LLNL-TR-840188

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Performance of Lithium-Ion Batteries with 3D Printed Anodes and Compressible Carbon Structures

F. Muto, M. Wood

September 23, 2022

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Performance of Lithium-Ion Batteries with 3D Printed Anodes and Compressible Carbon Structures

Lawrence Livermore National Laboratory
Francesca Muto
Mentor: Marissa Wood

Mentor Signature Marissa Wood

LLNL-TR-840188

Abstract

Carbon scaffolds have been shown to improve the performance of Li metal anodes in Li-ion batteries by acting as conductive hosts for Li metal plating and stripping. The scaffolds provide a more uniform electric field, and their 3D geometry enables smaller diffusion paths for the Li ions. In this project, several different types of carbon lattices were 3D printed, mechanically tested, and analyzed in coin cells. Planar and 3D printed graphite coatings were evaluated as the baseline, since graphite is a common anode material. The results showed that implementing a 3D graphite lattice into a coin cell improved the Li plating and stripping efficiency compared to the planar coating. However, since graphite can intercalate Li ions, other carbon materials were also explored that should act as better hosts for Li plating/stripping. To improve the compressibility of these non-graphite carbon scaffolds, five different carbon ink formulations were 3D printed in lattice configurations. SEM imaging and compression testing showed that both the final dimensions and the compressibility of the carbon lattices depended on the type of carbon precursors used. The two most suitable compositions were found to be those made with graphene oxide-resorcinol formaldehyde and graphene oxide-ammonium hydroxide. In the future, these formulations will be further refined to increase their mechanical strength, and their performance as scaffold hosts for Li metal anodes will be evaluated in coin cells.

Introduction

Despite recent advances in lithium-ion battery technology, there is a current demand for higher-capacity batteries. Li metal anodes can provide much higher capacities than conventional anodes, but they currently suffer from short lifetimes due to non-uniform Li plating and stripping that can generate needle-like dendrites that short the battery. Carbon scaffold hosts have been shown to facilitate Li metal anode cycling by providing a more uniform electric field, abundant Li nucleation sites, and a shortened path for ion transport (1-3). The focus of this project was to compare the morphology, mechanical properties, and electrochemical performance of different carbon scaffold host materials. This was achieved by fabricating different carbon lattices using 3D printing, characterizing them by SEM and compression testing, and evaluating their electrochemical performance in coin cells.

Methods

Baseline Electrode/Lattice Fabrication

Two methods of electrode fabrication were used: tape casting and 3D printing.

Graphite-based anode slurries were 92 wt% graphite, 6 wt% polyvinylidene difluoride (PVDF) binder, and 2 wt% carbon black. Additionally, a baseline slurry without graphite was made with 34.4 wt% carbon black and 65.6 wt% PVDF. In each case, N-methyl pyrrolidone (NMP) was used to dissolve the PVDF separately first, and the slurry was cast onto Cu foil with an adjustable doctor blade. Electrodes were dried at 70 ^{o}C, punched into ½” diameter disks, and dried again in a vacuum oven at 115 ^{o}C overnight.

The slurry used for 3D printing was similar to the slurry used in the tape casting method. However, since a higher viscosity is needed, less solvent (NMP) was added. The slurry was put into a syringe with a 200 µm nozzle and printed onto Cu foil by direct ink writing (DIW) using a Hyrel 3D Printer.

Compressible Carbon Lattice Fabrication

The compressible carbon structures were created using DIW as shown in **Error! Reference source not found.**. Slurries with different carbon materials were created with various gelling agents and crosslinkers in order to test which materials improve the mechanical properties of the lattices. The lattices were printed using a three-axis positioning stage (ABL 9000, Aerotech) where the motion was controlled by a G-code to create a 12 x 12 mm lattice with 800 µm spacing. If a gelling agent was used, the print was submerged in isooctane and then placed in an 80 ^{o}C oven for 3 days to allow sufficient time to gel. If needed, a solvent exchange was performed to change the solvent to water for freeze drying. All samples were freeze dried for roughly 24 hours. After freeze drying, the samples were carbonized under nitrogen for 2 hours with a 2 °C/min ramp rate using the appropriate carbonization temperature for that sample, ranging from 600ºC to 1000ºC. The samples were characterized by scanning electron microscopy (SEM) and compression testing. In order to determine compressibility, each sample was subjected to two tests using an Instron Universal Testing System. The first test was a cyclic test where the sample was compressed and decompressed, with each cycle increasing the stress by 10%. The second test was one single compression test at 1 mm per second, until there was a change in force of 40% or 800N of force was exerted.

