best mag
No. 88 Spring 2025
The international quarterly for the battery technology industry

Recombiner performance during normal and abnormal conditions

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Everyone in our industry understands the benefits of using recombiners in vented lead-acid or nickel-cadmium batteries. The benefit of their use during normal operating conditions is well known and has withstood the test of time for more than fifty years. But how many understand how the different designs react when the battery conditions are not normal, and an abnormal event occurs? Pete DeMar, founder of Battery Research and Testing examines the issues.

Recombiner plugs, as they are called in Europe, or recombination vents in the Americas, are all designed to do the same thing. They recombine the hydrogen and oxygen gas that is continuously generated during normal charging conditions –on float or equalise – from within the electrolyte, back into water vapour. That water vapour condenses on the walls of the recombiner body and as the water droplets gain size and weight, they eventually flow downward and back into the cell.

This return of the water back into the electrolyte, where it originated from, helps maintain the electrolyte level. This automatic replenishment of the water content in the electrolyte reduces the labor costs associated with an individual having to manually add water to the cells.

Pic 1: This picture shows how when a cell explodes, it can blow all four sides apart from the cover, and how it normally occurs in the head space where most of the gasses are located.

Safety in the battery room

Equally, and possibly even more important, is the fact that, when a recombiner converts those gases back into water it is simultaneously preventing those combustible gases from entering the battery room. The benefit of this reduction of combustible gases is understood and referenced in both the IEC62485-2 and the IEEE1635/ ASHRAE21 – 2022 documents. Both these documents provide guidance in performing the calculations as to air exchanges in order provide a safe environment in the building or room.

The IEC62485-2 goes so far as to state that if recombiner plugs are installed in the cells, the ventilation requirements can be reduced by 50%. The IEEE1635/ ASHRAE21 – 2022 document does not provide that same blanket endorsement but does state the benefits of recombiners.

That 50% reduction allowance is a conservative number, as most present day recombiners can recombine more than 90% of the gases generated during normal operations, with most advertising 98% or greater, and some promoting near zero water loss. It is realistic to state it is possible in some conditions that the HVAC could fail completely and, by the recombiners almost eliminating the off gassing, the battery room could remain a safe environment without any air exchanges at all. This of course would be determined by the individual use-case.

Development timeline

These devices have come a long way since their concept was originally discovered back in Thomas Edison's time. The first patents that I am aware of relating to the commercialisation of a recombination device were awarded to Harry A. Guthrie in 1939, and Palmer H. Craig in 1949. Palmer H. Craig's patent was the first design that resembled what we now can purchase from any recombiner manufacturer. Those devices were named the HydroCap, and they demonstrated that the process of returning the hydrogen and oxygen gas back into water was a real and doable process.

Now to fast forward to more modern times. Hoppecke realised the benefit of having recombiners in their cells to reduce the labor required for watering, so they designed their own version of a recombiner and introduced it to the public in 1971. It was so successful that other battery manufacturers, seeing the benefit of having a recombiner in their cells, decided to design their own, to help in the sales of their batteries.

Bater designed and manufactured a recombiner for use in their own cells, and at some point, also offered that unit to other battery manufacturers.

It is our understanding that the next recombiner manufacturer, was Sistemmi. They developed their unit in response to a request from a battery manufacturer that did not want to develop their own unit or use the Bater product, but did want to have one of their own to offer and, since they were already working with them in other ways, requested their assistance. Sistemmi, like Bater, provides their unit to multiple battery manufacturers for use in their products.

I am not positive about which of these next three were first, second, or third, but here are the other three recombiner manufacturers that I am aware of.

BAE had been offering the Bater-produced units along with their BAE cells, as do numerous other battery manufacturers and resellers, but wanted their own device – so they designed, developed, and now sell, their own recombiner. Philadelphia Scientific, which has been producing catalysts and

Pic 2: This picture shows a jar that was deliberately pressurised in order to create a rupture. Notice that the upper portion of the jar is connected to the cover, and that the side of the jar where it opened is near the midpoint of the jar.

catalyst-equipped vents for VRLA (valve-regulated lead-acid) cells for over 30 years now, decided to produce a recombiner for vented cells, and now has their second rendition of this product. Finally, there are the units produced by Flow System USA, with their Flux model units. They also developed their unit based upon a request from a specific battery manufacturer, for whom they were producing other items.

