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Abstract

Under the financial support of award DE-EE0007312, Group14 Technologies (G14) has progressed from the lab (~g) to lab-pilot (~kg) manufacturing of a novel silicon-carbon (Si-C) composite that is highly promising as an anode material for next-generation lithium-ion batteries. G14's Si-C is a drop in for graphite in lithium ion battery anodes, providing for increased energy density while lowering the cost on a capacity basis. At the foundation of the Si-C particle is an amorphous carbon scaffold, with its porosity fine-tuned for promoting intra-particle growth of the desired type and size (amorphous, nano-sized) of high capacity silicon, while also providing for internal volume to ameliorate silicon's expansion upon lithiation. Both the carbon and silicon within the Si-C composite are produced from readily available, low-cost precursors. At lab scale, we demonstrated the ability to produce Si-C capable of achieving capacity of 1000 mAh/g with minimum 500 cycle stability (up to 1000 cycles with pre-lithiation) in full cell, coin cell lithium ion batteries. Based on such lab experience, we down-selected process and equipment suitable for producing Si-C at lab-pilot scale. The chosen equipment was purchased, installed and commissioned at Group14's pilot manufacturing facility in Woodinville, WA. In turn, the ability to produce kg quantities facilitated the shipment of Si-C to various third parties. The promising feedback from such third parties included achievement of high first cycle efficiency (up to 92%) and 800 cycle stability in full cell, pouch cell lithium ion batteries. Beyond this highly promising electrochemical performance, it is important to note that G14's Si-C has also been developed for low cost. Based on estimated production costs, electrochemical performance data, and modeling employing the BatPaC model, we project <$125/kWh for lithium ion battery packs containing G14's Si-C.

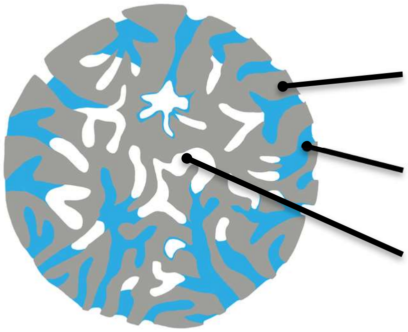
Background

The demand for advanced lithium ion batteries (LIB) is growing at a remarkable pace, particularly for electric vehicle applications. While this demand has catalyzed considerable advances in LIB recently,[1] additional progress is essential to position vehicle electrification on par with internal combustion. Such targets include cost reductions (i.e., <$125/kWh) fast charging capability (i.e., <15 min), and increased energy densities to allow >300 mile driving range between recharge.[2] Furthermore, such future battery advances must also achieve appropriate cycle life, lifespan, durability, safety, and other vehicle-specific requirements.

To this end, there is continued strong interest in developing new LIB anode materials, particularly silicon, which has 10-fold higher gravimetric capacity than conventional graphite. However, silicon exhibits large volume change during cycling, in turn leading to electrode deterioration and solid-electrolyte interphase (SEI) instability. The most common amelioration approach is to reduce silicon particle size (<150 nm), either as discrete particles or within a matrix. Thus far, techniques for creating nano-scale silicon involve high-temperature oxide or inactive metal alloying, multi-step toxic etching techniques, and/or other cost prohibitive processes. Likewise, common matrix approaches involve expensive materials such as graphene or nano-graphite, and/or require complex particle processing and coating. Thus far, very few silicon anode materials have been commercialized, with limited performance for broad adoption. To meet the growing need for a low-cost, high-performing silicon-containing anode material, Group14 Technologies, Inc. (G14) has developed a novel silicon-carbon (Si-C) composite whose manufacturing has been scaled from lab (~g) to lab-pilot (~kg) production with the financial support of award DE-EE0007312 as described herein.

Results and Discussion

A schematic of the rationally designed structure of G14's Si-C is presented in Figure 1.



Porous **Carbon** provides "scaffold" for silicon

Silicon within carbon pores for high capacity

Unoccupied void for silicon stabilization (minimizes expansion)

Figure 1. Schematic of G14's Si-C composite structure, wherein grey, blue areas represent amorphous carbon, silicon, and internal void volume, respectively. Note that features are not depicted in relative scale.