Cell Assembly

All coin cells prepared were half cells assembled in an argon glove box using a Celgard separator and a lithium metal counter electrode. The liquid electrolyte used was 1.2M $LiPF_6$ in 3:7 wt% ethylene carbonate: ethyl methyl carbonate. Cells were allowed to sit at least 3.5 hours before cycling to allow for sufficient wetting. Formation cycling was performed at room temperature by charging and discharging at C/10 for 3 cycles using a constant current constant voltage (CCCV) protocol. Additionally, lithium plating and stripping tests were done at room temperature at current densities of $0.1 mA/cm^2$, $0.2\ 1mA/cm^2$, and $0.5\ 1mA/cm^2$ for a maximum of 40 h per cycle.

Results & Discussion

Li Plating/Stripping for Planar and 3D Electrodes

The ideal lithium plating and stripping curve would show plating and stripping occurring for equal amounts of time, indicating that all the plated lithium was then stripped. The lithium plating and stripping results for the different cells can be seen in **Figure 1:** Lithium plating and stripping results for the baseline graphite, carbon black, and 3D printed graphite lattice cells. Graphite was used as a baseline since it is a common commercial anode material. However, for the graphite cells, we expect that some Li-ions will intercalate into the graphite and only some will plate onto the surface. The planar baseline graphite shows the smallest amount of lithium plating and stripping. The plating occurs for about 4 hours while stripping only occurs for 2 hours. For the graphite lattice, the plating time is significantly increased to almost 12 hours, showing the benefit of the 3D architecture. However, the stripping time is still much smaller at only 5 hours. The carbon black sample was created because Li ions should not intercalate into the carbon black, as they do in graphite, allowing for more Li plating. Indeed, the results from the carbon black cell show significantly more plating than both graphite cells; however the stripping is still significantly lower, occurring for less than half the time that plating occurred.

