

Bipolar Lead Acid – Eliminating the Lead

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Abstract:

ETP under an Army Phase II SBIR has developed a bipolar lead acid wafer cell with significantly improved cycle life and specific energy. Typically well suited for high voltage applications, the design was directed towards the 6TAGM battery. Removing the lead grids and intercell connectors, the design increased the specific energy by a factor of two. The design lends itself well to higher power higher voltage designs where further reductions in weight and increased capability naturally occur.

The doubling of specific energy occurred with baseline active material utilization. Further benefits can be obtained as improvements in active materials were incorporated.

Keywords: Battery; Lead-Acid; Pseudobipolar; Titanium; SnO₂; Titanium Silicide, Wafer Cell.

Introduction

High specific energy is a primary objective of designs of secondary batteries to be used in DOD applications. Lithium-ion (Li-ion) batteries are increasingly the choice for such applications due to their superior specific energy with respect to that of existing aqueous batteries. The disadvantages of Li-ion, such as cost and safety, have mandated reexamination of aqueous systems, particularly if increases in specific energy can be achieved.

Lead-acid batteries are still widely used, particularly when low cost and high power are needed, and the relatively low energy density is acceptable. Improvements in energy density of lead-acid batteries would greatly extend their market utility in many applications. Improved energy density can be achieved primarily through three approaches. The first is improvement in the utilization of the solid active materials (Pb and PbO₂). Utilization is typically limited to < 60%. This is caused by reduction in electrode porosity and electronic conductivity during discharge, caused by formation of (voluminous and resistive) PbSO₄ crystals. This can be mitigated in part through addition of conductive additives to the electrode masses, or through various means to retain high porosity. A second way to increase energy density is

to decrease the mass of various components of the battery structure, such as electrode grids and connectors. Finally, energy density can be improved through more efficient battery geometries (rather than prismatic or spirally-wound cells having lead strap current collectors with welded intercell connections).

Under sponsorship from the U.S. Army (Contract W56HZV-16-C-0059), Eskra Technical Products (ETP) is addressing the need for improved energy density lead-acid batteries. This is being done primarily through the second and third approaches mentioned; i.e. reduction in mass of battery components and improved construction. Improvements in active material have not been the focus of this program. ETP uses a “wafer cell” construction (Figure 1) that reduces the need for most of the supporting lead metal present in traditional lead-acid cells. This highly efficient design can potentially improve upon typical energy density by 100% or greater. The construction is similar to that of a true bipolar cell, except that both electrodes have their own supporting substrates. The individual cells, consisting of electrodes (active material supported on substrates), separator and electrolyte, are packaged in a polymer pouch, with open spaces on the back of both electrode current collectors as shown in Figure 1. Individual cells are stacked next to one another, with external (metal) current collector discs placed in the open circular spaces on the backs of the electrodes. Current flows from one cell to its neighbor, by passing through the external current collector discs, improving on the inherent high power performance of lead-acid batteries by increasing the area of intercell connection and minimizing resistive losses by eliminating grids and providing multiple, high area/short path parallel current paths between adjacent cells. With this design there is significant savings in weight, due to reduction of the mass of intercell connections., with placement of current collector foils external to the outermost cell electrodes of each twelve volt block, connected via current collector discs through openings in the cell package on the outside of the electrodes. The twelve volt, six cell blocks are connected in parallel to copper straps leading directly to the base of the external terminals on top of the battery (Figures 2 and 3). This series-parallel arrangement of cells and blocks lowers

the impedance of the battery.

An essential element of the design involves the substrates that support the active material in both electrodes. Lead metal can be used, although it has high specific weight (11.34 g/cm³). Metals such as copper and titanium have lower specific weight, but are reactive in contact with the sulfuric acid electrolyte, and at the potentials encountered during battery operation. The material chosen for the substrates should be inert with respect to cell materials and environment. This is accomplished through application of various protective coatings to substrate materials. As long as the coatings completely cover the substrates, and are electrochemically stable, lighter weight materials (such as Ti foil) can be used to support the electrodes.

In this paper we present progress in efforts to build very high specific energy lead-acid batteries. The target application has been the 6TAGM battery. Titanium foil is one of the electrode substrates considered for both positive and negative electrodes. Various positive electrode coatings are used, with high conductivity and electrochemical stability being required coating attributes. The literature and our half-cell experiments show SnO₂ and other proprietary materials to be functional as applied to titanium, copper and other metallic substrates. Thin lead coating of substrates or carbon/graphite polymer composite layers are a favored coating for the negative electrode. Projected energy densities are presented to contrast the relative merits of different material choices. The wafer-cell cell and battery construction is used in these calculations.