The scientific basis for the silicon-carbon composite that G14 developed can be elucidated through an understanding of the three core components: (i) amorphous activated carbon scaffold, (ii) amorphous nano-sized silicon, and (iii) unoccupied void space within the composite particle.

It is well known that non-graphitizable (hard) carbon is beneficial as a Li-ion anode material owing to its high gravimetric capacity (>400 mAh/g) and improved power performance over graphite.[3,4,5] The basis for this improved performance stems from the disordered nature of the graphene layers that allows Li-ions to intercalate on either side of the graphene plane allowing for theoretically double the stoichiometric content of Li-ions versus crystalline graphite. Furthermore, the disordered structure improves the rate capability of the material by allowing Li-ions to intercalate isotropically as opposed to graphite where lithiation can only proceed in parallel to the stacked graphene planes.

Despite these desirable electrochemical properties, amorphous carbons have not seen wide-spread deployment in commercial Li-ion batteries, owing primarily to low first cycle efficiency and low bulk density (<1 g/cc). Instead, amorphous carbon has been used more so as a low-mass additive and coating for other active material components of the battery to improve conductivity and reduce surface side reactions.

In recent years, amorphous carbon as a LIB battery material has received renewed attention as a coating for silicon anode materials. Such a silicon-carbon core-shell structure has the potential for not only improving conductivity, but also buffering the expansion of silicon as it lithiates, thus stabilizing its cycle stability and minimizing problems associated with particle pulverization, isolation, and SEI integrity.[6,7,8] Problems associated with this strategy include the lack of a suitable silicon starting material that is amenable to the coating process (discussed further below) and the inherent lack of engineered void-space within the carbon-coated silicon core-shell composite particle to accommodate expansion of the silicon during lithiation. This inevitably leads to cycle stability failure due to destruction of the core-shell and SEI layer.[9]

G14's Si-C is the result of three generations of developing Si-C composites leading to an inverse hierarchical approach whereby an activated (high surface area/pore volume) amorphous carbon is employed as a synthetic scaffold to host synthesis of nano-sized silicon. Compared to other types of possible structures for a composite material containing both silicon and carbon, we found this structure to have the greatest potential as anode material for lithium ion batteries, for example a greater potential for this structure to ameliorating silicon expansion upon lithiation,[10] as shown in Figure 2. To this end, we measured volume expansion of a Si-C composite incorporating bare nano silicon (▲), in addition to Si-C composites incorporating nano-featured silicon (■), and Si-C composites incorporating silicon oxide, denoted SiOx (●). The data were collected in coin cell, half cells, wherein the anode also comprised graphite blended to achieved capacity in the range of ~ 450 – 650 mAh/g. Interestingly, all of these Si-C composites exhibited a similar volume expansion with increasing capacity, for example the volume expansion for these anode materials was in the range of about 60-80% when blended in graphite to achieve a capacity of about 600 mAh/g. For reference, data are also depicted for graphite (●), whose data fall roughly within the extrapolation of the trendlines. Also included in Figure 2 are data for Si-C composites wherein we have synthesized silicon within the confines of porous carbon, denoted as “Group14 composite” (◆). As can be seen, the G14 Si-C composite exhibited extremely low volume expansion, as low as 26%, similar to our measured expansion for graphite anode.

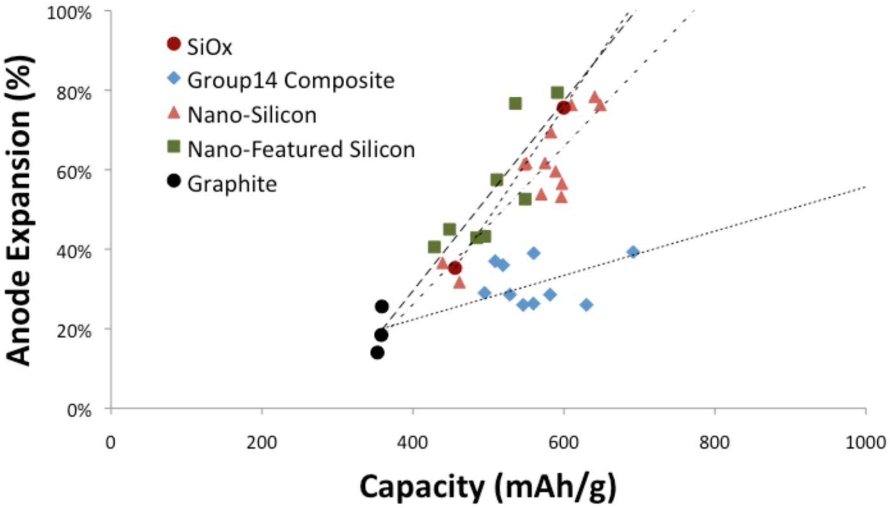


Figure 2. Anode volume expansion for various Si-C composites comprising different silicon types.[10]