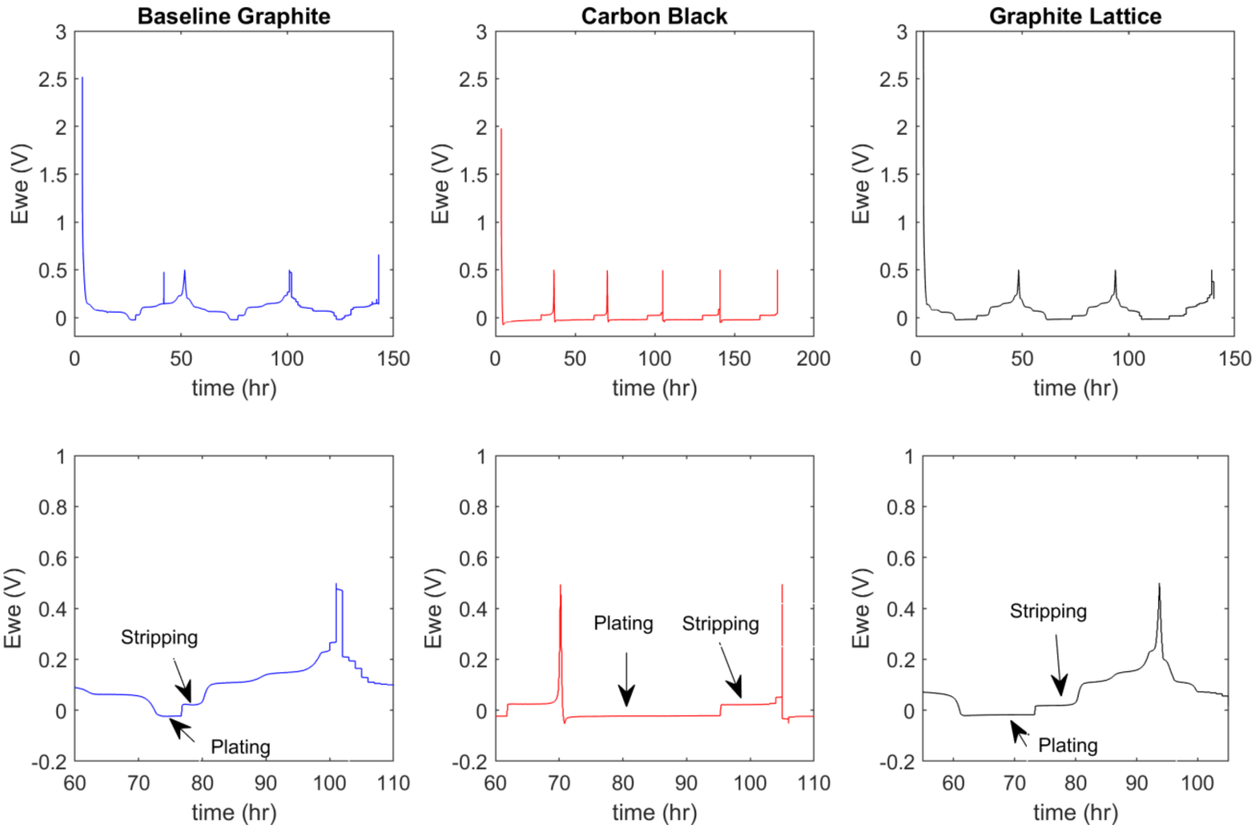


Figure 1: Lithium plating and stripping results for the baseline graphite, carbon black, and 3D printed graphite lattice cells. Row 1 is the voltage vs. time for the full length of time the cell was tested. Row 2 is a zoomed in view of one cycle where Li plating and stripping occurred.

Characterization of Compressible Carbon Lattices

While graphite is a conventional Li-ion battery anode material and thus serves as a good baseline for comparison, it is not an ideal host for Li plating/stripping because Li ions can intercalate into the graphite. Therefore, scaffolds made from different carbon materials are necessary to serve as hosts for Li metal anodes, but they need to be compressible and nonbrittle to maintain structural integrity in a battery cell. To improve the compressibility, carbon lattices made from several different formulations were 3D printed, post-processed, and then mechanically characterized. A sample of graphene was printed using an ink containing aqueous-based graphene oxide (GO) with hydroxypropyl methylcellulose (HPMC) added to increase the viscosity. The resulting sample showed filament widths of 130-160 μm as shown in **Figure 2**. This served as a baseline for the non-graphite carbon lattices. Other ink formulations included chitosan-glutaraldehyde (C-G) and GO-resorcinol formaldehyde (GO-RF). Compared to the baseline GO sample, both of these formulations showed increased shrinkage after carbonization, with much smaller filament widths (50 μm for C-G and 90 μm for GO-RF). This demonstrates that the type of carbon used for printing affects the final lattice dimensions and morphology.

