CAT® ENERGY STORAGE: ZINC-AIR TECHNOLOGY

A DETAILED LOOK AT THE INNER WORKINGS OF METAL-AIR TECHNOLOGY

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CATERPILLAR®

WORKING PRINCIPLE

Cat® Energy Storage solutions use proprietary rechargeable zinc-air cells at the core of the energy storage device.

Zinc-air cells use oxygen from the ambient atmosphere to produce electrochemical energy. As the air-breathing cathode – the positive electrode – is exposed to air, oxygen diffuses through this hydrophobic barrier to the cathode's catalytic active layer, where the reduction of oxygen is promoted in the presence of an aqueous alkaline electrolyte. The hydroxide ions that form due to oxygen reduction at the cathode react with zinc from the anode – the negative electrode – to form soluble zinc species in electrolyte. The cathode is an irreducible electrode, which means its physical size, electrochemical properties such as discharge impedance, and rate of oxygen reduction remain unchanged during discharge, unlike most other closed cell batteries.

THE ELECTROCHEMICAL REACTION:

Cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH$

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

Overall Reaction: $Zn + \frac{1}{2} O_2 \rightarrow ZnO$

Advances in the continuous fabrication of thin, high-performance gas electrodes in the 1970s enabled the mass production of the zinc-air button cell. The most successful applications of zinc-air batteries in the small form factor have been in medical devices, such as miniature hearing aids. However, these batteries are limited to disposable, single-use applications, as is the case with alkaline batteries (AAA, AA, C, D).

Reaction reversibility is the key to this breakthrough energy storage technology. This reaction becomes reversible and enables the world's first reliable, rechargeable zinc-air cell by leveraging the proprietary aspects of the advanced anode architecture, smart electronic controls, robust gas electrode design and additives. By enabling the rechargeability of the zinc-air cell, this advantageous battery chemistry has been lifted to a new level of cost effectiveness, usability and application reach.

BATTERY REACTIONS

This section highlights the electrochemical reactions occurring during charge and discharge of the zinc-air battery. In the discharged state, zinc exists in the electrolyte as a solvated ion $Zn(OH)_4^{2-}$, also known as zincate. The anode is charged by adding two electrons to the zincate ion, releasing four hydroxyl ions and depositing metallic zinc on to the anode current collector:

$$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$$

Potassium is present in the electrolyte as K^+ potassium ions. The alkaline electrolyte of potassium hydroxide remains, as there are equal amounts of OH^- consumed and produced. This is the same exact electrolyte constituent present in all nickel-metal hydride, nickel cadmium and primary alkaline batteries. The chemistry is ultra-safe and has traditionally been used in zinc-air hearing aid batteries.

The complementary reaction on the counter electrode consumes the OH^- to form water and oxygen gas, which releases electrons:

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

The oxygen gas generated leaves the cell through the oxygen vent port, with an oxygen generation rate between 50 and 150 ml/minute. Per the design, no electrolyte can leave the cell, and any electrolyte mist droplets that form inside the cell are typically between 0.5 and 1.5 microns in size. Although mist is not common, any mist formed is trapped by a mist elimination filter integrated into the top of the cell that captures the electrolyte droplets and returns them to the liquid portion inside the cell, thus preventing loss of electrolyte. Oxygen gas formed during charge is then routed through a manifold to the exterior of the battery cabinet (see Figure 1).

