

Noninvasive Detection of the Gases Inside the Sealed Batteries by the On-line Mass Spectrometry

Xiao Rong ZHOU, Pei Fang LIU, Lin ZHUANG, Jun Tao LU*

Department of Chemistry, Wuhan University, Wuhan 430072

Abstract: Mass spectrometer is connected through an adaptor to a sealed small battery to probe the gas phase changes inside the battery. The factors influencing the response time are analyzed with a simplified model. The feasibility of the new technique is demonstrated with a Ni-Cd battery, showing different profiles of MS intensities for O₂ and H₂. Compared with gas chromatography, this technique has the advantage of being noninvasive and should be useful for the study and diagnostic examination of small sealed batteries.

Keywords: Mass spectroscopy, gas evolution, batteries, overcharge, noninvasive.

Internal gas evolution is a commonly encountered phenomenon for batteries. In most cases gas evolution during charge, discharge or shelve, means a loss of capacity and, more seriously, may cause safety problems. It is therefore important to know the internal atmosphere in a battery and its change in different circumstances. There have been a few papers reporting the monitoring of the gas phase in batteries¹⁻⁴, mainly using chromatography. In the present communication we brief a new technique to probe the gas inside sealed batteries, *i.e.*, on-line mass spectrometry(MS).

In recent years there appeared a few papers reporting application of MS techniques to study the practical electrodes used in batteries, such as the negative and positive electrodes for lithium ion batteries⁵⁻⁸. In the present work, a whole battery instead of a single electrode was the object of test and the sealing of a battery served as the interface between the electrochemical system and mass spectrometer. The trace amount of gas leaked out through the battery sealing was used as the sample. Compared with the chromatographic approach, this new technique has the advantage of being noninvasive and more convenient for continuously monitoring the internal gases.

Experimental

A glass bottle fitting AAA size batteries was connected to the sampling valve of the mass spectrometer (ANALVA AGA-100 quadrupole mass spectrometer made in Japan) through a stainless steel adaptor, as shown in **Figure 1**. The test battery was connected

* E-mail: jtlu@whu.edu.cn

to an automatic charge/discharge device for galvanostatic charge or discharge. After warming up the mass spectrometer and evacuating the analyzer, the sampling valve was gradually opened till maximum opening to evacuate the adapter and the bottle. The battery was then subject to charge or discharge and MS spectra were recorded periodically at selected time intervals.

The response time of MS detection for the sealed battery

The influencing factors for the response time of the on-line MS detection can be analyzed based on the simplified flow path shown in **Figure 1** (lower). The gas leaks from the battery to enter the space of the glass bottle and the adaptor (called the chamber space in the text below). The flow rates through the leakage and the sampling valve (F_L and F_V) are determined by relevant resistances (R_L and R_V) and the pressure difference across the resistance ($P_3 - P_2$ and $P_2 - P_1$). Assuming the MS is able to reflect the change in the chamber space in real time, the response time of the measuring system is the response time of the chamber space to the pressure change in the battery. Based on this model, the response time of the on-line MS detection is deduced to be $\tau = R_V R_L V / (R_V + R_L) RT$, where V is the chamber space volume, R and T are the gas constant and temperature, respectively. Obviously, in order to reduce τ , one should reduce R_V , R_L and V as much as possible. This is the reason why the sampling valve should be kept fully open in the measurements.

MS detection of the gas phase change in Ni-Cd batteries

Typical results for AAA size Ni-Cd batteries are shown in **Figure 2**. Curve 1 shows the voltage change during charge and discharge. Curve 2 represents the MS intensity of O_2 which increases quickly after 1.45 V during charge and drops quickly to a low value on discharge. This is in agreement with the generally accepted oxygen cycle theory for sealed Ni-Cd batteries with the positive electrode capacity made intentionally smaller than that of the negative electrode. The displacement of the MS intensity peak from the dividing line between charge and discharge represents a delay in MS response about ten minutes in this experiment. The response time was quite long but still much shorter than the discharge or charge time, which are typically a few hours. Therefore this technique is able to reveal the main dynamic features of the changes in the gas phase inside the battery. It is possible to reduce the response time in the future by optimization.

