4.2%</td>
<td>-</td>
</tr>
<tr>
<td>LiFePO₄ Electrode</td>
<td>26</td>
<td>24%</td>
<td>3.7 mAh/cm²</td>
</tr>
<tr>
<td>Glass Fiber Separator</td>
<td>7.7</td>
<td>7.3%</td>
<td>-</td>
</tr>
<tr>
<td>Separator Paste</td>
<td>13</td>
<td>12%</td>
<td>-</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>38</td>
<td>35%</td>
<td>-</td>
</tr>
<tr>
<td>Graphite Electrode</td>
<td>4.2</td>
<td>4.0%</td>
<td>1.3 mAh/cm²</td>
</tr>
<tr>
<td>Nickel Current Collector</td>
<td>13</td>
<td>13%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 9: Composition of SCB on glass slide substrates shown in figure 43. As shown, the active materials represent 28% of the mass loading of this cell. There is room for further optimization, both by increasing the loading fraction of the active materials and improving the capacity matching of the cell. Loadings of electrodes are given based on entire electrode mass, while area specific capacities are calculated by multiplying the theoretical specific capacity by the active material loading.

The fabrication process for SCBs was extended based on flexible freestanding sheets as described above. These sheets were made using CMC and CNF in the electrodes, and CMC combined with silica particles and glass fiber in the separator. The fabrication process is shown in figure 44. Freestanding sheets composed of both electrodes and separator were fabricated, and laminated with excess separator paste. This resulted in a flexible trilayer sheet which could be folded into shape on a mold and dried. The resulting battery was
heat treated, resulting in a rigid composite maintaining the shape of the mold.

Figure 44: Process for fabricating SCBs conforming to a mold. (a) Freestanding electrodes made using CMC organic binder are flexible and can be curved. (b) Layups consisting of both electrodes, a glass fiber separator and separator paste are flexible and can be curved in order to conform to molds. (c) During drying and heating, the CMC is removed while the silicate binder cures. The result is a rigid battery stack matching the shape of the mold.

To assess the electrochemical performance of this production method, batteries were made from freestanding sheets cut to fit into a coin cell casing. These sheets were laid up as shown in figure 44 to make batteries with the cross-section shown in figure 45a. These were placed into coin cells and cycled. 45b-c shows some cycling results from these cells at C/20. Table 10 shows the composition of these cells at the stack level. This configuration represents an improvement in the capacity matching of the electrodes as compared to the glass substrate samples. The separator paste with 3% silicate loading was used in this sample in order to facilitate ion transport. However, the total thickness of the paste-coated
glass fiber was 137 μm. Subsequent cells will lower the separator thickness to improve rate.

Figure 45: A full SCB cell fabricated to fit inside a coin cell casing. (a) The design of this SCB, prefabricated as a freestanding SCB from electrode and separator sheets. (b) One discharge of this cell and the subsequent charge, normalized by graphite mass. Charge and discharge are both at C/20, with a trickle charge step. (c) Several cycles of this cell.

<table>
<thead>
<tr>
<th>Component</th>
<th>Loading (mg/cm²)</th>
<th>Fraction Total Loading</th>
<th>Total Area Specific Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFePO₄ Electrode</td>
<td>32</td>
<td>37%</td>
<td>3.65 mAh/cm²</td>
</tr>
<tr>
<td>Total Separator</td>
<td>18</td>
<td>21%</td>
<td>-</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>27</td>
<td>31%</td>
<td>-</td>
</tr>
<tr>
<td>Graphite Electrode</td>
<td>9.4</td>
<td>11%</td>
<td>2.3 mAh/cm²</td>
</tr>
</tbody>
</table>

Table 10: Composition of SCB on glass slide substrates shown in figure 45. This represents an improvement in capacity matching compared to the cell fabricated on glass slides shown in figure 43 and table 9. The graphite area specific capacity is within the range required for commercial cells.
7. Mechanical properties of structural ceramic batteries

For evaluation of SCB mechanical properties, full cells were made as described above from freestanding electrode and separator sheets. These sheets contained a CMC temporary binder as well as CNF. The sheets were laminated into full cell stacks using excess separator paste, dried, and heat treated to 500 °C for two hours in an argon atmosphere.

The samples used for mechanical tests were cut into a dogbone shape following the ASTM E8 standard plan shown in figure 46. This standard is designed to be used for the tensile testing of electrically conductive materials.

Figure 46: Template for a dogbone tensile sample, from [47]. Samples were made using the 'subsize specimen' dimensions, where G=25mm, W=6mm, and L=100mm. This sample size was chosen in order to allow easy processing in a 12cm deep furnace.

Composite materials require both strong and tough components in order to result in a robust composite structure. With this in mind, some samples were treated with poly(ethylene oxide) (PEO) before tensile testing. High molecular weight (N=5,000,000) PEO was used in order to provide maximal toughness at a low mass fraction of the total
composite. PEO was chosen due to its well-known propensity to conduct Li\(^+\) and therefore to improve structural performance without deteriorating rate capability.

![Composite image](image.png)

Figure 47: Tensile tests of full SCB stacks with varied amounts of PEO additive. (a) A dogbone sample in the Zwick mechanical tester. (b) Tensile test results. Composites exhibited 3.9 MPa tensile strength without PEO, which increased to 11.5 MPa with the addition of 2 wt\% PEO.