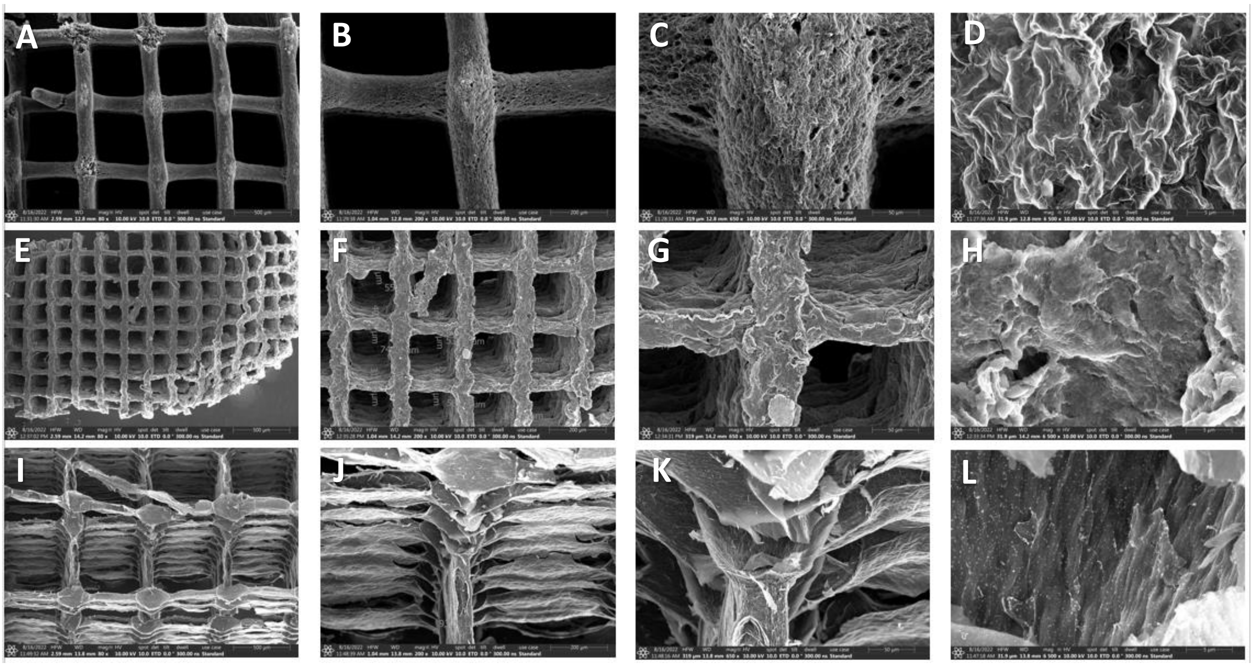


Figure 2: SEM images of 3D printed lattices with increasing magnification along the row. (A-D) is the standard GO formulation carbonized at 1000 °C with filament width of ~130 μm. (E-H) is Chitosan-Glutaraldehyde carbonized at 800 °C with filament width of 50 μm. (I-L) is GO-RF carbonized at 800 °C with filament width of ~90 μm.

Another approach was to use carbon nanotubes (CNT) due to their high conductivity, large surface area, and porous structure that studies have shown provide high charge transport 0. CNTs were combined with GO and cellulose to print the lattices shown in **Figure 3**. These lattices were carbonized at two different temperatures: 600 °C and 800 °C. Overall, these GO-CNT-cellulose samples are much more porous than the GO, C-G, or GO-RF lattices. The samples carbonized at 800 °C showed more shrinkage than the samples carbonized at 600 °C. More specifically, the filament width of the sample carbonized at 600 °C is about 350 μm, while the sample carbonized at 800 °C is 270 μm, showing a 26% difference in size.

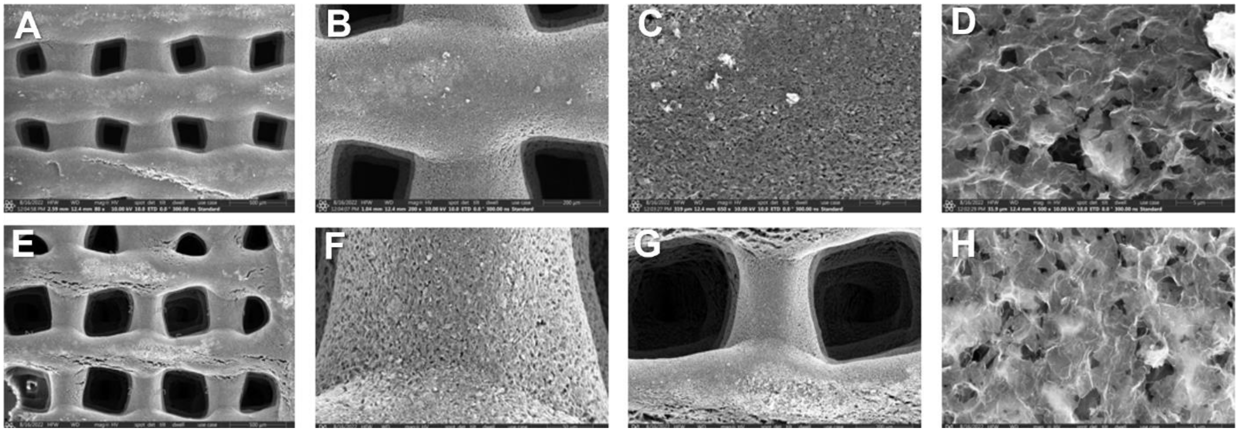


Figure 3: SEM images of 3D printed lattices with increasing magnification along the row. (A-D) is GO-CNT-Cellulose carbonized at 600 °C with a filament width of ~350 μm. (E-H) is GO-CNT-Cellulose carbonized at 800 °C with a filament width of ~270 μm.

