Journal of Zhejiang University SCIENCE A ISSN 1673-565X (Print); ISSN 1862-1775 (Online) www.zju.edu.cn/jzus; www.springerlink.com E-mail: jzus@zju.edu.cn



Experimental research on charging characteristics of a pressure-controlled VRLA battery in high-temperature environments

Hua ZHU † , Jin-jun TAN, Zhang-lu XU, Ji-sen XU

(Institute of Thermal Science and Power Systems, Zhejiang University, Hangzhou 310027, China) [†]E-mail: zhuhua@zju.edu.cn Received Arr. 27, 2008; Revision accented Oct. 8, 2008; Grosseheeled Dec. 20, 2008

Received Apr. 27, 2008; Revision accepted Oct. 8, 2008; Crosschecked Dec. 29, 2008

Abstract: Valve-regulated-lead-acid (VRLA) battery charging performed in high-temperature environments is extremely risky under overcharge conditions, and may lead to a subsequent thermal runaway. A new pressure-controlled charging method was adopted and the charging characteristics of the pressure-controlled VRLA battery in high-temperature environments were experimentally studied. The concept was tested in a large temperature gradient to obtain more details about the effects of users' accustomed charging and discharging modes on battery capacity. The premature capacity loss (PCL) phenomenon under high temperature exposure was analyzed. The results showed that the capacity loss could be recovered by charging using a large current.

Key words: Valve-regulated-lead-acid (VRLA) battery, Pressure-controlled charging method, High-temperature environments, Charging and discharging characteristics

doi:10.1631/jzus.A0820658 Document code: A

CLC number: TK1; TK02

INTRODUCTION

Compared with traditional flooded lead-acid batteries, valve-regulated-lead-acid (VRLA) batteries have advantages of minimized water loss and hydrogen evolution, no acid spilling, minimum maintenance, etc. They are widely used in the fields of telecommunications, electric power and traffic systems. But the VRLA battery is prone to thermal runaway because of its relatively low electrolyte volume and small thermal capacity. Unlike in the traditional flooded cell, there is no bubbling to carry heat away when it is overcharged. The enhanced internal-oxygen cycle and reaction may raise the electrolyte temperature, decrease inner resistance and increase the charging current. Such a vicious circle results in thermal runaway and ultimately leads to the destruction of the cell. Berndt (1993) suggested that thermal runaway arises because heat generation has an exponential relationship with temperature but heat dissipation has a linear relationship. A VRLA battery charging in a high-temperature environment is extremely vulnerable to overcharging. The situation becomes even more serious if thermal runaway occurs.

Tenno et al.(2002) proposed a modified model for overcharging of a battery based on a previous model (Tenno et al., 2001) by developing a new formula for electrode morphology, applying a charging factor to state-of-charge, electrode porosity and acid concentration, and considering the recombination of oxygen as a mass-transport limited gas evolution process. It was accurate for the prediction of the discharge-recharge cycle including deep discharge and overcharge by experimental calibration. Gu et al.(2002) developed a three-phase, electrochemical and thermal coupled model for VRLA batteries, which was an extension of the lead-acid model of Gu et al.(1998). Their new model focused on the internal oxygen cycle and its effects on the full charge and overcharge behaviors of VRLA batteries. Culpin (2004) discovered that separator dry-out was the critical parameter of transition from normal stable

418

behavior to unstable thermal runaway. Catherino (2006) pointed out that the electrolyte distribution in the separator played an important role in thermal runaway and that a modified separator could guide the displaced electrolyte return to the cell gap efficiently and minimize thermal runaway. Hao and Zhao (2005) studied the effect of temperature on sealed lead-acid battery performance at -50~4 °C and a discharging current $0.05C_{20} \sim 2C_{20}$ A (C₂₀ means 0.05C, where C is the rated capacity of the battery at 25 °C). They found that the battery capacity was guaranteed by the amount of acid stored in porous electrodes and their nearby separators. Zhang H.L. et al.(2007) and Zhang L. et al.(2007) also studied the effect of temperature on VRLA battery capacity. Sun (2003) reviewed the causes of thermal runaway in VRLA batteries and their countermeasures. Zhou et al.(2004) indicated that insufficient control of charging and discharging of the VRLA battery was the main reason for premature capacity loss (PCL), irreversible sulfation, thermal runaway and electrolyte dry-out.