Evidence of G14 Si-C structure was generated under the current project in collaboration with Dr. Chongmin Wang at Pacific Northwest National Laboratories (PNNL).[11] The data generated included confirmation of the nano-sized and amorphous nature of the silicon within G14’s Si-C by selected area electron diffraction conducted at PNNL. Furthermore, *in situ* TEM lithiation studies conducted at PNNL also provided evidence of low expansion upon 100% lithiation for G14’s Si-C (Figure 3).

We measured the electrochemical performance of G14 Si-C as a lithium ion anode material in house. Specifically, we measured the electrochemical performance of full cell coin cell lithium ion batteries wherein G14 Si-C was blended into the anode along with graphite.[12] These results are presented in Figure 4 (Wh/L vs. cycle) for three representative samples (denoted A, B, and C). These data are for full cell coin cells cycled at C/2 rate over a voltage window of 2.5–4.2 V, with a hold at a constant voltage of 4.2V until the current dropped to C/5, with a C/10 cycle conducted every 20 cycles, employing an electrolyte comprising 1M $LiPF_6$ in EC:DEC w/10% FEC, NCA cathode (provided by ANL), and a 5-15% anode excess (anode=5% CMC-SBR, 5% Super-C45, with the remainder of mass comprising ~16-19% Si-C, ~74-71% graphite). As can be seen from our in-house analysis, the G14 Si-C composite is capable of at least 500-600 cycle stability. For comparison, a representative graphite sample is also presented. It can be seen that the samples comprising a blend of the Si-C in graphite are capable of up to at least ~30% improvement in energy density compared to graphite alone.

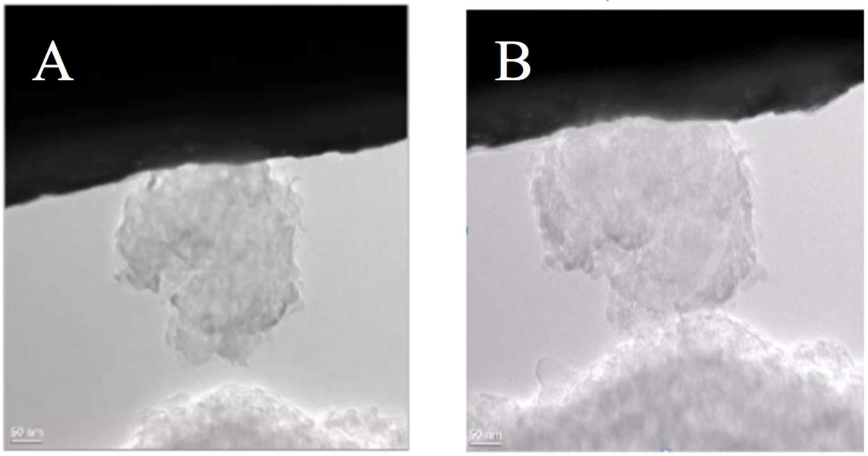


Figure 3. *In-situ* TEM for SCC-55 before (**A**) and after (**B**) lithiation. Data were measured in the lab of Dr. Chongmin Wang at PNNL, who reported areal expansion of individual G14 Si-C composite particles as low as 19% (particle shown exhibited 29%).[11] Based on the nature of the technique (lithium shorting with applied voltage bias) lithiation is assumed complete (100% lithiation).

