Lithium-Ion Battery Breakthroughs

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1. Introduction

I recently posted a paper arguing for a new battery design for really large batteries used in grid-scale battery energy storage systems. This is linked below

A New Form of Energy

https://energycentral.com/c/cp/new-form-energy

A strong argument can be made for high value applications to use improved lithium-ion (hereafter LiIon). Indeed, there are a number of emerging designs that use a high-silicon anode verses the currently ubiquitous graphite anodes. I wrote about one of these about six months ago in a paper linked below. Also, this design could be suitable for future electric vehicles.

Future EV Batteries

https://energycentral.com/c/ec/future-ev-batteries

There is also demand for a premium lithium-ion battery that offers substantially higher energy density than LiIon batteries used in current EVs. The first subject of this post, NanoGraf, seems to fill this niche with their initial offering.

This post will also explore several new battery technologies that will allow the optimization of various LiIon battery components. The overall goal is to end up with a family of these batteries that are safer and have optimized performance and pricing for their target applications.

2. Applications

Certainly portable devices like smart-phones and laptops represent a major target for NanoGraf. However, there is a specific customer with even deeper pockets than typical users of portable electronic devices: the U.S. Department of Defense.

NanoGraf technology was developed, optimized, and patented by our team working in collaboration with researchers at Northwestern University and Argonne National Laboratory.[1]

NanoGraf's technology utilizes a proprietary doped silicon alloy material architecture to achieve category-leading performance and solutions to long-standing Si anode technical hurdles. The proprietary combination of silicon-based alloys and a protective inorganic and organic coating helps stabilize the active material during charge and discharge.

Whereas current graphite-based anodes offer a capacity of 372 mAh/g, NanoGraf material can be customized to achieve capacities between 550 mAh/g and over 1400 mAh/g, delivering higher cell level energy density and best-in-class rate capabilities for high discharge applications.

[1] NanoGraf Technology page, https://www.nanograf.com/technology

NanoGraf, an advanced battery material company and enabler of the world's most energy-dense 18650 lithium-ion cell, today announced that it won a $1 million development contract from the Department of Defense to produce a more powerful, longer-lasting 4.3Ah lithium-ion battery. The cell will provide U.S. military personnel with enhanced run-time for the equipment they rely on to operate safely and efficiently.[2]

Soldiers carry upwards of 20 pounds of lithium-ion batteries to power communication devices, goggles, helmets, and more. Battery-powered technology helps soldiers achieve their missions, but the weight can result in fatigue and mobility issues, putting soldiers at risk. Improved battery performance is key to the U.S. military's success and ability to provide excellent communications and keep soldiers safe. NanoGraf's batteries will continue to improve run time on U.S. soldiers' equipment, resulting in increased overall performance.

This is the second Department of Defense project won by NanoGraf. In 2021, the company developed the world's longest-running 3.8Ah 18650 cylindrical lithium-ion cell, at 800 watt-hours per liter (Wh/L).

"When people talk about range anxiety with electric vehicles, it's about the inconvenience, whereas in the military, it can be about life or death," said Dr. Francis Wang, CEO of NanoGraf. "We're honored to have this opportunity to enable enhanced survivability and effectiveness to our Soldiers and Warfighters with greater runtimes for their critical electronic devices."

3. Why Silicon?

Graphite, a pure form of carbon, is a critical material for battery anodes. Graphite's physical structure allows it to store lithium ions, which merrily migrate to the anode when the battery is charged. Unlike cathodes, which can be composed of various combinations of chemicals (cobalt, nickel, manganese, lithium, iron, phosphorus et al), all current anodes used in EV batteries are composed mainly of graphite.[3]

However, there is another candidate for this key position. Silicon is lighter, and can potentially store more energy, than graphite. Some battery designs use small amounts of silicon mixed in with the graphite to improve battery performance, and finding ways to incorporate more Si in anodes is a major focus of battery research.

NanoGraf, a Chicago-based materials developer that was formed in 2012 (under the original name SiNode) has developed a novel silicon-based anode material that it says has the long-term potential to replace graphite-based anodes, increasing both energy and power density while offering excellent cycle life.

