What Is Your Sensor Telling You? Not All Sensors Are the Same.

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Abstract

Off gassing of hydrogen from lead acid batteries is a known phenomenon and a potential safety hazard due to the low flammability limit of hydrogen in air. This has led to the development of multiple hydrogen alarm systems and sensors for battery monitoring, and other gas sensors for Li Ion battery monitoring. Not every sensor is the same, and it is important to know how the sensor works before selecting one for a system. Knowing how the sensor operates is important to selecting the best suited sensing technology for a given application. Maintenance and placement of the sensor are also key to accurate and effective monitoring of a battery system. This paper will cover the various sensor technologies on the market, their pros and cons for battery applications, and recommended practices for using sensors and alarm systems for battery monitoring.

Introduction to Gas Sensing

Since the days of the canary in the coal mine, there has been a need for gas sensors. Multiple gas sensing technologies have been developed throughout the years, each with its own advantages and disadvantages. Hydrogen, in particular, is a highly combustible gas that is liberated from lead acid batteries over the life of the battery. Currently, multiple hydrogen alarm systems are available on the market that employ hydrogen sensors to detect flammable levels of hydrogen in air. In an industry evaluation of common commercial hydrogen alarm systems, three primary sensing approaches were identified: catalytic bead, solid state metal oxide semiconductor, and chemi-resistive ceramic sensing elements. (Note that lithium ion battery electrolyte gas sensors are due to enter the market soon, but this evaluation was based on current products in the market, and as such, these specific sensors have been excluded from this paper). In this paper, these primary sensing methodologies will be reviewed and evaluated for their use in lead acid battery monitoring applications.

Hydrogen is a flammable gas at low concentrations with a low activation energy, so it can easily ignite. The lower flammability limit (LFL) of hydrogen is 4% in air. Monitoring of hydrogen evolution from lead acid batteries, therefore, is an important safety measure to ensure that flammable levels are not reached in an application. To this aim, gas sensing has been widely adopted in lead acid battery intensive applications. Hydrogen alarm systems on the market generally have warning and alarm settings at 1% and 2% hydrogen in air, respectively, corresponding to 25% and 50% of the LFL. Furthermore, development is underway to leverage hydrogen off gas sensing to predict the state of health of lead acid batteries, based on the duration, frequency, and magnitude of hydrogen evolution. Though such approaches are still under development, it is the goal to use gas detection along with other traditional battery monitoring methods to identify battery health, and address potential problems prior to failure.

The functionality of hydrogen alarm systems is dictated by the gas sensor employed within the system, so the fundamental mechanism of the gas sensing element is very important. How the sensor measures the desired gas, along with the specifications of the sensor, will dictate how well the alarm system works. In the following paper, the operation and performance of various commercial gas sensors will be discussed, along with the advantages and disadvantages of each for lead acid battery monitoring.

Gas Sensing Technologies

The catalytic bead sensor is one of the three primary gas sensing technologies currently used within hydrogen alarm systems for gas monitoring. Catalytic bead gas sensors have a simple design that utilizes a Wheatstone bridge circuit of thin platinum wire coils. One of the platinum wire coils is covered in reactive catalyst to promote oxidation of combustible gases. The other platinum wire coil is coated with a nonreactive oxidation inhibitor. This inert coil is the reference resistor in the Wheatstone bridge, while the other coil has the catalytic bead which reacts in the presence of combustible gases. A diagram of the Wheatstone bridge is shown in Figure 1, where the unknown resistance of the active bead is measured by the known resistance of the reference bead. The sensor response is characterized based on the resistance change between the active bead and reference bead. The reference bead, therefore, must be inert to combustible gases for proper operation. Most combustible gas sensors are calibrated to methane gas since it has a saturated single bond that requires the sensor to operate at the highest temperature in comparison to other hydrocarbons[i]. Sensor manufacturers then provide correction factors for the sensor response to other combustible gases like hydrogen, or integrate the correction factor into the alarm system. The sensor or alarm system should always be tested with the specific gas of interest to ensure that it operates properly.

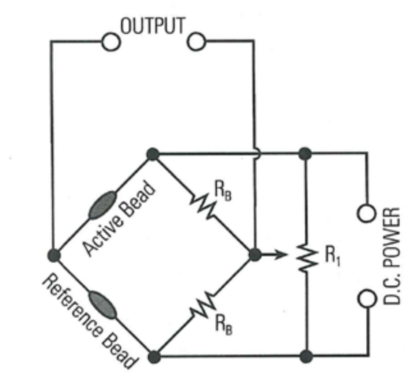

Figure 1. Wheatstone bridge diagram for catalytic bead sensors.

