

Revitalizing Lead Battery Technology for Tomorrow's Growing Markets Utilizing Today's Sustainable Infrastructures

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INTRODUCTION

In order to satisfy the increasing demands of energy storage in the near future, novel battery technologies that are sustainable and safe, inexpensive and high performance are urgently needed. In particular, as various types of hybrid drivetrains proliferate the consumer vehicle market, battery technologies with high energy and power densities are required for automotive applications. On the other hand, the transformation of our energy infrastructure into renewable sources is driving massive demands for distributed energy storage, requiring reliable and safe battery systems for stationary applications.

Lead-acid technology is the most deployed rechargeable battery. It is generally safe, relatively inexpensive, and has adequate performance for today's automotive, traction, and stationary applications. Due to the large battery manufacturing base and complete recycling infrastructure, leadacid the most sustainable among all secondary battery technologies.

> Although its incumbency has been challenged by more advanced technologies, lead batteries are still preferred in automobile SLI (starting, lighting, and ignition), small-scale traction, and back-up power applications (Figure 1).

Despite its widespread deployment, lead-acid technology suffers from several drawbacks that could limit its applications to advanced hybrid automobiles and grid-scale renewable storage. In particular, lead batteries typically have poor performance under deep discharge, partial-state-of-charge, high-rate cycling, and dynamic charge acceptance. These performance limitations are not inherent to the chemistry, but rather to the architecture of the battery. Specifically, in traditional monobloc batteries, current must flow parallel to the surface of the electrode and concentrate to the tab of the grid collector. As a result, a non-uniform current density distribution develops over the surface of the electrode, which accelerates failure mechanisms such as sulfation and stratification, thus preventing the proliferation of lead battery technologies to applications with stringent performance requirements.



Figure 1: The current lead battery market is divided into transportation, traction, and stationary applications, summing up to a total market size of about \$40 billion dollars.

TECHNOLOGY

Gridtential Energy Inc. has developed Silicon Joule® technology to advance lead-acid's performance with innovations in battery architecture and electrode material. The Silicon Joule battery adopts a bipolar configuration, in which electrochemical cells are arranged electrically in series and hence current flows perpendicular to the surface of the electrodes (Figure 2).

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The bipolar configuration eliminates non-uniform current density distribution across the electrodes to delay traditional failure mechanisms such as sulfation and stratification. In addition, the current conduction path length in a bipolar battery can be much shorter than that in a monobloc, resulting in efficient current delivery and therefore higher energy and power densities. The adaption of bipolar architecture in the Silicon Joule technology is made possible by the introduction of silicon wafer current collectors that isolate individual cells hermetically.





Figure 3: Silicon current collector used in Silicon Joule® technology. The surfaces of the silicon wafer are rendered compatible with lead-acid electrochemistry by the formation of a contact layer followed by deposition of an adhesion layer using solar processing technologies.



Figure 4: Cell construction of the Silicon Joule battery. Commercial positive and negative active materials are pasted onto plastic grids for mechanical support. The pasted grids are isolated with an absorbed-glass-mat separator and sandwiched between current collectors. Silicon wafers are light and stiff, impervious to sulfuric acid, have high thermal conductivity but low coefficient of thermal expansion. Silicon Joule® bi-plate is processed to render its surface resistant to electrolyte corrosion and also compatible to leadacid electrochemistry (Figure 3).

The seamless integration of silicon wafer current collectors into the bipolar architecture results in a energy storage platform that is high performance, energy and power dense, flexible to meet specific needs but also scalable to a range of applications.

Silicon Joule® technology is manufactured by exploiting high-volume and low-cost solar wafer processing tools, and also compatible with the ubiquitous and sustainable lead recycling base. Our silicon wafer current collectors can be processed by trailing-edge solar manufacturing equipment. The process sequence is relatively simple, the individual steps of which are developed and mature. Silicon Joule® battery is constructed such that active materials are applied on plastic grids that act as mechanical support during the pasting and curing processes (Figure 4).

The pasted grids are stacked and sealed with silicon wafer collectors and absorbed glass mats to become a battery. The cell compartments are filled with sulfuric acid electrolyte and formed with pastespecific formation procedures before shipment. Silicon Joule® technology is designed to have maximum compatibility with existing manufacturing technologies, and it improves the performance of commercial lead batteries by an architectural, not chemistry, modification. This means that each commercial battery manufacturer can retain its proprietary advantages in paste formation, market positions, and distribution channels.