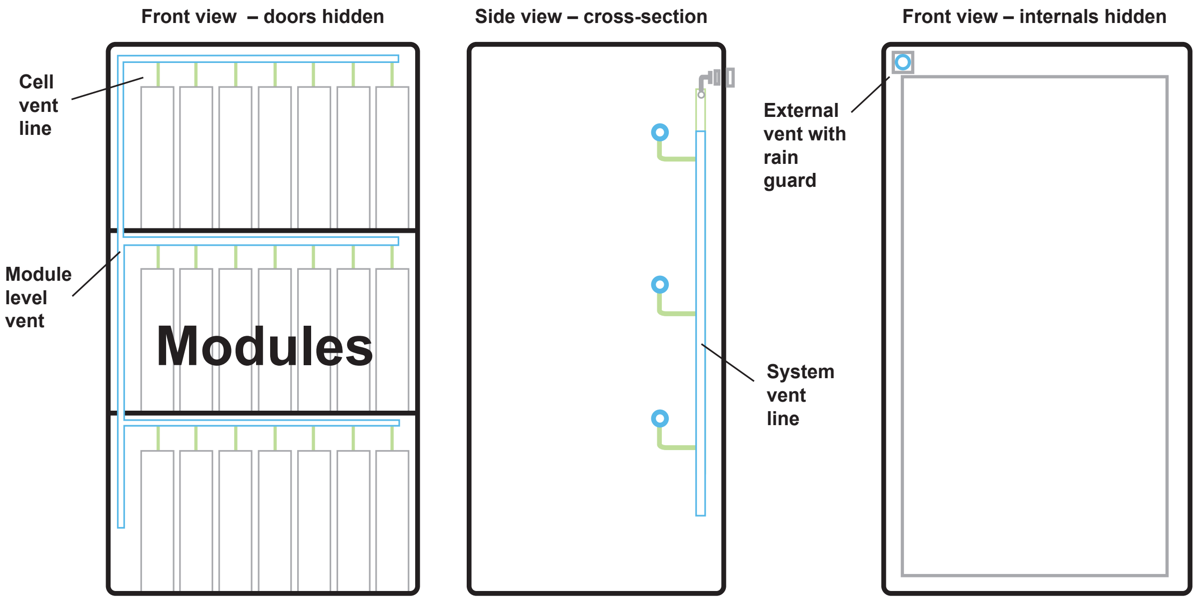

Figure 1: Cat® Energy Storage module layout

All gases are directly vented out of the cabinet, which has ~1000 times the air flow compared to vented gases. Unlike other batteries, zinc-air batteries have electronics directly affixed to the cells, as well as an electronics panel for power circuits inside the cabinet. The cabinet and venting are designed to make the system and associated electronics robust, reliable and safe.

During discharge, the two reactions that take place during the charging cycle are reversed. Metallic zinc on the anode current collector is oxidized and reacts with hydroxyl ions in the electrolyte, forming dissolved zincate and releasing electrons that are then available to the load:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$$

The consumed hydroxyl ions are replaced via the reduction of oxygen from the air in the air cathode, consuming the electrons released during the oxidation of zinc:

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^-$$

No gas is released during this process.

SELF-DISCHARGE

Similar to alkaline batteries, the Cat Energy Storage system self-discharges under idle conditions, albeit at a very low rate. The following reaction occurs during self-discharge, resulting in a small amount of hydrogen generation:

$$Zn + 2\ OH^{-} + 2H_2O \rightarrow Zn(OH)_4^{2-} + H_2$$

Self-discharge rates are typically between two to five percent per month, depending on ambient conditions. Any generated hydrogen leaves the cell through the vent port. Zinc-air flooded battery chemistry is inherently safer than other pasted electrode chemistries due to the fact that the cell vent equilibrates the pressure inside of the cell to the outside ambient pressure.

OVER-CHARGE

Zinc-air chemistry is extremely resistant to over-charge. As the electrolyte is water-based, no thermal runaway reactions are possible. Any over-charging results in electrochemical splitting of water, and the gases are vented through the cell vent. Furthermore, a smart battery controls system at the cell level monitors and stops charging when a cell reaches the target voltage during charge.

OVER-DISCHARGE

During discharge, cell voltage is monitored by the smart controls and monitoring electronics, and discharge is stopped when a cell reaches the target voltage. Similar to over-charge, there are no thermal runaway reactions possible, even if the voltage falls below the target voltage. Caterpillar's zinc-air energy storage system has proprietary controls to reduce or eliminate any effects of zinc passivation, thereby maintaining the cell performance.

THEFT DETERRENCE

There are two primary reasons why zinc-air technology is not an attractive target for thieves. While lead has a high street value, especially in emerging economies, the zinc used in zinc-air storage has no scrap value. Any other metals used in zinc-air storage systems are too difficult to harvest and have little value.

The second reason why zinc-air technology is not attractive to thieves is the nature of the technology itself. A lead-acid battery can easily be repurposed for other uses, and anyone can put a meter across the positive and negative posts of a lead-acid battery to read a voltage.

On the other hand, a system using zinc-air technology cannot be used in isolation, and no voltage can be read outside of the complete system. Lacking an air source to supply the cathode for the chemical reaction, along with the integration of the modules with electronic controls, the zinc-air energy modules will not function and are useless.

For more information, visit ***www.cat.com/powergeneration***.

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