Normal operations
Every one of these units, during normal operations, will recombine most of the gases back into water. The very key words in that sentence are "during normal operations". By this I mean that under all conditions that are acceptable to any battery manufacturer – which includes being within the respective manufacturer's recommended float or equalise charging values, coupled with any recommended voltage adjustments required because of the ambient temperature – these units will recombine the gases being generated, back into water without any issues.

Abnormal events
Users of any of the above-listed manufacturer's products can feel comfortable that their device will function correctly during normal operating conditions. But what happens if an abnormal event occurs?

My definition of an abnormal event is anything that does not normally occur within the battery. The three abnormal events that can and do occur, are:

1. **The failure of the charging system control**, which allows the battery-string voltage to increase substantially above what is acceptable to the cells, which causes an overcharge situation where excess gas is generated and available for recombination.

2. **A thermal runaway event**, where the increase in the current flow through the cells creates excess gas which is available for recombination.

3. **An ambient temperature** that increases the electrolyte temperature and where there is no lowering of the battery voltage to correct for that overcharge situation, which then increases the gas available for recombination.

Pic 3: This picture shows two units from an off-grid site that when being removed from their cells, separated the body from the base. It is our belief that the plastic was negatively impacted due to excessive internal heat generation.

In all three of the above stated conditions, the cells will generate substantially more gas than the recombiner was designed to safely recombine.

A misunderstood technology
Stating that recombiners are one of the least understood parts of a battery system is a massive understatement. As testimony to that statement is an incident from a few years ago where it was reported that a cell in the battery string had ruptured and released electrolyte and plastic pieces onto the floor – and that this event was due to the failure of the pressure relief valve in the recombiner to release, which

caused the pressure inside the cell to reach a point where it caused the cell to rupture. The blame for this event was placed upon the recombiner. However, the pictures of the cell and the battery area told a very different story.

One picture showed the battery string with the position of the damaged cell in the rack. Other pictures included close ups of the upper portion of the jar, just below the cover, which showed that all four sides of the jar had been forcibly separated. A substantial piece of the rear of the jar was hanging downward and still attached to the jar by the model sticker. A large piece of the front of the jar was located a few feet away from the battery rack, and various plastic pieces of the jar and the recombiner were scattered around.

Failure mechanisms

There are two very basic rules that help demonstrate the difference between a cell that ruptures and one that explodes. With a cell that ruptures due to excessive head-space pressure, the longest side of the cell (front-to-back or side-to-side) will crack approximately halfway up from the bottom, as this is the point where the plastic will allow the maximum deflection. When this occurs, the electrolyte will flow out of the cell and most of it will end up running down the side of the jar, and onto the floor in that area. It does not get ejected numerous meters or feet away from the side of the jar. The jar does not break up into numerous pieces and will not be found scattered around the room some distance from the cell. Nor will the vent or recombiner be ejected from the cell.

When a cell explodes, the explosion is the result of the gases within the cell being ignited by an arc occurring in the gases, and the result of that explosion is that multiple parts and pieces will be ripped from the cell. This can be from all four sides but does not have to be. Frequently, the cover is completely separated from the sides of the jar, pieces of the cell are scattered some distance from the cell, the electrolyte is ejected some distance from the cell, and the location where the most damage to the cell is to the upper portion of the jar. It will extend downward slightly but not be present in the lower third of the jar, and a vent or recombiner will typically be ejected from the cover.

Interpreting incident reports

This incident was reported as a rupture but what occurred was an explosion. Those reporting on that event were surely well intended but were not experienced in differentiating between the two types of events. So, they erroneously assigned to the recombiner the blame for an event that was not caused by the recombiner.

With the understanding that we needed to be more suspect of any reports on issues that occurred with cells with recombiners, we began paying more attention to everything available to us to help us understand the root cause or causes of what we were looking at.