All of the abovementioned researchers tried to control the incidence of overcharging and thermal runaway of the VRLA battery using an electrical parameter. In this study, a new charging method for VRLA batteries—a pressure-controlled charging method—is proposed and adopted, which prevents the thermal runaway phenomenon effectively by cutting off the occurrence of overcharging at normal ambient temperatures. However, VRLA batteries may have to be operated in high ambient temperature environments due to geographical location, weather, usage, etc. So it is important to investigate the charging behavior of the pressure-controlled VRLA battery at high ambient temperatures with the users' accustomed charging and discharging modes.

PRESSURE-CONTROLLED CHARGING METHOD

The pressure-controlled VRLA battery (Fig.1) was proposed and patented by Zhejiang University (Xu *et al.*, 1999). The pressure-controlled switch P linked to the VRLA battery at the top via a short tube is composed of a chamber with an adjustable electrical connecting point and a metallic membrane with a signal juncture. When the VRLA battery is fully charged, its inner pressure increases to a threshold



1: power module; 2: control module; 3: voltmeter; 4: pressure gauge; 5: amperemeter; 6: VRLA battery; 7: compound pressure-controlled charger; P: pressure gauge; S: signal wire

Fig.1 Experimental setup of a pressure-controlled VRLA battery

value that activates switch P. A signal from P to the control module by wire S causes a decrease in the charging current and the cell pressure declines slowly.

EXPERIMENTAL RESULTS

Fig.1 is a sketch of the experimental setup. A 12 V 12 A h VRLA battery was tested in a DHG-9123A (made in Shanghai, China) thermostatic container at 35~55 °C. Current and voltage during the charging and discharging of the battery were measured using a JL5135 DC (made in Hangzhou, China) numerical amperemeter and a voltmeter, respectively. The pressure inside the battery was read using a pressure gauge. Copper-constantan thermocouples at the bottom of the battery were used to measure the temperature of the battery. Users' established charging and discharging methods were used in the tests. Charging of the VRLA battery was terminated after only a short period of time, when the pressure-controlled switch was activated and the battery was discharged using a fixed resistance or load. Battery performance was investigated in a large temperature gradient where charging in a high-temperature environment was followed by discharging at normal temperature.

Fig.2 shows the variation in the temperature and voltage of the tested battery during the charging process at an ambient temperature of 35 °C. The sharp turning point in the cell voltage curve in Fig.2 corresponds to the activation of the pressure-controlled switch and the reduction of the charging current by the control module. During the charging process, the battery temperature increased gradually from 33 °C to 38 °C, and then remained steady for about 1.5 h before it increased in the next step. About 4 min at 39 °C, the

pressure-controlled switch was triggered by the increasing cell pressure and the charging current was reduced by the control module. Thus it can be seen that the pressure-controlled charging method is effective for the VRLA battery. The triggering threshold pressure of the pressure-controlled switch can be adjusted to an appropriate value for use in different environments.



Fig.2 Temperature-time curve and cell voltage-time curve at 35 $^\circ \mathrm{C}$

Fig.3 shows the cell voltage curves of a VRLA battery charging at different ambient temperatures. The action of the pressure-controlled switch occurred earlier with the increase in ambient temperature. The turning point when charging at 55 °C was nearly 0.22 h ahead of that when charging at 45 °C. Also, the switch activation moment during charging at 45 °C was about 0.35 h ahead of that during charging at 35 °C. The early activation of the pressure-controlled switch indicates the increased temperature control sensitivity when a battery is charged in a high-temperature environment. This protects the battery from overcharging and reduces the possibility of thermal runaway. With the increase in ambient temperature in the charging process, the average cell voltage decreases. The average cell voltage of charging at 55 °C is lower by about 0.14 V than that at 45 °C. The average cell voltage of charging at 45 °C is 0.14 V lower than that at 35 °C.