After taking SEM images of the samples, compression tests were performed to compare the mechanical properties of lattices made with different carbon materials. The results are shown in **Figure 4** and indicate that three carbon lattice formulations have improved compressibility relative to the baseline GO formulation.

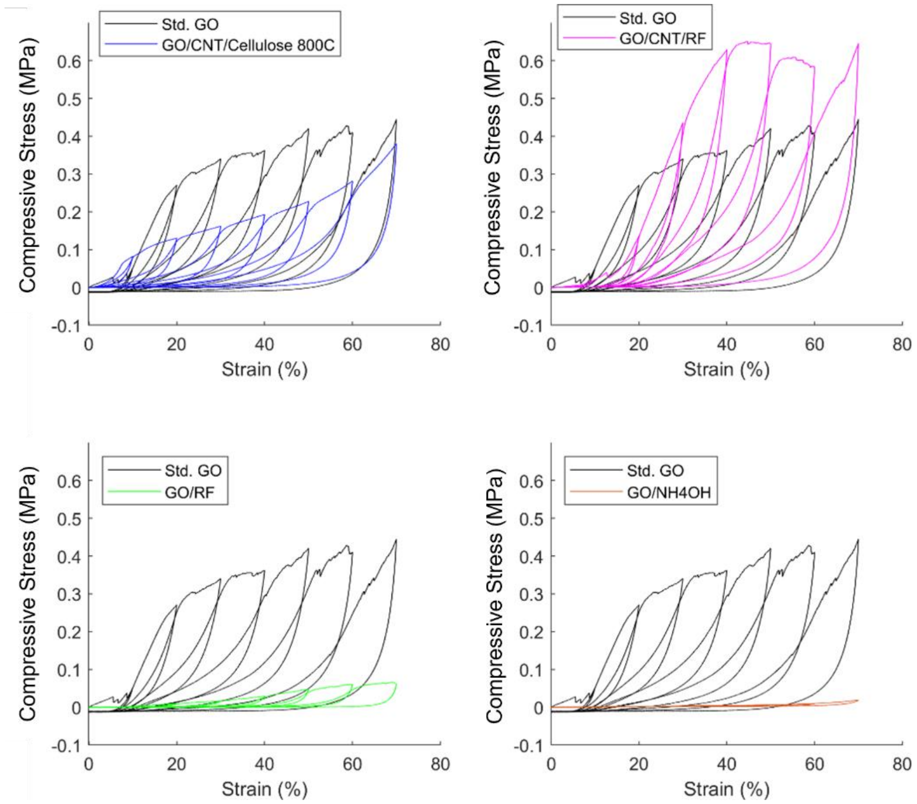


Figure 4: Stress vs. strain curves for 3D printed lattices made with different carbon materials.

The Young's modulus was calculated for each sample and can be found in **Table 1:** Young's modulus of printed lattices made with different carbon materials.. In terms of compressibility, a low Young's modulus is desired. The Young's modulus of the GO-NH_4OH formulation (0.04 MPa at 60% strain) is the lowest of all, indicating that this formulation is the most compressible, followed by the GO-RF formulation.

Table 1: Young's modulus of printed lattices made with different carbon materials.