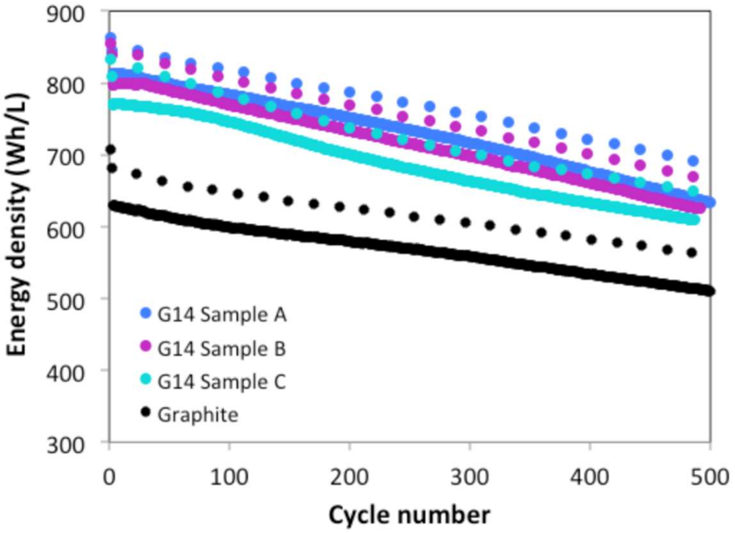


Figure 4. Volume energy density (Wh/L) in full cell coin cells for three representative Si-C samples.[12]

It was of interest from DOE interactions to assess electrochemical performance employing device-level enhancement in combination with G14 Si-C. Specifically, we explored the effect of prelithiation of an anode comprising a blend of Si-C and graphite.[12]

Prelithitation was accomplished by an electrochemical contacting method prior to cell assembly. The data are presented in Figure 5 as retention for full cell coin cells employing methods as described above. For comparison, a representative graphite sample is also presented. As can be seen, the G14 Si-C composite when blended with graphite in an anode is capable of 1000 cycle stability when employing pre-lithiation as an example of a device-level enhancement.

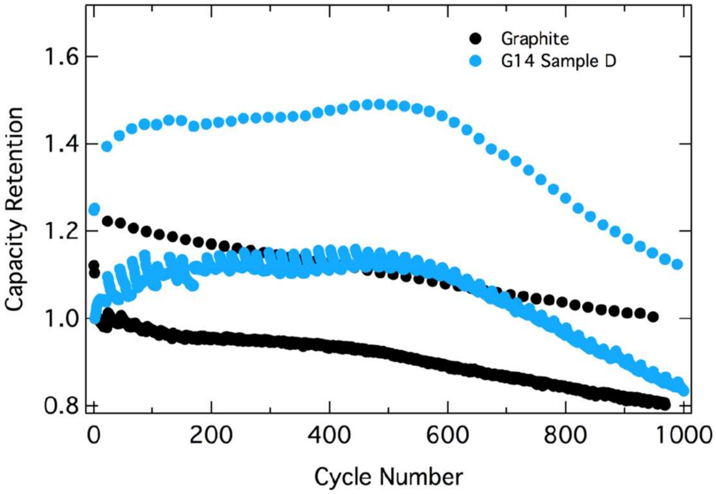


Figure 5. Example device-level enhancement: cycle stability of prelithiated Si-C.[12]

Based on the promising data generated at lab scale, we down-selected process and equipment suitable for production of G14 Si-C at lab-pilot quantity scale. Specifically, the down-selected equipment was a rotary kiln, and the down-selected process was chemical vapor infiltration of a silicon-containing precursor gas on porous carbon scaffold in a rotary kiln. To this end, an appropriate vendor was selected, and the appropriate equipment was purchased, installed, and commissioned at G14's pilot manufacturing facility located in Woodinville, WA. The establishment of production of G14 Si-C in kg quantities over the period of a few days facilitated sampling of material to various 3rd parties for their evaluations, and their subsequent feedback.

Among the feedback received by various 3rd parties was confirmation of high capacity as well as high first cycle efficiency (FCE) for G14 Si-C.[13] An example is depicted in Table 1 for data generated in Swagelok half cells, collected in triplicate (three individual cells). The anode comprised 90% G14 Si-C, 5% conductivity enhancer, and 5% SBR-CMC binder. Lithium metal provided the counter electrode and reference. The electrolyte was 1 M $LiPF_6$ in 3:7 ethylene carbonate:diethylene carbonate to which 10% fluoroethylene carbonate (FEC) was added. Cycling was accomplished at a rate of C/25 between 5 mV and 1.5V.