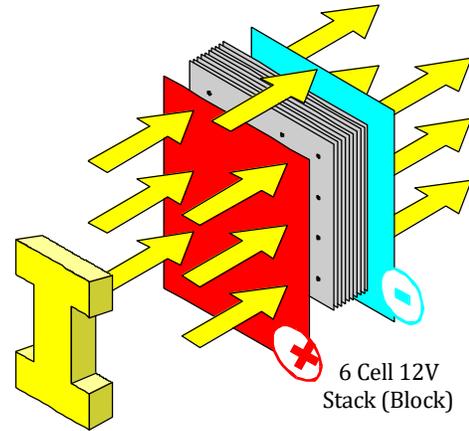
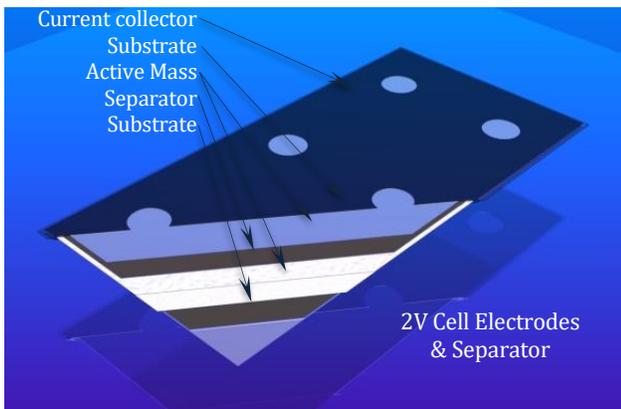


Figure 1. ETP Pseudobipolar "Wafer Cell."

ETP found that forming titanium silicide on the surface of the positive electrode prevented corrosion of the positive current collector. This coating was formed by reacting the surface of the titanium with silicide gas. An alternative method was also to coat the surface of the titanium foil with titanium silicide. The negative electrode will operate when coated with a thin lead, graphite or carbon. Raw copper foil can be used if the cell potentials are carefully monitored.

The cell formation process was performed with open cells and then fully sealed after a charge discharge cycle at the top of charge. Cycling afterward maintained cells operating below 4 psi. Successful formations required that red lead be added to the SLI positive paste mix to allow the formation to initiate.

ETP Battery Design

A battery of particular interest is the 6TAGM. A 12 V battery is constructed through parallel connection of multiple 12 V modules or blocks. Each 12 V block consists of six individual wafer cells, stacked adjacent to one another, and electrically connected in series. Figure 2 shows a 12 V battery schematically, consisting of five individual 12 V blocks/modules. Blocks are connected back-to-back, and are connected to battery posts as shown.

Figure 3 is a photograph of a high power, 450 volt Ni-MH battery, consisting of series-connected 48 volt blocks that contain multiple individual wafer cells. The construction is similar that that of the lead-acid battery described in this paper. Not shown are the current collecting straps that conduct current to the battery posts. This battery was built at Electro Energy, Inc., by one of the authors of this paper. It shows significant improvement in energy density (Wh/l) relative to commercial Ni-MH batteries, particularly in high voltage configurations. It was also capable of extremely high power output, > 1 MW.

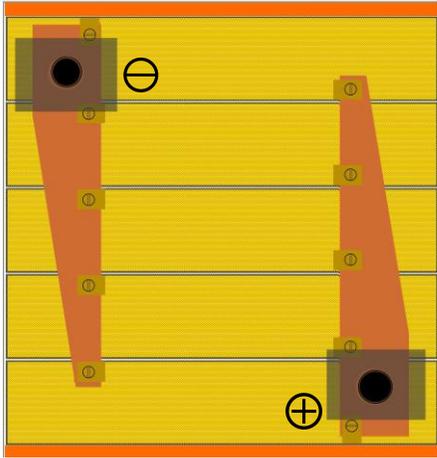


Figure 2. Wafer-Cell 6TAGM Construction Schematic, Top View of Block / Bus Configuration



Figure 3. Wafer-Cell NiMH Battery Construction

Design Calculations

ETP's wafer-cell construction is contrasted with that of traditional 6TAGM batteries through a series of design calculations. These calculations are for batteries such as depicted in Figure 2. Active material utilizations typical of automotive and commercial starting batteries are used. The baseline conditions for calculations are shown in

Table 1.

Table 1. Baseline Conditions for Battery Calculations.

Component	Value
Housing Thickness (inch)	0.375
Capacity (Ah)	154
Voltage (V)	12
Positive Active Material Utilization	0.462
Negative Active Material Utilization	0.600
Acid Specific Mass (g/cm ³)	1.310
Separator Porosity (Compressed)	0.88
Acid Capacity/Solids Capacity	2.0
Compression (kPA)	170
Temperature (Deg C)	25
Width (inch)	10.512
Height (inch) – excluding terminals	8.071
Packaging Thickness (inch)	0.012
Number of Intercell Cu Connectors/Cell	8
Intercell Cu Connector Thickness (in)	0.006
Intercell Cu Connector Diameter (in)	0.92

Figure 4 shows results of calculations done to contrast the traditional 6TAGM design and the ETP wafer cell design. For the calculation, thin Ti foil (12 μm) was used as the positive electrode substrate, with a thin SnO₂ or TiSi₂ equivalent coating (1.5 μm). For the negative, a 12 μm Cu foil was used, with an 85% graphite filled polyvinylidene fluoride (PVDF) coating (50 μm). The battery consisted of five, 12 volt modules, along with a metal housing, current collector straps, metal (steel) ribbed reinforcing plates at the ends of the battery, and a gas-inflated bladder to maintain pressure on the cells. As shown, the active material fraction is significantly higher in the ETP design. This is due to reduction in the weight of battery containment and conductive/connection components. This savings results in a 61% increase in specific energy (58 Wh/kg vs. 36 Wh/kg of the production 6TAGM).