Silicon Joule® technology can be configured into different sized batteries for automotive, traction, or stationary applications. Our 24V U1-sized battery offers a drop-in replacement for traction applications. In addition, we are working with several partners to develop batteries for hybrid automobiles, telecom backup, and industrial applications (Figure 5).

Gridtential built over 250 Silicon Joule® batteries to demonstrate its superb cycling performance. The alpha platform is a 6V maintenance-free battery with a capacity rating of 8.1Ah at 10-hour discharge (5.4Ah at 2-hour discharge) (Figure 6).



Cridtential[®]

PERFORMANCE

We subject a collection of alpha batteries to standard constant-currentconstant- voltage charging followed by constant-current discharge, and the batteries consistently achieved > 700 cycles at the 10-hour rate, and > 1200 cycles at the 2- hour rate, while remaining > 80% energy efficient throughout their cycle lives under 100% depth of discharge (Figure 7, Figure 8).

We have also demonstrated the voltage scalability of the technology from 6V to 12V, and observed similar cycling performance at both voltages (Figure 9). Our alpha batteries have good cycling performance even at elevated temperatures. In particular, it achieved > 250 cycles at 40°C (Figure 10).

We have also demonstrated the adoptability our battery platform by partnering with commercial lead-battery manufacturers. In particular, we have introduced paste chemistries from seven partners into our alpha platform, and demonstrated similar performances when compared to our baseline (Figure 11). Silicon Joule® technology can be adopted for a spectrum of applications, such as deep-discharge industrial, fastdischarge stationary, and high-power automotive.



Figure 7: Alpha battery cycling performance. (*Left*) Discharge capacity versus number of cycles. (Right) Energy efficiency versus number of cycles. All three batteries (464, 475, and 495) have a rated capacity of 8.1Ah at the 10-hour rate. The batteries were charged with a constant-current-constant-voltage scheme and discharged with constant-current to a voltage limit. The charging current was 0.81A with a voltage limit of 2.45V. The discharge current was 0.81A and the discharge voltage limit was 1.75V. As can be seen, our batteries consistently achieved > 500 cycles with 10-hour discharge, with energy efficiencies > 80% throughout their lives.





Figure 8: Alpha battery cycling performance at high current rates.

(Left) Discharge capacity versus number of cycles.

(Right) Energy efficiency versus number of cycles. All three batteries (399, 434, and 464) have a rated capacity of 8.1Ah at the 10-hour rate. The charging current of the batteries were 1.75A (399), 2.50A (434), and 0.81A (464), with a constant-voltage limit of 2.45V. The discharge currents were the same as the charging currents, to voltage limits of 1.60V (399 and 434), and 1.75V (464). The cycling performance is > 1200 cycles at C/2, > 900 cycles at C/4, and > 700 cycles at C/10.



Figure 9: Demonstration of voltage scalability of alpha batteries.

(Left) Discharge capacity versus number of cycles.

(Right) Energy efficiency versus number of cycles. Batteries 464 and 475 are 6V units whereas 412 and 421 are 12V units. All units were discharged at the 10-hour rate. It can be seen that the slow capacity fade over > 600 cycles are independent on the stack voltage.







(Left) Discharge capacity versus number of cycles.

(Right) Energy efficiency versus number of cycles. Battery 368 were cycled at 20 °C and battery 376 were cycled at 40 °C. Both units underwent a constant-current-constant-voltage charge scheme and a constant-current discharge scheme. The charge and discharge currents are both 2.5A. The charge and discharge voltage limits were 2.45V and 1.60V, respectively.





(Left) Discharge capacity versus number of cycles.

(Right) Energy efficiency versus number of cycles. The 5 units (464, 529, 577, 600, and 631) have pastes from different commercial lead battery manufacturers.



COST

Silicon Joule® technology is designed to combine the scalability and economics of solar and lead infrastructures. The silicon wafer current collectors can be processed by trailing-edge commercial solar manufacturing equipment with little or no modifications. Individual biplate fabrication steps follow typical solar process flow: ingot conversion, brick and slice, clean and texture, metallization and electroplating. These processes are all well developed, commercialized, and have proven productivities (Figure 12).



SUBSTRATE MATERIAL Low Purity Si Custom Size



SILICIDE CONTACT LAYER Solar Metallization



SEALED WAFER FRAME Leak-Proof Wafer Bonding



PbSn ADHESION LAYER Industrial Electroplating

Figure 12: Process sequence of silicon wafer current collector.

1) Low purity silicon raw material is first cast into an ingot. The ingot is then cropped and sliced into custom-sized wafers according to the dimensions to the battery.