In 2021, the company developed a 3.8 Ah cylindrical lithium-ion cell for the US Department of Defense, which the company claims is the world's most energy-dense 18650 cell. Soon to be in commercial production, the cell is designed to give military personnel more runtime for their electronic equipment…

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[2] Hayleigh Criss, NanoGraf, "NanoGraf Wins $1 Million Development Contract from United States Department of Defense to Produce Next-Generation Battery Technology for the U.S. Army," March 28, 2022, https://www.nanograf.com/media/nanograf-wins-1-million-development-contract-from-united-states-department-of-defense-to-produce-next-generation-battery-technology-for-the-us-army

[3] Charles Morris, Charged, "How NanoGraf is commercializing the "world's most energy-dense" 18650 battery cell with stable silicon oxide," Feb 15, 2023, https://chargedevs.com/newswire/how-nanograf-is-commercializing-the-worlds-most-energy-dense-18650-battery-cell-with-stable-silicon-dioxide/

Charged recently spoke with NanoGraf Chief Operating Officer, Connor Hund, about graphite, silicon, and the quest for more powerful, longer-lasting batteries.

Charged: You have a new technology, which involves silicon-based anodes. Is it about replacing graphite, or just using less graphite?

Connor Hund: More about using less graphite. Graphite historically has made up the entirety of the anode, but currently, most commercial cells that you find in the market use 5 to 8% silicon oxide in the anode. What we're able to do with our next-generation silicon anode material is to increase that percentage up to 20, 25, 30% currently, with higher expectations in the future.

Silicon stores 10 times the amount of energy that graphite does, but it's a fundamentally less stable material, which is why you aren't able to build the whole anode out of silicon. It'll fracture and swell over time with too much in the anode, but that's fundamentally the benefit—you get more capacity in the battery if you're able to use more silicon in a stable way.

Charged: So, when the ions are stored in the material, silicon expands a lot more than graphite does. What's the percentage of the volume expansion?

Connor Hund: Swelling can be about 10 to 15% with graphite. It can be north of 50% with silicon, with first-generation silicon oxide materials, and we typically show about a 15 to 20% improvement on that when you use our silicon. It'll still expand more than traditional graphite, but we're able to do it in a stable way that fundamentally comes from the way that we're prelithiating the silicon oxide core. That sort of enables that reaction to happen earlier in the manufacturing process, and that enables a fundamentally more stable material.

Normal anode material will come into contact with lithium within the battery. What we're doing is injecting lithium into that core initially. We've sort of pre-swelled the material already, before we're putting it into a battery.

Charged: So the volume of the material is already larger, and when the lithium ions go in, that means the expansion is going to be less?

Connor Hund: Yes, that's a bit of a simplistic way to describe it. You'd have to get the full explanation at the PhD level, but that's essentially what's happening.

Charged: Most of our readers are pretty familiar with how batteries work, but take me back a little bit and explain how the lithium ions get stored in graphite and/or silicon during charging.

Connor Hund: The anode is the negative side of the battery, and there's a lithium-ion flow between the anode and the cathode, which is the positive side. Those are separated by a separator material, or membrane, and when you're at a full state of charge versus an empty state of charge, that determines which side of the battery those lithium ions are on.

Charged: We know that there are different kinds of carbon, very specific kinds of carbon that are used in anodes. Is that also the case for silicon?

Connor Hund: Yes, there are two main types of silicon—silicon oxide and silicon carbide. And if you look up NanoGraf versus a lot of our competitors, they're not pairing the silicon with oxygen the way that we are. With ours, it's the same elements, but it's protected better, and that comes down to the prelithiation, as well as our surface coating material that we put around that silicon oxide core. And that also protects it from fracturing, swelling, etc.

The beauty of our material is that it drops into existing manufacturing processes, so we're able to increase the percentage of silicon in the anode, increase the energy density, without changing manufacturing processes, or using expensive input materials that some of our competitors have to use.

No shade at our competitors, because what they're doing is impactful, but Sila and Group14 would be examples of companies that use silicon anodes, but with a fundamentally different type of architecture, and different materials than what we're using…

Charged: What's your business model? Will you be licensing your technology to battery makers?

Connor Hund: We'll be a materials manufacturer producing our silicon anode material. That's the first part of it. But we also have a completed battery cell that we're able to sell on the market—a cylindrical 18650. We're able to work with cell manufacturing partners to use our material to enable the world's most energy-dense cylindrical 18650 [at 810 Wh/L and 4.0 Ah capacity]. That's our initial product that we're going to market with.

The Department of Defense funded the development of that battery cell, but we'll sell it commercially as well. It will be in commercial production in Q3 of 2023. We have a new manufacturing facility in the West Loop, Chicago. That's under construction currently, coming online in the first half of 2023, and that's where we'll be housing our manufacturing going forward. We've on-shored our production to that facility at the pilot scale, and we're also scaling up production within that facility.