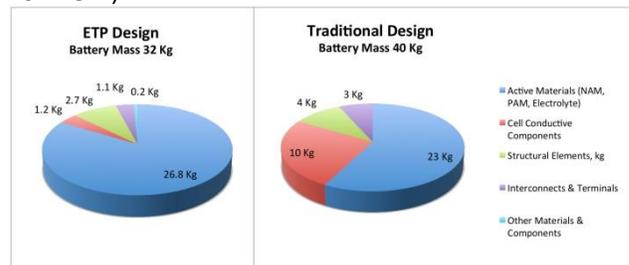


Figure 4. Mass Fractions of Battery Components for 6TAGM Lead-Acid Battery.

Table 2 shows the effects of different supporting (non-active) materials, namely the material used in the housing (Titanium or Steel), and the electrode substrates. As shown, the use of thin titanium or copper for the electrodes improves specific energy by approximately 10-15% over 152 μm lead foil, which in turn offers a 40% increase over a conventional 6TAGM design. The housing material made a smaller difference. The designs use very conservative material utilization values typical of production 6TAGM batteries, and offer opportunities for ongoing, stepwise improvement in energy density, specific energy and specific power with further development of active material utilization strategies described in the literature.

Experimental

Full single pouch cells, such as shown in Figure 5, were built to evaluate substrate performance. Cell construction initially used lead foil as the substrate for both electrodes for concept verification. Electrodes were prepared using standard pasting processes. Typical paste compositions are shown in Table 3.

Table 2. Effects of Substrate Type, Block Count & Housing Material.

12 Volt Blocks	Positive Substrate	Negative Substrate	Housing	Q Wh	Specific Energy Wh/kg	Energy Density Wh/l

5	12 μm Ti / 1.5 μm SnO ₂	12 μm Cu/ 50 μm Graphite filled PVDF	Ti	1850	58.0	133
4	12 μm Ti / 1.5 μm SnO ₂	12 μm Cu/ 50 μm Graphite filled PVDF	Steel	1830	55.8	132
5	152 μm Pb	152 μm Pb	Steel	1750	50.4	126
Present Production Lead-Acid 6TAGM:				1440	36	103



Figure 5. Single full scale 6TAGM pouch cell electrode, rear face with.

As with the half cell tests, cells were held in compression (Figure 6) and evaluated using Arbin battery testers. After initial formation (C/20 to 2.55 V, 2.55 V for 36 hours), cells were subjected to repeated charge/ discharge cycles. Discharges were typically done at C/20 rate to 1.7 V, and charge was also done at C/20 rate, to 2.55 V, and then 2.55 V to C/30 cutoff current. After testing cells were disassembled and autopsied.

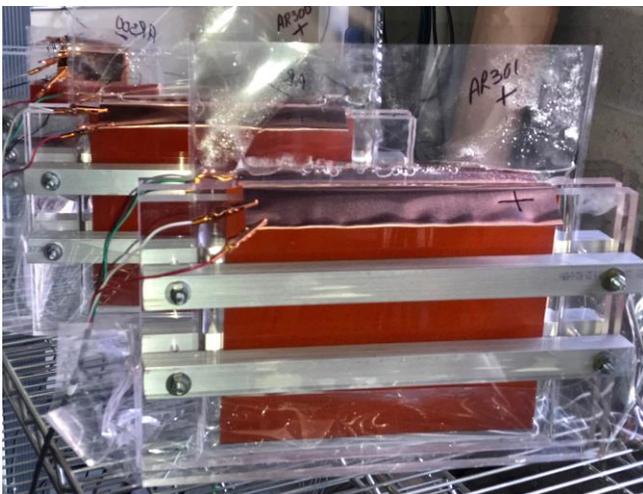


Figure 6. Full Scale 6TAGM Cells Under Test

Summary

A wafer cell construction of lead-acid batteries is proposed that will dramatically improve the specific energy over traditional designs. The pseudobipolar arrangement reduces the amount of support and conduction material (non-energy producing material) needed by 67%. The design approach to lead acid batteries greatly increases energy density and impressively eliminates the principle wearout modes of lead-acid – positive material cycling deterioration and in non-lead substrate implementations, does away with positive grid corrosion. Cycle life is multiplied by the high compression enabled by the design, and the design is ideal for high voltage batteries, which in contrast to conventional designs, result in elimination of interconnect and bus components, further reducing weight and freeing up additional volume for active materials. And experiments have shown the design capable of operating fully sealed, providing submodule and battery charge management capability via inexpensive pressure transducers.

The design is particularly suited to low and high voltage aircraft, heavy duty and tactical vehicles and other high vibration, high voltage and high power applications.

In contrast to other high performance batteries, this design approach is inherently safe, requiring minimal charge and discharge control subsystems and no supplemental containment in safety-critical applications. Acknowledgements

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