2) High throughput solar metallization is employed to form a silicide contact layer onto both sides of the wafer.

3) The wafer is edge-sealed by wafer bonding techniques.

4) PbSn adhesion layer is deposited onto the current collector by industrial electroplating technologies.

The Silicon Joule® battery is also designed to be compatible with existing lead battery manufacturing. Comparison of the process sequences of a lead monobloc and the Gridtential bipolar battery illustrates the similarities. A typical lead monobloc process involve grid casting, oxide manufacturing, pasting and curing, welding of straps and lugs, followed by boxing, and finally electrolyte filling and formation. Existing lead battery manufacturers can produce a Silicon Joule® battery after slight modifications of the monobloc process flow. In particular, instead



of the welding and boxing steps, a stack-and-seal procedure is used to package the battery. Also, as pre-fabricated silicon bi-plates can be purchased, grid casting can be eliminated (Figure 13).

AGM VRLA



Figure 13: Comparison of typical AGM VRLA and Gridtential bipolar battery manufacturing. Manufacturers of Silicon Joule battery can purchase silicon biplates and eliminate grid casting. A simple stack-and-seal assembly step replaces welding, boxing, and sealing steps.

By integrating high-volume and low-cost solar manufacturing into existing lead battery infrastructure, Silicon Joule® technology is highly scalable and easily commercialized compared to other technologies that requires novel processing techniques and custom manufacturing equipment. In addition, it offers an adoptable architectural enhancement to existing lead batteries, both in terms of performance and manufacturability.



SAFETY

Unlike lithium-ion chemistries that contain moisture-sensitive materials, lead-acid technologies are generally safe due to its aqueous electrolyte. Safety hazards of lead batteries usually fall into the following categories: thermal runaway, hydrogen build up, and electrolyte leaks. Silicon Joule® technology excels in safety from both materials and design perspectives.



Figure 14: Simulated temperature distribution of a 12V U1 Silicon Joule battery to illustrate thermal performance of the technology. The model simulates the battery under 2.5V float voltage at 40 °C. The simulations show uniform heat throughout all the cells.

First, silicon's thermal conductivity (130 W/m K) is much higher compared to that of lead (34.7 W/m K). Heat generation during battery cycling is distributed by the silicon wafer current collector to the environment effectively. The efficient thermal management enables higher temperature of operation and also increased threshold for thermal runaway (Figure 14).

Second, as individual cell compartments are isolated in the bipolar configuration, each cell has its own headspace and pressure valve relieve valve. In other words, there is no shared headspace for hydrogen build-up and therefore less likely for explosions to occur during operation (Figure 15).

Third, the battery package is made of plastic and sealed with plastic welding techniques, similar to existing lead-acid batteries. Electrolyte leaks should not be more likely to occur compared to best-inclass lead batteries



Figure 15: Mechanical design of a 24V Silicon Joule battery. Individual cells are hermetically sealed to their neighbors with silicon wafer current collectors. As there is no shared headspace for hydrogen accumulation, hydrogen explosions should be less likely to occur during its operation.



SUSTAINABILITY

In the Silicon Joule[®] battery, silicon wafers are used as current collectors and they replace lead grids in traditional lead-acid monoblocs. As a result, the amount of lead used in the battery is significantly reduced (Figure 16). The Silicon Joule[®] battery is not only much lighter compared to traditional monoblocs, it also has higher energy and power densities. In addition, the Silicon Joule[®] battery introduces neither new elements nor known "poisons" into existing lead recycling streams. Not only is the battery compatible with lead recycling infrastructures, less energy



is required to recycle our batteries due to the reduced amount of lead in them. As opposed to many novel technologies, Silicon Joule® extends the sustainability of the most sustainable battery in the planet.

UNIQUENESS

Gridtential is building a unique battery technology with an unconventional collaborative approach. Gridtential's management includes a technology advisory council consisting of representatives from the lead industry to advise and steer the company's technical direction. This structure ensures that Gridtential is positioned to benefit the whole industry inclusively. Silicon Joule® technology is widely available because of our license business model, and we believe that our customer's success is our success.

Figure 16: Comparison of mass distributions of AGM stop-start monobloc and Silicon Joule® bipolar batteries. As silicon wafers replace lead grid current collectors in the Silicon Joule® battery, the amount of lead used is greatly reduced. The mass distribution of the Silicon Joule® battery is skewed towards pastes and electrolyte, resulting in an energy dense package.