The catalytic bead operates at an elevated temperature to facilitate the reaction with the combustible gas. The operating temperature is in the range of 400°C to 600°C, which aids in promoting the catalytic reaction with combustible gases and stability of the sensor. The reaction of the combustible gas with the catalytic bead is an oxidation reaction, so oxygen is necessary for the sensor to operate. The catalytic bead sensor is simple to fabricate, and has a long operating life. These sensors have been on the market for many years and are commonly used in hydrogen alarm system. Over time, catalytic bead sensors can lose sensitivity due to poisoning, and burning when exposed to high concentrations of combustible gases.

The second sensor technology in wide use today is solid state metal oxide semiconductor gas sensors (MOS sensors) that use n-type and p-type semiconductor materials to detect gas. Researchers have identified that n-p junctions within semiconducting materials are very sensitive to background gases. Further development of this sensitivity, along with the addition of a metal oxide layer on the semiconducting material, led to the development of this gas sensing technology.

In air, at temperatures between 150 and 400°C, oxygen is absorbed at the surface of the metal oxides by trapping electrons from the bulk, with the overall effect of increasing the resistance of the sensor for n-type materials[ii]. For specific gas detection, the gas reacts with the absorbed oxygen on the metal oxide, which results in a change of the sensor resistance. This resistance change of the material is proportional to the concentration of gas being measured by the sensor; hydrogen is indicated by a reduction in resistance. Figure 2 outlines a simple design of the MOS sensor, which has the metal oxide layer on top of a silicon substrate. Two termination leads serve as power inputs to provide heat to the sensor. The collector lead of the sensor measures these changes in resistance.

Unlike catalytic bead sensors, MOS sensors offer greater discrimination of the types of gasses that can be measured. Varying the semiconducting material, processing techniques, and operating temperature can tune this sensing technology to detect a variety of gasses - not just combustible gasses. Solid state metal oxide semiconducting gas sensors, however, can be susceptible to background gasses, or have cross-sensitivity, which could trigger false alarms. There are some filters and design configurations that can help mitigate this sensitivity, but this is an inherent characteristic of this sensing technology.

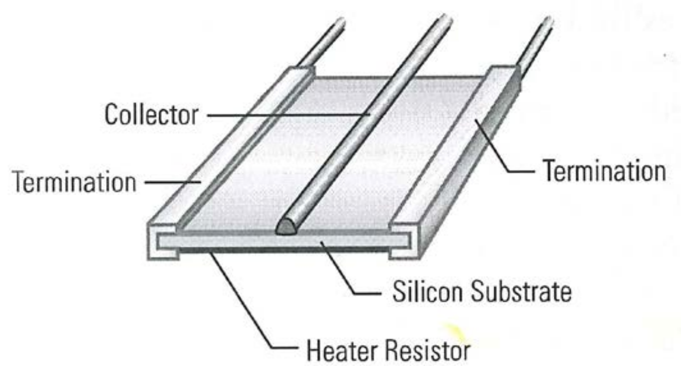

Figure 2. Solid state metal oxide semiconductor sensor diagram.

The third major sensor technology in use today, chemi-resistive ceramic sensors, combine some of the key characteristics of these other two sensor technologies. A ceramic active layer, that has catalytic properties for a particular gas, is operated at an elevated temperature of 100 – 300°C. In the presence of the desired detection gas, the catalytic reaction of the ceramic active layer changes the resistance of the sensor. Figure 3 depicts the chemi-resistive ceramic sensor. An internal heater maintains the element at the elevated temperature. Resistance is measured across interdigitated electrodes, which are deposited onto a ceramic substrate onto which a gas sensitive ceramic coating material is deposited. Chemi-resistive ceramic sensors can be made highly selective to a particular gas species, offering a significant advantage over MOS and catalytic bead sensors when false alarms due to cross-sensitivity are a risk. Like the catalytic bead and MOS sensors, chemi-resistive ceramic sensors require oxygen to be present in the background gas environment to sense reducing gases and to recover quickly to baseline conditions upon removal of the gas species.

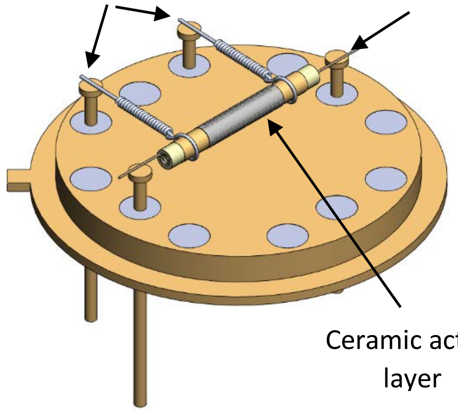

Figure 3. Solid model of chemi-resistive ceramic sensor.