Table 1. 3rd Party data for G14's lab-pilot scale manufactured Si-C: Confirmation of high capacity and high FCE.[13]

Cell #	Capacity (mAh/g)	First Cycle Efficiency (%)
1	1658	89
2	1710	89
3	1601	90

Swagelok half-cell, working electrode 90/5/5 AM/C/SBR-CMC, Counter electrode and reference: Li metal, electrolyte: 1M $LiPF_6$ in EC/DEC 3:7 with 10% FEC, formation: CC charge-discharge at C/25 between 5 mV and 1.5V.

The measured capacity for the Group14 Si-C was 1601-1710 mAh/g. The measured first cycle efficiency was 89-90%. The charge and discharge curves are presented graphically in Figure 6. The three curves in green, red, and blue, depict the individual charge/discharge curves for the three replicate cells.

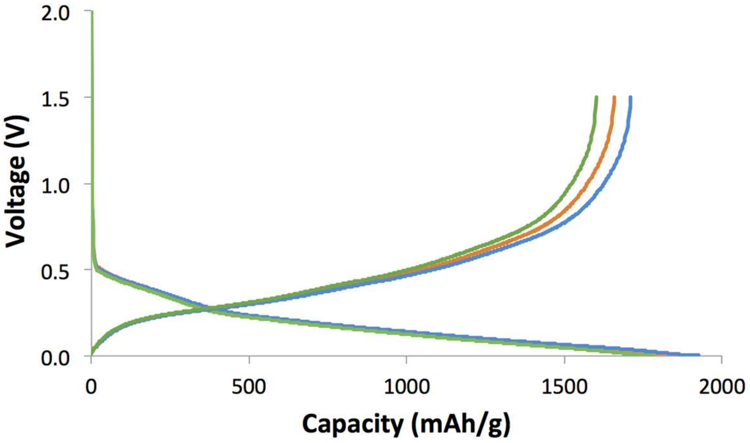


Figure 6. 3rd Party data for G14's lab-pilot scale manufactured Si-C: Confirmation of high capacity and high FCE.[13]

Yet another example of positive 3rd party feedback regarding G14 Si-C's high FCE is presented in Table 2. In this example, the anode comprised a blend of Group14's Si-C with graphite to yield a gravimetric capacity of ~550 mAh/g reversible capacity. The data presented in Table 2 are for half cell, coin cell format, wherein the anode comprised ~12% Si-C diluted in graphite. The data were generated for two different samples. The measured FCE was 90.5% to 92.0%. These data were also employed to back calculate the capacity and first cycle efficiency of non-diluted Si-C. The calculated value for capacity was 1918 to 2092 mAh/g, and the calculated value for first cycle efficiency was 88.7 to 92.1. It is important to note that Sample 2 had a lower surface area than Sample 1 with a consequently further improved (lowered) first cycle efficiency. It is remarkable to note that for Sample 2 the calculated first cycle efficiency for the non-diluted Si-C was higher than the case for the blend of Si-C diluted in graphite.

Table 2. 3rd Party data for G14's lab-pilots scale manufactured Si-C: Confirmation of high capacity and high FCE (graphite blend).[13]

Sample	Initial Charge Capacity (mAh/g)	Initial Discharge Capacity (mAh/g)	FCE (%)	Calculated Capacity [no dilution] (mAh/g)	Calculated FCE [no dilution] (%)
1	604	547	90.5	1918	88.7
2	604	556	92.0	2092	92.1

Data for half cell coin cells, anode ~12% Si-C diluted in graphite, counter electrode Li metal, discharge: 0.1 C CC-CV 5 mV 0.005 C cutoff, charge: 0.1 C CC 1.5V cutoff.

The same 3rd party also generated data for cycling performance in full cells (see Figure 7). The anode gravimetric capacity was ~ 550 mAh/g and the anode density was ~1.6 g/cm^3 (therefore the anode volumetric density was ~880 mAh/cm^3.