Fig.4 shows the discharging characteristics of a VRLA battery after charging at different ambient temperatures. All the current curves declined with time when the battery was discharging under a constant resistance or load. Comparing the different

charging temperatures, the discharge capacity resulting from charging at 55 °C was about 0.6 A·h less than that at 45 °C. The discharge capacity due to charging at 45 °C was nearly 0.3 A·h less than that at 35 °C. In general, the relationship between capacity and temperature is as follows:

$$C_{t_1} = \frac{C_{t_2}}{1 + K(t_2 - t_1)},\tag{1}$$

where C_{t_1} and C_{t_2} (A·h) are the capacities of the battery in the ambient temperatures t_1 and t_2 (°C), respectively, *K* is temperature coefficient of capacity, and t_1 and t_2 (°C) are the temperatures of the electrolyte.



Fig.3 Cell voltage-time charging curves in different high-temperature environments



Fig.4 Current-time discharging curves under large temperature gradients

It can be inferred from Eq.(1) that the depth of discharge is reduced with increasing temperature if the discharge capacity is constant. Thus the battery life will be extended if it is fully charged at a high temperature (usually below 50 $^{\circ}$ C) and discharged at

normal temperature (Zhu, 2002). From Fig.4, the lifetime of the battery in the test should also have been prolonged theoretically as the depth of discharge was reduced with the increasing temperature. But unfortunately the battery suddenly failed to discharge after a series of cycles. Four possible reasons for the unexpected decay of the capacity of the battery are as follows: (a) The battery was not fully charged; (b) Positive active material (PAM) was softening and shedding; (c) Part of the battery unit was in short circuit; (d) Sulfation of electrodes took place. Case (d) can be excluded because the possibility of sulfation of electrodes occurring in such a short period of time is very low. Case (b) may occur as charging and discharging of the battery in a relatively large temperature gradient might destroy the tight combination of PAM. The softening and shedding of PAM will seriously affect the battery capacity and the life of the positive plate. The decay of the capacity is irreversible if it is caused by Case (b), (c) or (d). Only the degradation caused by Case (a) is reversible as its capacity can be recovered by charging in a large current.

The curves in Fig.5 show the discharge characteristics at normal temperatures after the 2nd and 3rd recovery charging using an applied current of $2.5C_{10}$ $(C_{10} \text{ means } 0.1C, \text{ where } C \text{ is the rated capacity of the}$ battery at 25 °C). The discharging voltage of the battery at the beginning was above 12 V, and a cell voltage-drop of 2 V (or multiples of 2 V if more than one cell was involved) did not occur instantaneously in the process of discharging, thus Case (c) can be excluded. Fig.5 shows that the capacity of the battery had effectively recovered after charging under a large current 2~4 times. So Case (a) was the main reason for the decay of capacity of the battery. The users' accustomed charging and discharging modes deepen the undercharging of the battery unit with increasing environmental temperature. The large temperature gradient could not compensate for the negative impact of undercharging, although the life of the battery could be extended by the reduction in the depth of discharge of the battery with the increasing temperature. The 3rd discharge capacity was about 0.96 A·h more than the 2nd one (Fig.5a). So the last step of charging using a small current plays an important role in the charging process. The main purposes of the last step are: (1) to supplement the loss of capacity by self-discharge, (2) to maintain the internal-oxygen



Fig.5 Current-time curves of discharge of recovery test. (a) Current-time curves of discharging after recovery charging in the current of $2.5C_{10}$; (b) Current-time curves of original and recovery states

cycle, and (3) to equalize the state of charge among battery units. Artificially reducing the time of charging when small currents are applied may cause some battery units to be undercharged frequently. So the sudden decay in the capacity cannot be prevented and the life of the battery is largely shortened in this way. Fig.5b shows that the discharge capacity of the battery after the 4th recovery charging is about 93.2% of the original capacity. The capacity of the battery can be restored by charging using a large current.