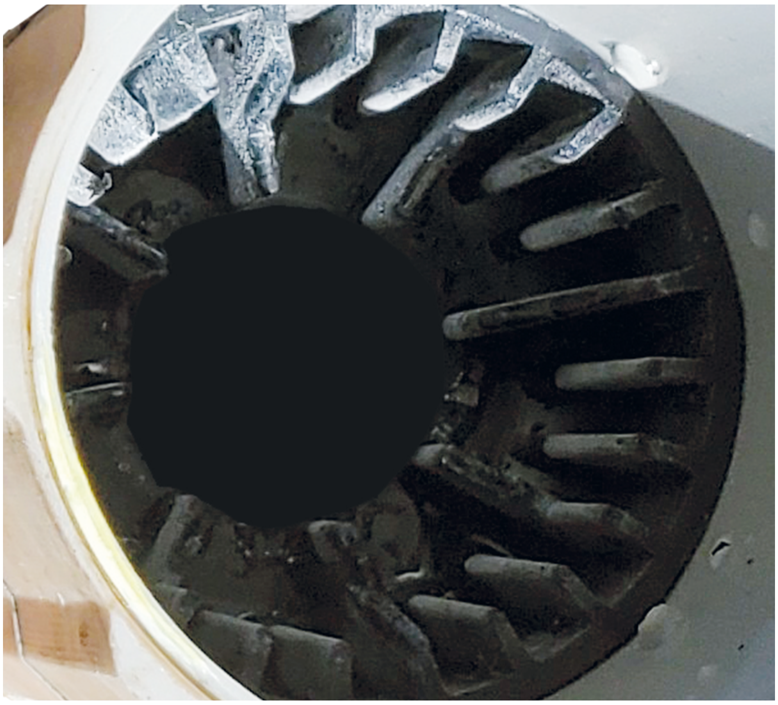
The first incident that made us realise there is a lot more to recombiners than we had previously understood occurred in an off-grid application – we were accidentally copied on the report that included pictures. The pictures are what led us to our present investigation, which will be reported on after completion of that investigative testing program.

The first picture that we saw of this off-grid battery showed three recombiners and the base (the part that secures the assembly onto the cover, were gone from the recombiner, and were reported as being inside the cells. It was explained that when the individual that owned the battery went to check the electrolyte levels in the cells that three of the recombiners simply broke apart when he twisted them to remove them. The remainder of the units came out as they normally do.

That picture showed what appeared to be a clean separation, with no indicator of the cause. There was another picture that showed the inside of one of the recombiners. The user had been instructed to cut one apart and take pictures and send them to the manufacturer. At first glance, that picture appeared that everything in there looked normal. However, later on, while looking at that picture with more magnification, it was noticed that there were three of the raised support structure ribs, that showed some slight irregularities. Those irregularities were dimples on the top of those ribs. Those dimples looked like they were the beginning of the plastic melting, but which had not progressed any further. There were 24 ribs and only three showed any irregularities, but there were those three. The remaining 21 ribs looked just as they should.

It needs to be understood that the battery enclosure was a home-built insulated cabinet – as are many of these remote off-grid applications – and it was designed to both insulate the batteries it from the heat in the summer and the cold in the winter. This location is in the desert. There was no outward appearance that indicated any issue with the units.

The charger was set at a fixed value, which was within the voltage range recommended by the battery manufacturer. We assume it did not have a temperature compensation circuit, which could have adjusted the voltage up or down depending upon the temperature of the battery. It is believed that because it is in Arizona and it was summer, the battery cells were substantially above 25°C (77°F), that the battery voltage was set for 25°C (77°F), and the cells were subsequently being overcharged. This overcharging generated more gas than the recombiner could control and the excess recombination created internal temperatures above what the plastic was designed for, which ended up with the initial melting that we observed.



Pic 4: This picture shows the beginning of the catalyst core support structure melting, due to excessive internally generated heat due to the inability to control the amount of gas being recombined.

Understanding the issues

Upon trying to understand this issue, we surmised (guessed or expected) that the catalyst core had reached such a temperature that it exceeded the HDT (Heat Deflection Temperature) of the plastic in that retainer basket, and that excess temperature also impacted the area where the bottom of the body connects to the part that sticks down into the cell and which has the bayonet tabs.

Because of this incident we began to wonder just how much else about recombiners, that we had originally thought were about equal, we did not really understand.

Testing program

Because of this desire to understand and be able to explain the differences in the way recombiners could respond during an unusual event, we began a testing program. Our testing program consists of running six-hour duration tests on each of the different recombiner manufacturers' products. Each test being run is at a fixed current and the cell voltage is allowed to go to wherever it needs to go to, for us to be able to force the current that want to use, through the cell. The currents that we utilise are 10, 20, 30, 40, & 50 amps.

The pass/fail criteria are simple, does the unit remain physically intact with no melting, and secondly does it function as normal upon return to a normal operating condition.

While these are abnormally high currents to have on a fully charged cell, these currents can and do occur during any one of the above-listed events.