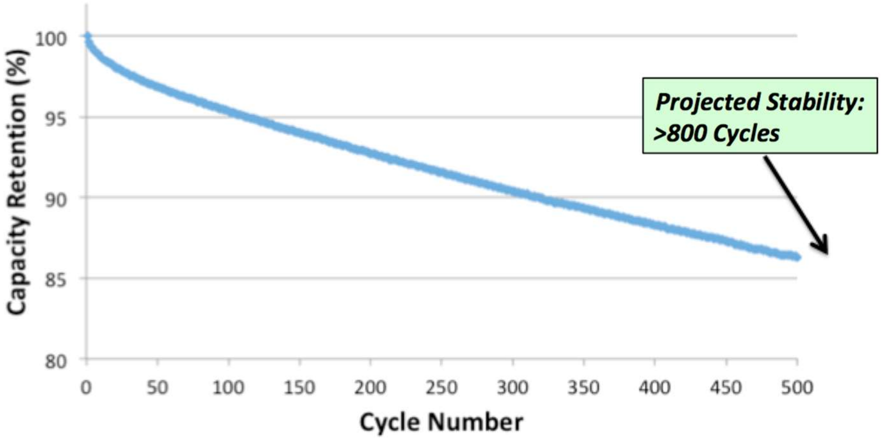


Figure 7. 3rd Party data for G14's lab-pilot manufactured Si-C: > 800 Cycle stability.[13]

Presented are the average data for two full cell pouch cells, anode ~12% Si-C diluted in graphite, NMC 622 cathode, cycled at 1C rate between 4.3V (CV charge 0.05C cut-off) and 3.0 V, electrolyte 1M $LiPF_6$ in EC:EMC:DEC = 3:5:2 v/v% + Additive. As can be seen, Group14's Si-C is achieving a projected stability (i.e., capacity retention of 80%) of greater than 800 cycles.

Beyond high first cycle efficiency and cycling stability, another attractive attribute of Group14's Si-C is projected low cost at full scale volume. To that end, we used BatPaC model (2018 version 3), developed by Argonne National Lab, to validate the cost benefit of including G14 Si-C material in a battery pack.[13] We chose this model since it has a comprehensive list of considerations to evaluate the battery pack cost and has been used by EPA for cost estimations of battery technologies.

For the BatPaC cost calculation, we used default values provided in the model with few exceptions. In the "chemistry" part of the model, our input parameters in the model are NMC622 cathode, capacity of the graphite/G14 Si-C blend, and cost of anode active material. Other input parameters are not changed as we expect G14 Si-C graphite blend to have similar resistance and electrode density as pure graphite based on preliminary data from our customers.

For the cost calculation, we assumed that the specific capacity of Si-C material is 1500 mAh/g. G14 has the ability to tune the capacity based on Si content of our composite and as such we are able to produce material with capacity as high as 1900 mAh/g.

Our baseline case assumed a $40/kg selling price, which is based on a detailed cost of goods sold model at full scale volume, taking into account projected raw material costs, labor costs (standard U.S. rates), electricity costs, process yields, equipment depreciation, etc. As a sensitivity analysis, we also considered the case for a higher (e.g., $50/kg) and a lower (e.g., $30/kg) Si-C selling price than the $40/kg baseline selling price.

We have examined scenarios wherein G14 Si-C was blended into the anode from 0-50% wherein we considered the cost of a unit battery pack assuming 200,000 units manufactured per year. For the pack design, we picked 88 kWh battery with 300 mile range (typical objective for a sedan type vehicle). As can be seen in Figure 8, from the assumptions above and employing the BatPaC model, we project that blending G14 Si-C into the anode of lithium ion batteries can achieve the project goal of attaining <$125/kWh.

