THERMAL PHENOMENS IN LEAD ACID BATTERIES

Jiří Neoral

Doctoral Degree Programme (2), FEEC BUT E-mail: xneora01@stud.feec.vutbr.cz

> Supervised by: Petr Bača E-mail: baca@feec.vutbr.cz

ABSTRACT

This article deals with thermal phenomens which affect lifecycle, capacity and performance of lead acid batteries focused on thermal runaway.

INTRODUCTION

In automobile industry, mainly diesel nad petrol engines are used. It's efficiency is limited and greenhouse gases are made, mainly CO2. Emisions of such gases created by automobiles are consiradably high percentage of it's total production. Therefore and because of limited amount of petrol there is a demand for alternative drives. As an alternative could be used engine powered by battery. Lead acid battery is the oldest secondary cell ever used. Since it was created methodology of production was developed wery well. But there are still some issueswhich limit its possible usage in electrical or hybrid vehicles. Nowadays VRLA (Valve Regulated Lead Acid batteries) are popular. One of the phenomens VRLA batteries have to face is Thermal Runaway. During Thermal Runaway batteries characteristics change and it can lead to total destruction of battery.

VRLA BATTERIES

VRLA is a stand for "Valve regulated lead acid battery" VRLA are bettiries with overpreassure valve. When preassure inside of battery rises to critical limit, valve opens and releases to atmosphere oxigen, hydrogen and vapour. By loss of vater inside battery drains and its internal resistance rises. VRLA is known as maintainance-free battery, which has better characteristics then battery with flooded electrodes and it can be used in any position. VRLA batteries cannot be used in high temperature environments, because its characteristics are affected by loss of watter inside and substrate corrosion. Recomended highest temperature for usage of VRLA is 60 °C. For higher temperature rises significantly probability of destruction. Main reason of destruction is draining of water inside of battery.

VRLA batteries are made as AGM batteries (Absorbed Glass Material), which contain electrolyte absorbed in separator made of glass microfibers and in active mass of electrodes. Self-discharge is small typically between 1-3% per month therefore storage time can be longer. Freezing of electrolyte isn't probable. AGM contain electrolyte strengthen by SiO₂. Small minims create cross-linked structure. Charging by low current helps to avoid over creation of gasses and cell destruction. [2]

NEGATIVE IMPACTS DURING USAGE

SELFDISCHARGE

Both electrodes are thermodynamically instable, therefore electrodes can react with lotion releasing hydrogen on negative electrode and oxygen on positive. Lead dioxide can react chemicaly with lead substrate. Selfdischarge rises with H_2SO_4 concentration and high temperature.

CORROSION

Corrosion decreases Ah capacity and available current. It creates sediments too. Rate of corrosion is influenced by time when battery stays discharged after usage, by depth of discharge and temperature of battery during inactivity.

THERMAL EFFECTS

Batteries are dependent for it's purpose on electrochemical processes of charge and discharge. Chemical reactions inside of battery are temperature dependent. Ideal temperature for battery usage is between 15 and 25 °C. In higher temperatures batteries can provide more power at the expanse of lifetime.

THERMAL BALANCE

Rate of thermal change in time $dT / dt (K \cdot s^{-1})$ can be expressed as:

$$dT / dt = \left(dQ_g / dt - dQ_d / dt \right) / C_b \tag{1}$$

where dQ_g/dt , is heat generated in unit of time $(J \cdot s^{-1} \text{ nebo } W)$, dQ_d/dt is heat dispersed by unit of time $(J \cdot s^{-1} \text{ nebo } W)$, C_b is thermal capacity of battery materials.

Thermal capacity is defined by equation:

$$C_{b} = \sum m(i)C_{p}(i) \tag{2}$$

where m(i) is a weight of part number i, $C_p(i)$ thermal capacity of part number i $(Jg^{-1}K^{-1})$.

Battery is in stable state, when heat created is equal to heat derived $dQ_{e}/dt = dQ_{d}/dt$

When heat created rises above level of heat derived, it can lead to rising of internal temperature and battery destruction. This phenomen is called "Thermal runaway".

SOURCES OF HEAT INSIDE OF BATTERY

Thermal losses are made by current transition through internal resistance of battery during charging and discharging. This kind of heat is known as Joule heat. Therefore batteries designers focus on keeping internal resistance of battery as small as possible.

Apart from Joule heat chemical reactions occur inside of batteries where some of them can be exothermic (create heat) and some of them endothermic (absorb heat). During heating of battery the problem usually is with exothermic reactions. Thermal state of battery is dependent on surrounding environment. If batteries temperature is higher than temperature of surroundings, batteries temperature decreases, if surrounding temperature is higher, battery absorbs temperature from its surroundings.

HEAT REMOVAL

There are several ways to remove heat from battery. One of them is heat conductions through batteries parts, thermal radiation to surrounding. Most common cooling is through side walls of container.

THERMAL RUNAWAY

Thermal runaway is defined as increase of charging, or residual current by rising internal temperature. Starting residual current going through battery leads to temperature increase inside of battery, which leads to increase of internal current, which increases temperature again until temperature gets to critical level causing battery destruction.

Thermal runaway occurs in VRLA batteries. Its sources are increased internal temperature and batteries overcharge. It leads to state when heat created inside of battery rises faster, then can be drained. It can cause melting and cracking of containers. Hydrogen sulfide and sulfur dioxide can be created. [1]

THERMAL SENSOR

Thermal sensor with specific needs had to be selected. Demand was focused on:

miniature size

stability in acidic environment

high thermal sensitivity

With regards to needed paramaters, platinum resistive sensor embedded in glass mass was selected acording to DIN EN 60 751 standard by JUMO měření a regulace s.r.o. It is based on platinum spike with connections, where sensor is protected by glass tube. It is necessary that sensor is fixed and connections are protected from sulphuric acid. Connections are soldered to connections of sensor and then fixed by epoxy resin. [3]

EXPERIMENT

Experiment was realized through automated measuring device programed in VEE environment. Experiments were evaluated in MS Excel software.

Cell ws charged untill it reached 2,45 V. Current gets residual on level of 50 mA (1). If cell is still charged, current doesn't change but voltage rises to second charging level above (2,45 V). Charging reactions on positive electrode stop working, water electrolysis starts. This usualy causes thermal runaway (2). Manual impact (3).



Charging and discharging

Very steep peek is an impact of small lead sulphate layer. It's creation and destruction lasts for a few ms. All other thermal changes last longer, because it deals with greater volume of active mass (4). During discharge internal resistance rises and it causes creation of Joule heat. Small crystals of lead sulphate are created but because of high temperature by high current it melts and internal resistance drops, so does temperature (5). Charging above limit voltage of 2,45 V shows increas of temperature. This is caused by Joule heat generated by charging (6). Temperature drops caused by current decrease to residual 50 mA (7). Rising of temperature appers when cells are charged without stoping by constant current. It is caused by Joule heat and electrochemical heat of exotermic reactions (8).

CONCLUSION

Thermal effects in batteries were studied. Thermal runaway was described. Sensor for later measurements was selected and preliminary experiments were realised.

REFERENCES

- [1] D. Pavlov, B. Monahov, A. Kirchev, D. Valkovala, Thermal runaway in VRLAB Phenomena, reaction mechanisms and monitoring, Journal of Power Sources 158 (2006) 689 - 704
- [2] D. Rand, P.T. Moseley, Valve regulated lead acid batteries, ISBN: 0-4445-0746-9, 2004
- [3] Thermal sensors manufacturer, http://www.jumo.cz