Tensile test results are shown in figure 47b. As expected, samples undergo brittle failure. The cell stack achieves an ultimate tensile strength (UTS) of 3.9 MPa with no PEO added. This relatively low strength is due to the brittle failure of individual struts at low deflection. Once an individual strut fails, it is useless in bearing further load. PEO was therefore expected to improve the mechanical properties of the structure by coating struts and allowing them to deform while still contributing to structural integrity.

The result of adding small amounts of PEO is also shown in figure 47b. As shown, the addition of PEO increases the stiffness of the material. It also increases the UTS of the
battery stack by nearly a factor of three to 11.5 MPa. This series of tests demonstrates that SCBs can be fabricated that are able to bear load, and points to ways in which their performance might be improved further.
8. Conclusions and Future Outlook

In this work, we have established a genuinely new strategy for the production of structural batteries. The Structural Ceramic Battery (SCB) architecture uses an inorganic polymer binder and thus provides the benefits of a composite electrode while providing structure from an inorganic adhesive. We have established sodium trisilicate as a water-processable binder material that is earth abundant and environmentally friendly. Electrodes made using this binder have rate capabilities commensurate with electrodes employing conventional PVDF and can be cycled at least 750 times with little degradation. In addition, we have established a manufacturing method for SCBs that is expected to be compatible with mass-production. Avenues for further improvement of the SCB system are suggested by this work.

8.1. Adjusting binder chemistry to optimize rate

A major area for improvement is to increase the Li\(^+\) ion conductivity of the ceramic binder. Increasing the mass fraction of the binder will improve the fracture toughness of the material, as shown by the fracture toughness measurements presented above. However, increasing the mass fraction of sodium silicate will lower rate capability. These trade-offs may be best managed by increasing the rate of charge transport through the binder material.

One route to do this is to change the cation. Sodium silicate was chosen as the focus
of these tests because it is an extremely earth abundant material that is already mass produced. Using lithium silicate instead, however, may improve charge transport. There is evidence for this in the improvement of rate capability with heat treatment, improved capacity with cycle number, and the redistribution of Na⁺ with heat treatment observed via TEM. Further investigation of the role of cation distribution within these electrodes is likely to prove interesting, as preliminary results have already shown.

Another way to improve ion transport through the ceramic electrolyte would be to change the anion. Phosphates have been used as ceramic adhesives similar to silicates. In addition, the well-studied solid electrolyte Lithium Phosphorous Oxynitride (LIPON) can be formed by treating lithium phosphates in a nitrogen atmosphere. This and other strategies for using solid electrolytes as binders may enable improved multifunctionality.

8.2. Optimize mechanical properties

The mechanical properties of the material may be optimized via several routes. One is to further improve the mechanical properties of the binder itself. This may be done by altering the binder chemistry as described above, or by introducing organics as described in the geopolymer section. Another route could be to expand the work on PEO by using a gel electrolyte in the pores of the SCB. This could drastically increase the toughness of the composite.

Furthermore, additional mechanical tests must be done on these materials in order to
optimize their properties. For example, three-point bending and vibrational tests should be done to prove out these materials prior to integration in vehicles.

8.3. Demonstrate large-scale packaged cells

Above, the fabrication of large-format (15 cm²) cells on substrates and larger (80 cm²) battery stacks were demonstrated. A manufacturing method was shown that can produce cells designed to fit molds of varied curvature. Large-scale packaged cells must next be developed and optimized in order to bring the benefits of SCBs to vehicles.

8.4. Improve energy density

Lastly, the compatibility of this strategy with a wider range of active materials must be demonstrated. Above, the use of an SCB strategy with graphite and LiFePO₄ electrode materials was shown. The material has also been shown to be compatible with Li₄Ti₅O₁₂. Further tests must be done to demonstrate compatibility with materials exhibiting higher energy density. In particular, NMC and NCA materials as well as protected metallic lithium anodes are the most promising candidates. Because SCBs represent a fabrication strategy to produce load-bearing batteries that are in principle compatible with a range of active materials, it is envisioned that SCBs will improve in energy density along with the state of the art as new active materials become available.
References

[1] In Greeuw et al. 1984, $E_A$ and $\mu_0$ were measured for the mobility of Li$^+$ ions in thermally oxidized silica by fitting transient ionic currents to a diffusion model. These data were taken in the temperature range 100°C - 500°C. In order to find the room temperature diffusivity for the present work, ionic mobility was calculated from these measured quantities then diffusivity was determined by the Einstein relation.

[2] $5 \times 10^{-19}$ cm$^2$/s was calculated from the data given in Snow et al, 1965. $3 \times 10^{-18}$ cm$^2$/s was calculated from the equation given in Verhoogen, 1952. These are clearly only estimates, as they are room temperature diffusivities calculated from high-temperature experiments, and could miss low-activation-energy diffusion mechanisms dominant at lower temperatures.

[3] Calcium-containing minerals are sometimes used in geopolymers. Calcium can function as a network modifier and improve the strength of geopolymer monoliths. Unlike in portland cement, however, calcium is not one of the main constituents and geopolymers can be made without it. See Li et al, Cement and Concrete Research 40.9 (2010): 1341-1349.


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