Final test and results

At this point in time, we are in the process of testing the last of the six different manufacturers' products, and what we have observed with the differing designs has been eye-opening. It is intended that the results of this testing program will be presented at Battcon 2025, but of course that is dependent upon whether the selection committee determines the paper worthy of publishing at their venue. I also intend to provide additional information on this program in the next publication of this magazine – if the editors determine it worthwhile of course.

Recombiner performance during normal and abnormal conditions

In the Spring issue of *BEST*, Pete DeMar provided explanations on the background of recombiners, their benefits, the variety and motivation behind the different manufacturers of these devices, how they compare during normal operations, and then explained his observation of an abnormal issue, which eventually led him to question how different designs performed during abnormal conditions.

Everyone should accept the fact that normally stationary batteries are operated within what are the acceptable voltage and temperature considerations for their respective manufacturer's requirements. Everyone also should acknowledge that there are times when batteries are required to operate outside of those requirements. These instances are what are considered 'abnormal events'. Every manufacturer's recombiners will function as expected during normal operations, but that is not the case for all of them when there is an abnormal event.

We can relate these normal and abnormal conditions to driving a car down a highway. Normally the car operates within the speed limit (96–112kph/60–70mph) and the car is designed for that 'normal' operation and will function for many years without failure. However, there are times when we exceed the limit for a short duration of time, such as overtaking another vehicle, which all vehicles can handle without suffering any damage. Then there are times when the vehicle is required to severely exceed the normal speed limits for extended periods (160–200kph/100–120mph). If the vehicle is not designed for that usage, bad things can happen, such as the engine expiring. All vehicles can handle normal operations without damage, but only vehicles that are designed for those excessive speeds can withstand those operations.

Just as with a vehicle that is designed to handle excessive conditions, as well as normal conditions, the same applies for recombiners. If the recombiner is not designed to handle abnormal events, it can suffer damage which can render it damaged or non-functional.

As explained in the Spring issue, in order to test the various recombiners' ability to handle unusual events we performed extended duration (six-hour) tests. During those tests we forced currents through the cells that were in substantial excess of what occurs during normal operating conditions. We did this to create an abnormal amount of excess gas in the head space. This excess gas, if allowed to contact the catalyst material, would create an increase in temperature due to the exothermic reaction.

The current flow rates that we used were 10, 20, 30, 40, and 50 amps. Your initial thought might be that those values seem excessive. However, in almost all except for the smallest battery installations, the chargers that are installed to support the normal loads, plus support the recharge following a discharge event, can exceed 50 amps. The charging source is what in an abnormal event will be providing the voltage and current to create those currents.

As far as we are aware, there are a total of six manufacturers of recombiners that supply products in Europe and/or North

Fig 1

and South America. Of those six, two of them are battery manufacturers which, per our understanding, only provide their recombiners for use in their own batteries, either with new battery orders or for retrofit into existing battery strings of their product. There may be exceptions to this that we are unaware of.

There is one battery manufacturer who produces a recombiner that, in addition to supplying their recombiners with their batteries, also provides their recombiner to other battery manufacturers for usage in their cells, as well as to resellers of batteries and battery related products.

The other three recombiner manufacturers are not battery manufacturers and they supply their products to various battery manufacturers, resellers, and end users.

Fig 1 shows a recombiner from each of the six manufacturers that we are aware of. Each of the units shown has the capability to recombine the gases generated during normal operations for up to approximately 1,500Ah. There is a total of 10 different recombiner models available that we are aware of presently. Three of the manufacturers have other models, with one having one lower amp hour model, one having two lower amp hour models, and one having a larger amp hour model.

As can be seen by the differences in the physical size of the recombiners, size does not dictate how much gas a unit can recombine back into water. In addition, how a recombiner looks does not indicate its ability to safely function during any of the three abnormal events described in the Spring edition. Those three events being:

- a failure of the charging system controls
- a thermal runaway (presently called a thermal walkaway in the US) or
- an extended elevated temperature without a reduction in the battery float voltage.

All three of those abnormal conditions can generate gas volumes that are substantially greater than any that the recombiners were originally designed to recombine the gas for. How a recombiner responds to any of those abnormal conditions should be an important consideration to anyone purchasing recombiners for usage in their battery strings, if they want to protect their battery systems.