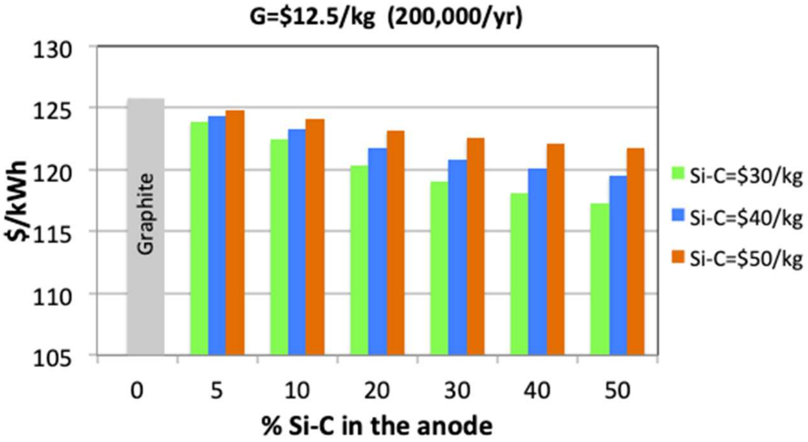


Figure 8. Cost model (BatPaC 2018 v. 3) using increasing amount of Si-C in the anode for 88 kWh battery pack for 300 mi range vehicle, Si-C cost of $30/kg, $40/kg, and $50/kg, 200,000 battery system manufactured per year, graphite cost of $12.50/kg, NMC622 cathode.[13]

Summary of Project Goals

A summary of major project milestones and deliverables is presented in Table 3. Over the course of the project we advanced from lab to lab-pilot scale manufacturing of G14 Si-C. Specifically, we demonstrated ability to produce Si-C at pilot scale in excess of the 1 kg goal. Importantly, the product performance of the pilot-scale synthesized Si-C has been validated in the lab. This performance includes demonstration of gravimetric capacity well in excess of 1000 mAh/g, successfully demonstrating the achievement of the second aspect of the final project goal. Regarding the objective to achieve a predicted 1000 cycle stability, we have achieved this goal in combination with device-level enhancements, as discussed above. Based on our in house electrochemical testing, G14 Si-C has the ability to boost anode energy density by at least ~30% with at least 600 cycle stability. Furthermore, we have obtained 3rd party feedback of achieving even greater stability, for example >800 cycle stability. Importantly, this result was obtained for lab-pilot scale manufactured G14 Si-C. Finally, we have employed the BatPaC model to determine that incorporation of G14 Si-C into the anode of lithium ion batteries can achieve < $125/kWh. Given this information, in discussion with the DOE we have agreement that G14 Si-C has met the project milestones and deliverables as described in Table 3.

Future Directions

G14 has developed a novel Si-C composite that has been proven by industry-leading battery manufacturers to dramatically increase anode capacity with at least 90% first cycle efficiency and 800 cycle stability. This technology is anticipated to lower the cost of Li-ion batteries on a $/kWh basis by 30%, enabling electric vehicle cost parity with internal combustion engines.

The next step for development of G14 Si-C is to advance to a commercially relevant pilot manufacturing scale. As the next step in this endeavor, we plan to advance the current process equipment type to a scale representing 10 kg produced in an 8 h work shift. In addition to the current rotary kiln, we will de-risk process scaling by assessing two other equipment types, namely a vertical bed type reactor and a horizontal bed type reactor. Based on our process assessment at the 10 kg scale, we will subsequently down-select and advance the most promising approach to a scale representing 100 kg produced in an 8 h work shift. In parallel, we will correspondingly scale production of the porous carbon scaffold. It is important to note that G14's employees are veterans of prior experience at EnerG2 before the spin-out of G14, including construction of an ISO 9001/ISO 14001 certified manufacturing plant that has produced 100s of tons of porous carbon for customers worldwide. Beyond scale up of G14 Si-C, we also plan to conduct "deep dive" structure-function studies, as well as expand our in-house full cell capabilities, which will substantially facilitate not only scale up activities but also customers' evaluation and ultimate qualification of G14 Si-C in commercial battery products.

Table 3. Summary of project schedule status.

Milestone/Deliverable	% Complete	Anticipated Date		Actual Date	
		Start	Completion	Start	Completion
Synthesize 1x10g Si-C with 1000 mAh/g; predicted 1000 cycles; < $125/kWh projected cost	100%	1/1/17	6/30/17	1/1/17	6/16/17
Validate performance of at least one pilot-scale-synthesized material in the lab	100%	4/1/17	6/30/18	6/9/17	12/31/18
Complete installation and commissioning of all new process equipment	100%	6/1/17	3/31/18	6/9/17	3/31/18
The synthesis of 1 kg completes a demonstration 1000 mAh/g and predicted 1000 cycles at < $125/kWh at full scale volume	100%	9/1/17	6/30/19	6/9/17	6/30/19

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