Author's comment: There are a huge number of battery form factors, even if you limit the discussion to just LiIon batteries. For instance, Tesla is evolving all of their EVs to 4680 batteries (cylindrical, 46mm diameter and 80mm long). The above described battery (18650) is a cylindrical battery with an 18mm diameter and is 65mm long. An excellent resource for dealing with any type of battery is referenced here.[4]

Charged: Are there any other customers you can talk about?

Connor Hund: I can say that premium consumer products are another initial market for our battery cells. I don't want to go into specific customer names, but you could think about customers that have a desire for long-lasting battery cells for portable products.

The electric vehicle market is definitely the medium-term vision for the company. We're using premium markets and Defense Department funding to scale up the company into commercial production. Then the future roadmap is to scale up production further, and pursue those more mainstream cost-competitive markets. That's the roadmap, but it's probably on more of a three-year time scale to be selling commercially into those EV markets.

[4] https://en.wikipedia.org/wiki/List_of_battery_sizes

4. Funding

NanoGraf appears to be using a combination of venture capital and funding from government contracts to ramp up the production of their silicon anode material and their initial battery cell designs.

NanoGraf, an advanced battery material company and enabler of the world's most energy dense 18650 lithium-ion cell, today announced a contract award from the U.S. Government. The contract will fund the onshore manufacturing of high-performance silicon anode materials as the first large-volume silicon oxide manufacturing facility in the U.S. At peak production, NanoGraf will produce 35 T/Y, enough material to provide enhanced power for various battery applications.[5]

The 18-month contract complements NanoGraf's existing domestic material production strategy and the company's additional plans to support the electric vehicle market by 2024. NanoGraf will produce 35 tons of silicon anode material per year as the company scales to 1,000 tons per year to support the EV market. With NanoGraf's proprietary silicon oxide material design, material prices will be on par with the cost of lower-performance graphite anodes.

NanoGraf, an advanced battery materials company and enabler of the world's most energy-dense lithium-ion 18650 cell, today announced that it has raised $65 million in an oversubscribed Series B funding round.[6]

The funding round was co-led by Volta Energy Technologies and CC Industries (CCI) with participation from GIC, Emerald Technology Ventures, Material Impact, Arosa Capital, Nabtesco Technology Ventures, and TechNexus. Existing investors including Hyde Park Angels, Evergreen Climate Innovations, and Goose Capital also participated in the round. NanoGraf had previously raised a total of $27 million in funding from a mix of venture, angel and non-dilutive funding sources…

5. The Future: Optimize Everything

I spent a day researching and writing the above (as a first draft). I went to bed at my usual 9:00 PM, then I woke up in the wee hours of the morning and started thinking about this article, and gained a better understanding of the big picture.

We (the world's population) are in the midst of a war against past generations understanding of the right path forward. In the 19th Century we (mostly Europe, but also big cities in the U.S.) were in the midst of a crisis. Our main source of energy was coal. However coal is a dirty fuel, and many places had horrible air pollution. Then the developing electric utility industry enabled coal-burning generation plants to be moved away from big cities, but this only put a bandage on the problem of coal emissions. Then we discovered that we could drill for oil and natural gas. We built large gas-fueled and hydroelectric generating plants. This helped to mitigate the air pollution from coal.

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[5] Hayleigh Criss, NanoGraf, "NanoGraf Wins Contract from U.S. Government to Develop First Large-Volume Advanced Silicon Anode Manufacturing Facility in the U.S." Dec 1, 2022, https://www.nanograf.com/media/nanograf-wins-contract-from-us-government-to-develop-first-large-volume-advanced-silicon-anode-manufacturing-facility-in-the-us

[6] Hayleigh Criss, NanoGraf, "Battery Startup NanoGraf Raises $65 Million Series B to Scale North American Production of Silicon Anode Products," Fab 14, 2023, https://www.nanograf.com/media/battery-startup-nanograf-raises-65-million-series-b-to-scale-north-american-production-of-silicon-anode-products

In the mid-20th century only a few scientists were warning about greenhouse gas, but now you know the rest of that story: climate change. Thus requires a major restructuring of the energy-industry unlike any we have seen. Also, this will use many new tools.

5.1. Renewables, Storage and Rapid Expansion

We have developed renewables that now have better economics than most other electricity sources, but they are intermittent. We have also discovered that we can use electro-chemical battery energy storage systems to mitigate the intermittency, but we need to build many more of these. Plus still more batteries for all types of transportation, and every type of portable electronic and electro-mechanical device. Understand that we are at the very beginning of this development and expansion.

Above all else we will need to optimize everything for their intended use-cycles and life cycles, starting with the batteries.