CONCLUSION

(1) The pressure-controlled method can effectively reduce overcharging and potential for thermal runaway of the VRLA battery in high-temperature environments by employing a pressure-controlled switch, resulting in a decrease in the average voltage of charging with increasing temperature.

(2) Artificially cutting down the time of charging in a small current may result in some battery units being undercharged and will cause a loss in battery capacity. Such a decay in capacity is likely when charging in a high-temperature environment.

(3) The decay in capacity owing to long-term undercharging can be largely recovered by charging in a large current $2 \sim 4$ times.

References

- Berndt, D., 1993. Maintenance Free Batteries (1st Ed.). Wiley, New York, p.306-310.
- Catherino, H.A., 2006. Complexity in battery systems: Thermal runaway in VRLA batteries. *Journal of Power Sources*, **158**(2):977-986. [doi:10.1016/j.jpowsour.2005. 11.005]
- Culpin, B., 2004. Thermal runaway in valve-regulated lead-acid cells and the effect of separator structure. *Journal of Power Sources*, **133**(1):79-86. [doi:10.1016/j. jpowsour.2003.09.078]
- Gu, W.B., Wang, C.Y., Liaw, B.Y., 1998. The use of computer simulation in the evaluation of electric vehicle batteries. *Journal of Power Sources*, **75**(1):151-161. [doi:10.1016/ S0378-7753(98)00119-0]
- Gu, W.B., Wang, G.Q., Wang, C.Y., 2002. Modeling the overcharge process of VRLA batteries. *Journal of Power Sources*, **108**(1-2):174-184. [doi:10.1016/S0378-7753(02) 00043-5]

- Hao, X., Zhao, Y.C., 2005. Effect of temperature on sealed lead-acid battery performance with absorb electrolyte. *Marine Electric & Electronic Technology*, 3:52-54 (in Chinese).
- Sun, C., 2003. A review of thermal runaway in VRLA battery and countermeasures. *Chinese LABAT Man*, 3:134-136 (in Chinese).
- Tenno, A., Tenno, R., Suntio, T., 2001. Charge-discharge behaviour of VRLA batteries: model calibration and application in state estimation and failure detection. *Journal of Power Sources*, **103**(1):42-53. [doi:10.1016/S0378-7753 (01)00830-8]
- Tenno, A., Tenno, R., Suntio, T., 2002. Evaluation of VRLA battery under overcharging: model for battery testing. *Journal of Power Sources*, **111**(1):65-82. [doi:10.1016/ S0378-7753(02)00276-8]
- Xu, J.S., Feng, X.L., Wang, J.Y., 1999. The Pressure-controlled Sealed Battery. Patent No. CN97249861.3, China.
- Zhang, H.L., Xu, J.Q., Wang, P., Bo, X., 2007. Effect of environmental temperature on VRLA battery and measures. *Telecommunications for Electric Power System*, 178:44-46 (in Chinese).
- Zhang, L., Wei, X.B., Zhang, G., 2007. Analysis of the relationship between temperature and capacity on sealed valve-regulated lead-acid battery. *Diesel Locomotives*, 403:19, 20, 26 (in Chinese).
- Zhou, Z.M., Zhou, J.H., Ji, A.H., 2004. Practical Technology of VRLA Battery. China Electrical Power Press, p.48-55 (in Chinese).
- Zhu, S.R., 2002. The Technology of Lead-acid Batteries (2nd Ed.). China Machine Press, p.78 (in Chinese).