There is a slow decrease in MS intensity for all gaseous components in the first 3 hours of charge, including O_2 , N_2 , H_2O and H_2 . This decrease may be attributed to the successive evacuation of the system as revealed by the change of analyzer pressure (curve 4). After about 3 hours of charge, all gaseous components (except O_2) showed a slow increase in MS intensity during overcharge and the increased MS intensity vanished slowly on discharge to form a hump on these curves. A similar hump can also be seen on the curve of analyzer pressure (curve 4). The hump may be attributed to the pressure

Figure 1 Connection between a battery and the MS data for the MS spectrometer(upper) and corresponding flow path(lower)

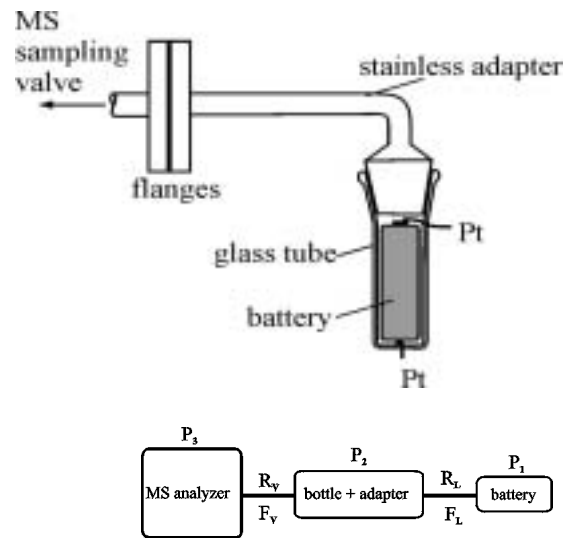
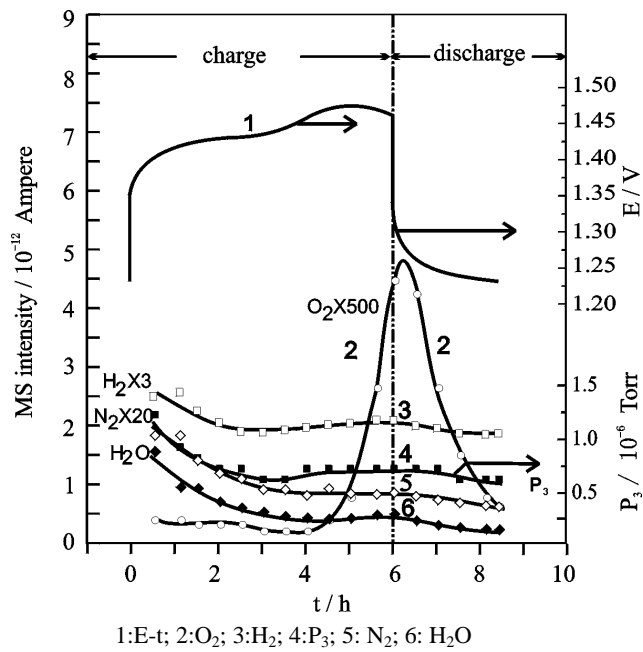


Figure 2 Charge(0.25C) and discharge(0.25C) processes of an AAA size sealed Ni-Cd battery



increase inside the battery due to battery warming which should be most severe during overcharge. The MS curves for H₂O, N₂ also showed approximately the same hump. The N₂ signal was mainly due to the air captured in battery during manufacturing. The MS curve shape for H₂ indicates that the hydrogen was mainly produced in previous overcharges and the hydrogen could stay in the battery for a quite long time because of the lack of effective mechanism of hydrogen cycle. Therefore measures should be taken to depress hydrogen evolution during charge for safety and long service life and the on-line MS appears to be a convenient technique to evaluate the situation of hydrogen evolution and diminishing for sealed batteries.

After about 8 hours of on-line MS measurement, the battery showed no detectable weight loss in experimental error, showing the noninvasive advantage. This new method is a useful tool for the study and diagnostic examination of small sealed batteries.

Acknowledgment

This work was supported by National Natural Science Foundation of China (Project No. 29833090). The authors thank Professor Chuan Sin CHA for suggesting this experiment and helpful discussions.

References

1. M. Kanda, M. Yamamoto, K. Kanno, *et al.*, *Journal of Less-Common Metals*, **1991**, 172-174, 1227.
2. T. Sakai, A. Yuasa, H. Ishikawa, *et al.*, *J. Less-Common Metal*, **1991**, 172-174, 1194.
3. S. Bruckenstein, R. R. Gadde, *J. Am. Chem. Soc.*, **1971**, 93, 793.
4. G. Diehl, U. Karst, *Anal. Bioanal. Chem.*, **2002**, 373, 390.
5. P. Novak, J. C. Panitz, F. Joho, *et al.*, *J. Power Sources*, **2000**, 90, 52.
6. M. Winter, R. Imhof, F. Joho, *et al.*, *Journal of Power Sources*, **1999**, 81-82, 818.
7. R. Imhof, P. Novak, *J. Electrochem. Soc.*, **1999**, 146, 1702.
8. M. Lanz, P. Novak, *J. Power Sources*, **2001**, 102, 277.

Received 18 June, 2003