All electrochemical batteries have three major components: the cathode (positive side of the battery, that is, where a conventional current (positive charges) leaves a discharging battery) the anode (negative side, where a conventional current enters a discharging battery) and the electrolyte / separator between the anode and cathode.[7] Most of the LiIon battery's optimization so far has been done on the cathode, and thus we have a wide range of cathode chemistries, and one-size definitely does not fit all applications. Now it's the anode's time, and we are also starting to work on the electrolyte / separator.

5.2. Solid-State Batteries

A large majority of current lithium-ion battery designs use a liquid or gel electrolyte, and all of these, to varying degrees, are flammable. This provides the major push for batteries with solid-state separators in lieu of electrolytes.

I have written on Solid state batteries before, see the post linked below:

New Battery Technology: *In this post we will look at three lithium-ion battery designs that include solid electrolytes and metallic lithium anodes.*

https://energycentral.com/c/ec/new-battery-technology

Recently, after I completed most of this post, I encountered another solid-state design using metals for solid-state batteries.

A team from Florida State University and Lawrence Berkeley National Laboratory has developed a new strategy to build solid-state batteries that are less dependent on specific chemical elements, particularly pricey metals with supply chain issues.[8]

Bin Ouyang, an associate professor in the Department of Chemistry and Biochemistry, first developed the idea for this work while finishing his postdoctoral research at the University of California, Berkeley, along with his co-first author Yan Zeng, and their postdoctoral adviser Gerbrand Ceder.

[7] This tends to be a very confusing issue, because almost any DC electrical device has a cathode and anode, and current-flow conventions tend to vary for each device, and for batteries charging verses discharging. The best source for batteries came from the site here: https://www.anl.gov/science-101/batteries

[8] Kathleen Haughney, Florida State University News Release, "Powering Up: Research team develops strategy for better solid-state batteries," Feb 23, 2023, https://news.fsu.edu/news/science-technology/2023/02/23/powering-up-research-team-develops-strategy-for-better-solid-state-batteries/#:~:text=A%20team%20from%20Florida%20State%20University%20and%20Lawrence,Their%20work%20was%20published%20in%20the%20journal%20Science.

In their study, they demonstrated that a mix of various solid-state molecules could result in a more conductive battery that was less dependent on a large quantity of an individual element.

“There’s no hero element here,” Ouyang said. “It’s a collective of diverse elements that make things work. What we found is that we can get this highly conductive material as long as different elements can assemble in a way that atoms can move around quickly. And there are many situations that can lead to these so-called atom diffusion highways, regardless of which elements it may contain.”

Solid-state batteries operate almost the same way as other batteries — they store energy and then release it to power devices. But rather than liquid or polymer gel electrolytes found in lithium-ion batteries, they use solid electrodes and a solid electrolyte. This means that a higher energy density can occur in the battery because lithium metal can be used as the anode. Additionally, they have lower fire risk and potentially increase the mileage of electric vehicles.

However, many of the batteries constructed thus far are based on critical metals that are not available in large quantities. Some aren’t found at all in the United States. Given that the U.S. and many other countries plan to replace all vehicles with electric vehicles by 2050, there is an enormous strain being put on the supply chain for critical metals.

The research team considered the straightforward path of using one element to replace commonly used ones, but that approach raised its own supply chain issues. Instead, the team approached the problem by designing materials that weren’t beholden to one specific element. For example, instead of creating a battery made with germanium, which rarely appears naturally in high concentrations, the team created a mixture of titanium, zirconium, tin, and hafnium.

“With such a feature, we need to assemble those elements in a way so that we have many ‘good’ local configurations which can form a network for the fast transport of atoms or energy,” Ouyang said. “Think of it as a highway. As long as there is a connected highway for atom diffusion, the atoms can move quickly.”

This study opened a new area of research for Ouyang and his colleagues as they work to build more efficient solid-state batteries.

Government, research and academia have heavily invested in the development of solid-state batteries because batteries that contain liquids are more prone to overheating, fire and loss of charge. Smaller solid-state batteries already power devices like smartwatches and pacemakers. Still, many manufacturers believe that breakthroughs in this area could mean solid-state batteries could one day be helping electric vehicles or aircraft.

Other scientists contributing to this work are Young-Woon Byeon and Zijian Cai from Berkeley Lawrence National Laboratory, Jue Liu from Oak Ridge National Laboratory and Lincoln Miara and Yan Wang from the Samsung Advanced Institute of Technology.

Final author’s comment: Some of the above described metals don’t sound particularly common. Hopefully, these are just interim designs on the way to a large family of elements that can be used in mixtures that are optimized for various applications. Some of these should be less exotic.