There are no stationary battery models that, when fully charged and in normal operation conditions, require two or more amps of float current to remain in a fully charged condition, unless they have an internal issue. Most models will require less than one amp, and the normal operating temperature of a recombiner in any cell is just a few degrees above whatever the ambient temperature is. Also, the units functioned successfully with 10 amps of current flowing through them.

Fig 2 shows our test set up. We inserted the recombiner to be tested into the cell and proceeded to increase the current flow to that desired for the respective test and then monitored the recombiner case temperature throughout the test.

We utilised lead-selenium instead of lead-calcium cells for our test cells, so that we could observe whether the Arsine or Stibine gas would be controlled by the filtering material utilised to protect the catalyst material. Pass/fail criteria:

- the recombiner would maintain external and internal structural integrity throughout the six-hour test period with no melting or plastic bubbles blowing out the sides, or the cores collapsing onto the cover, or internal melting
- the recombiner would be functional throughout and following the six-hour period
- when a recombiner failed a test, we did not test it again at a higher rate.

General observations:

- the recombiner case temperature would normally reach its upper limit at the respective current flow within 30 to 45 minutes of the beginning of the test period
- the three recombiners that passed all the tests (10, 20, 30, 40, and 50 amps) achieved their maximum temperature during their 30 amp test and their temperature did not increase during their higher current tests
- the three recombiners that failed the testing all failed during their 30 amp tests.

Fig 2

In one test, the recombiner temperature climbed from its beginning temperature of 23°C (73°F) to 94°C (201°F) over the first two and a half hours of the 30 amp test, and then it gradually declined back down to near the starting temperature by the end of the test. We attribute this occurrence to a poisoning of the catalyst material by the gases which rendered the catalyst material non-functional.

With all the other tests, the recombiner remained at its elevated temperature until the current flow was removed. We attempted to repeat this test on the same recombiner the following day, but it would not increase in temperature above the ambient, which meant that it was essentially dead. We then repeated the test on another identical recombine, and it functioned as expected, which we interpreted as the filter material in the first recombiner not protecting the catalyst material as intended.

What controls the amount of heat that is generated during the recombination process? The catalyst core (the ceramic part that holds the catalyst material) determines how hot the core will get, which determines how hot the body of the recombiner gets. It does this primarily because of four things:

First is the material the core is made out of. Second is the size of the pores in the core that the gas must pass through which limits/restricts the gas flow. Third is the thickness of the walls of the core which also limits the amount of gas that can get to the catalyst material at any one time. Last but not least is the amount and type of catalyst material utilised within the core. All of these must be considered and are a part of the delicate balance that each manufacturer must consider when designing a recombiner.

What determines how the plastic parts of the recombiner react to the heat generated during the recombination process? The HDT (heat deflection temperature) rating determines when a plastic will soften and no longer retains its rigidity. All plastics have different temperatures at which they will deform or melt. Within the six different manufacturers units that we tested, we recorded external body temperatures that ranged from a low of 77°C (170°F) to a high of 193°C (380°F).

It was observed that some units would melt or deform with an external temperature as low as 93°C (200°F) and some would remain intact and fully functional as high as 293°C (380°F). This is attributed to the HDT of the plastic that the respective designers selected for their unit.

It is important to understand that all of the recombiners functioned as expected during normal charging and even up through their 10 amp tests, which indicates that the designers had indeed considered gas generation that was substantially above what would be normally required. However, they did not take into consideration abnormal events of greater magnitude, which can occur with any of the three situations stated previously – charging source runaway, thermal runaway or an elevated ambient temperature without a reduction in the charging voltage.

Our observations made one thing clear: if we couldn't predict how a recombiner would respond to abnormal events, it’s unreasonable to expect users to. Despite differences in size, all recombiners appear outwardly normal – proving that appearance offers no clue to their behaviour under stress.

It must be understood that every recombiner is designed to perform the same fundamental function. They simply recombine the hydrogen and oxygen back into water. Where they differentiate from each other is how they prevent themselves from generating heat that is greater than what their plastic is designed to remain intact at, and how they prevent the catalyst material from becoming poisoned.

To help individuals assess whether a recombiner can withstand prolonged abnormal events, we developed a straightforward form that can be used to request key information from the manufacturer. Based upon the answers they provide the individual can then determine if that recombiner is the best for their application. The recombiner comparison form is available by requesting it at info@batteryresearch.com.

Hopefully this information will be of benefit to users of recombination devices.