The operation of all three of these primary gas sensing technologies leverages a change in a resistive circuit to identify the presence and concentration of a desired gas. How this change in resistance is generated determines the performance of the sensor. Each of these approaches offers robust gas detection capability, but generally a particular technology is best suited for a given application based on its unique requirements.

Advantages and disadvantages for battery applications

Typical characteristics important to battery monitoring are outlined in Table 1. Cross-sensitivity and operating temperature are key parameters for an installation. Many battery applications are indoors under controlled temperatures where this may not be a concern, but outside applications or those in which other hydrocarbons could be present would need to consider these parameters. Combustible gas sensors frequently suffer from false positive responses since they can respond to many different gases. To prevent false positive responses, combustible gas sensors should not be selected for installations where hydrocarbons or carbon monoxide could be present. In applications where cross-contaminants are not expected, combustible gas sensors may be a viable option for hydrogen detection.

Detection range, calibration interval, and life of the sensor are key characteristics in the operation of the alarm system. Stand-alone hydrogen alarm systems generally detect the full range of the lower flammability limit. There are some gas sensors that can detect hydrogen at concentrations greater than the LFL, but the alarm system is only concerned with the LFL.

Technology	Cross-Sensitive	Operating Temp.	Detection Range	Calibration Interval
Catalytic	Yes	-10 – 50°C	100% LFL	3 months
MOS	Yes	-10 – 50°C	100% LFL	3 months - 1 year
Chemi-resistive	No	-20 – 80°C	100% LFL	1 Year

All gas sensors are susceptible to drift, poisoning, or inhibition from detection. Some sensing technologies can be more prone to these issues than others due to the sensing mechanism. Catalytic bead sensors can easily drift out of calibration due to effects on the catalyst or consumption of the catalyst during operation. A shorter calibration interval is recommended for these types of sensors to ensure the sensor is accurately detecting the gas. Installation location is also a consideration for using these sensors due to the need to calibrate often; thus, the sensor should be located in a place that is easy to access.

Silicon gases (for example, from gasket and RTV sealants) are a common contaminant of all sensor technologies that can poison the sensor over time. Some manufacturers use filters to mitigate this poisoning effect. It is best not to use silicone sealants or have any uncured silicone near the sensor installation. Even fully cured silicone can still off-gas and poison the sensor, so it is best to reduce the amount of silicone exposure to the sensor.

Other contaminant gases can inhibit the sensor's detection capability, like halogen compounds commonly found in refrigerant gases and fire extinguishers. Catalytic bead sensors can temporality lose the ability to function, but can recover after operating in clean air for a significant amount of time. Chemi-resistive ceramic sensors can be blocked from operating properly from these halogen compounds as well, and can be permanently damaged as the concentration of these compounds increases over time. These are not the only type of gases that can inhibit gas detection, but these are the commonly known gases and compounds that can affect standard sensor chemistries. The manufacturer's literature should designate the types of gases and compounds to avoid.

Over-exposure to combustible gases, hydrogen, and/or reducing gases can damage sensors and prevent the sensor from operating properly. The three sensor technologies described above all require oxygen in order to operate properly, and are typically calibrated in air. The sensors can, therefore, perform improperly when the oxygen concentration is less than 21%. The sensor performance can also be affected when the oxygen concentration is much greater than 21%. Small deviations from an air background may result in erroneous sensor output; large deviations (such as very low oxygen concentrations or reducing environment) can permanently damage the sensor. A review of the product literature should be conducted to ensure the sensor is operating in an atmosphere that is proper for the system.

Installation

An instruction manual or other product literature is generally provided with sensors and alarm systems that indicates the best practices for the product. Knowing how these sensors operate and what gases and compounds can affect these sensors aids in the selection of an ideal sensor location for installation. In the case of hydrogen sensors and hydrogen alarm systems, it is important to place the sensor at the highest point in the room. Hydrogen is an extremely buoyant gas and will quickly disperse to the highest point in the room. The sensors should, therefore, be placed in this location to maximize the likelihood of exposure to any hydrogen present within a room or cabinet.