Lattice Composition	**Young's Modulus (MPa) (20%)**	**Young's Modulus (MPa) (40%)**	**Young's Modulus (MPa) (60%)**
Standard GO	2.72	2.72	2.74
GO-RF	0.06	0.3	0.64
GO-CNT-RF	2.37	7.33	4.93
GO-CNT-Cellulose, 800 C	1.85	1.5	1.6

GO-NH4OH	0	0.01	0.04

Conclusions

The morphology, compressibility, and electrochemical performance of several different types of carbon lattices were investigated to determine their suitability as scaffold hosts for Li metal anodes in Li-ion batteries. The carbon lattice provides a more uniform electric field and abundant Li nucleation sites to help prevent Li dendrite formation and improve the cycling stability of Li metal anodes. Graphite was used as a baseline material since it is a common commercial anode in Li-ion batteries. Comparing a tape cast, planar coating of graphite with a 3D printed graphite lattice, we found that more Li was able to plate onto the surface of the lattice compared to the planar graphite, showing the benefit of the 3D structure. However, since the Li ions can also intercalate into graphite, other carbon materials are better suited to act as scaffold hosts for Li plating/stripping.

To develop a compressible scaffold from non-graphite carbon materials that can maintain its structure in a cell, five different carbon formulations were 3D printed in lattice geometries and then subjected to compression testing. The SEM images showed that the morphology of the lattices is dependent on the type of carbon used. Out of the five, the GO-NH$_4$OH and GO-RF formulations showed the best compressibility and were selected as good scaffold candidates moving forward. Their electrochemical performance in cells will be tested in the future to compare with the graphite baseline.

Professional Development

<u>New Skills and Knowledge</u>

While working on this project, I learned new skills and refined some that I already possessed. This internship was the first time I was ever exposed to a Direct Ink Writing printer, freeze dryer, tube furnace, and compression tester. Now as a daily user, how this equipment works is second nature to me. Some skills I refined were my glovebox use, electrode fabrication, and battery testing. This internship allowed me to dig deeper and learn not only how to do these things, but the reasoning behind why we do it the way we do. For example, instead of following a recipe without question I started to think critically about why we were using these specific components.

Impact on Career Planning

This experience solidified my interest in renewable energy, especially in the field of batteries. This program has made me realize that not only do I want to pursue a master's degree, but I want to pursue my degree in materials science. Throughout my time at LLNL, I attended seminars and connected with people in the materials science division. Through this experience, I realized that my career goals more closely align with pursing a degree in materials science.

Relevance to DOE Mission

The mission of the Department of Energy is to secure the security and prosperity of the United States by addressing energy challenges. This project is contributing to this mission by improving the performance of Li-ion batteries, which are in high demand as the world quickly moves toward renewable energy (for example, with the quick rise of electric vehicles). This project aims to develop carbon materials that can serve as hosts for high-capacity Li metal anodes to increase the energy density of Li-ion batteries and next-generation solid-state batteries in the future.

Acknowledgements

I would like to thank Marissa Wood for her guidance throughout my project, as well as providing me with all the necessary training and materials I needed during my time here. I would also like to acknowledge Lawrence Livermore National Laboratory for hosting me during this appointment.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This research was supported in part by an appointment with the AMO Summer Internships program sponsored by the U.S. Department of Energy (DOE), EERE Advanced Manufacturing Office (AMO). This program is administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by ORAU. All opinions expressed in this paper are the author's and do not necessarily reflect the policies and views of DOE, ORAU, or ORISE.

References

(1) Zhang, A., Fang, X., Shen, C. *et al.* (2016). A carbon nanofiber network for stable lithium metal anodes with high Coulombic efficiency and long cycle life. *Nano Res.* 9, 3428–3436.

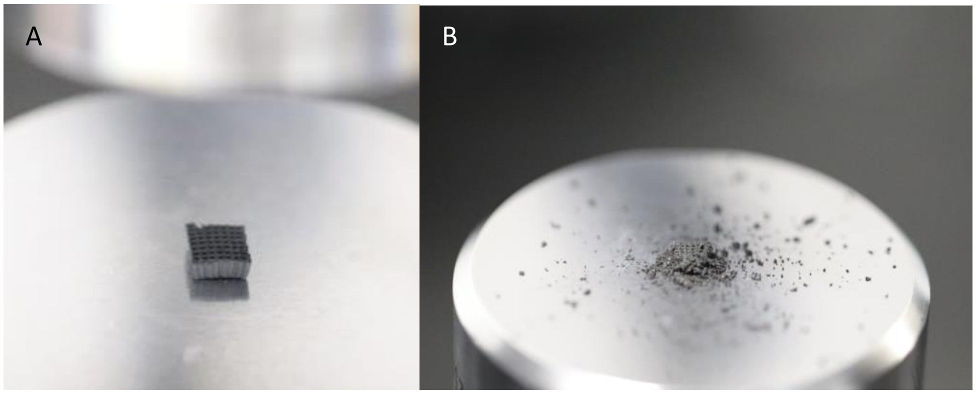
(2) Xu, Y., Wang, L., Jia, W. *et al.* (2019). Three-dimensional carbon materials as stable host for dendrite-free lithium metal anodes. *Electrochimica Acta*, 301, 251-257.