The proximity to sources of silicones and refrigerant gases should be considered for the installation location, as they are known contaminants to gas sensors. The installation location should be far from any windows sealed with silicone sealants, air conditioning units, coolant lines, or other locations where these gasses could be present. Because it is important to regulate the temperature in most battery applications for optimum battery performance, identifying a location for sensor installation that is far from possible refrigerant gas sources may prove difficult.

The best location for installing the sensor for battery monitoring, and number of sensors necessary for a particular installation, is determined on a case-by-case basis. Every room is different, and the battery installation also varies by room. At a minimum, one sensor should be placed at the highest point in the room in a location to which the gas can freely move without barriers. Ideally, the sensor will be located directly over the batteries, as this will ensure that as the hydrogen accumulates and increases in concentration, it will be detected by the sensor. To increase monitoring of large battery installations, multiple sensors should be used. These sensors can be placed in multiple locations above the installed batteries. As the hydrogen is generated, it will flow to the ceiling of the room and spread across the ceiling. Hydrogen differs from other combustible gases in that it is the lightest of all gases and as such, diffuses rapidly from the source[iii]. Since hydrogen will distribute across the ceiling, another configuration for sensor installation is to install sensors in the corners of the room. As the gas concentration increases and spreads across the ceiling, the four corners will read the equilibrated concentration of that the whole ceiling has achieved. This approach should not be used if the ceiling over the batteries is not flat. False, and non-flat ceilings can build-up hydrogen in areas without the sensors in the corners detecting it. As the concentration builds, it may be too late to mitigate the hydrogen concentration in the false ceiling, or in pockets that may be higher than the corners.

Calibration of sensors is a necessity, so the sensors should be located in a place that can easily be accessed in order to perform calibrations over the life of the sensor. Most ceilings are not easy to access. Tubing can be used to direct the flow of the calibration gas to the sensor. To this aim, calibration kits often come with tubing to aid in the calibration and testing of the sensor. Sensors cannot be installed and then left alone for permanent operation, sensors require regular maintenance for proper operation and to achieve the full life of the sensor. Accessibility, proximity to contaminants, and the location to which hydrogen is most likely to migrate are the main factors in determining the installation location of the sensor.

Operation

Under normal conditions, the sensor and alarm system will operate properly and may never trigger an alarm or indicate hydrogen concentrations above baseline or threshold conditions. If the alarm does reach threshold levels, however, there is typically a light indication, a mechanical relay, and/or an audible alarm. Safety measures should be designed into the system that are appropriate for the application. These may include configuring the alarm system's relays to initiate ventilation, shut down specific systems, or communicate the issue to a downstream or remote monitoring station. Some alarm systems are configurable to allow relays to be set either normally-open or normally-closed to accommodate these different response actions.

As previously mentioned, some gases and compounds can poison the sensor, or inhibit the sensor from operating. The sensor or alarm system should have designed-in error states to indicate when the sensor is not operating properly. Error states are generally provided for a loss of power to the device and to indicate out-of-range operating conditions or output levels. If care is not placed on the sensor selection and installation, there can be a higher risk of these error outputs. The instruction manual should be carefully reviewed for each application - especially the warnings, installation instructions, and possible outputs, and what they mean for proper operation of the system.

It should be noted that false alarms from contaminants or interfering gases are a common problem among gas sensors that often do not trigger an error state. Safety measures should always be taken in response to an alarm state; however, if a false positive is suspected, the area around the sensor should be investigated for possible contaminants. This may include silicones, refrigerants or interfering gases such as carbon monoxide, VOC's, or combustible gases. If the area is contaminant free and the sensor was installed properly, the manufacturer should be notified for further assistance with troubleshooting and diagnostics. Knowing how the sensor operates will aid in determining between true notifications of increased hydrogen, or if the sensor has failed or has been damaged.

Summary

There are multiple sensor technologies on the market for gas sensing. When using gas monitoring for battery applications, it is important to select the correct sensing technology for the application. The location for installation, the accessibility to the sensor for maintenance, and the proximity to possible contaminants should all be considered before selecting a gas sensor or alarm system. The manufacturer instructions and recommendations should be followed to ensure proper operation of the system. Once the sensor is installed properly, regular maintenance, including calibrations with the desired gas to be detected, shall verify the system operates as it should during normal operating conditions. Sensor technology is continually improving; owners of battery systems should perform due diligence and evaluate the market before selecting a sensor for an application. Making a sensor for the market is more of an art that a predictable scientific event[i]. Selecting the correct sensor for an application can also be an art, but knowing the technology behind the gas sensor will help in the selection, installation, and operation throughout the life of the system.

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