(3) Zhu, Y. Li, J. Saleh, S. M. Pham, H., et al. (2020). Towards high-performance Li-ion batteries via optimized three-dimensional micro-lattice electrode architectures. *Journal of Power Sources, 476, 228593.*

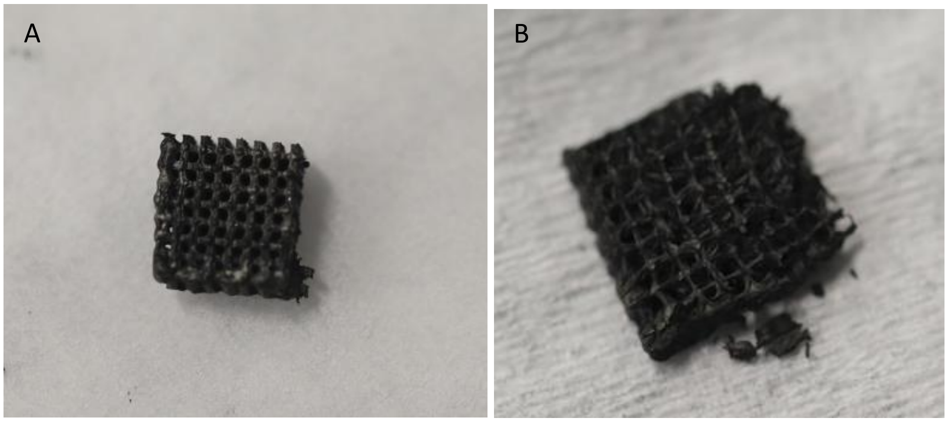
(4) Wu, C., Zhang, S., Wu, W., Xi, Z., Zhou, C., Wang, X., et al. (2019). Carbon nanotubes grown on the inner wall of carbonized wood tracheids for high-performance supercapacitors. *Carbon, 150*, 311-318.

Appendix

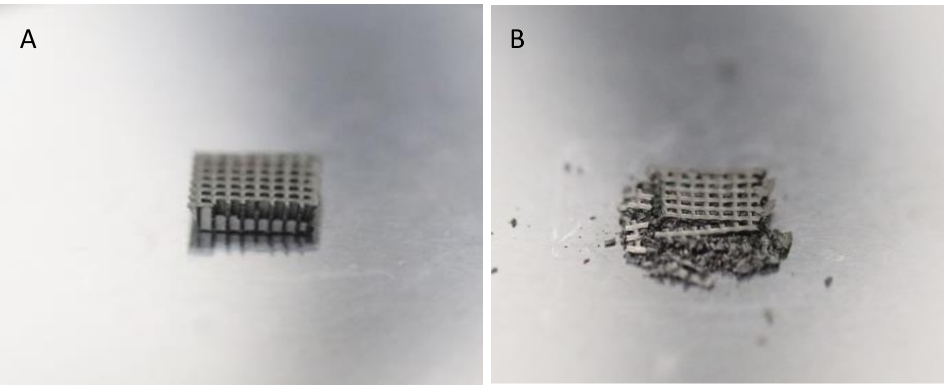
Images of Samples Pre and Post Compression testing



A- 1: Standard GO (A) Prior to compression (B) Post compression



A- 2: NH_4OH (A) Prior to compression (B) Post compression.



A- 3 GO-CNT-RF (A) Prior to compression (B) Post compression.