THE GASSING BEHAVIOUR OF LEAD–ACID NEGATIVE ACTIVE MATERIAL AND DEVELOPMENT OF A QUALITY CONTROL TEST FOR LEAD OXIDE PURITY

B. CULPIN*, M. W. PILLING and F. A. FLEMING

Chloride Advanced Research, Wynne Avenue, Swinton, Manchester M27 2HB (U.K.)

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Summary

Maintenance-free (M.F.) batteries are widely applied, particularly in the areas of automotive SLI and stand-by power. The M.F. characteristics are due to low evolution of hydrogen and oxygen from the plates on open circuit and during constant potential overcharge, thus obviating the need for 'topping up'. M.F. batteries use a non-antimonial alloy, typically Pb/Ca/Sn, and care is required in the selection of lead feedstock for oxide production to ensure low levels of undesirable impurities. Feedstock lead was analysed for impurities in an attempt to define their safe limits and to see if secondary lead could be used in M.F. batteries. The large number of impurities present, however, together with uncertainties in analytical accuracy led us to a more pragmatic test which measured the gassing rate directly. This served as a rapid method for evaluating lead supplies, a suitable quality control technique for factory use, and a research tool for evaluation of individual impurities and synergistic effects.
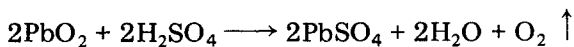
Introduction

One of the main trends in lead–acid battery design over recent years has been the introduction of low maintenance or maintenance-free (M.F.) batteries, particularly for automotive and stand-by applications. In these, regular topping up of the battery is avoided and many M.F. automotive batteries are fully sealed so that water addition is impossible. Batteries operating on the oxygen recombination principle are also entering both market areas and these batteries rely on an hermetic seal for successful operation, again making water additions impossible.

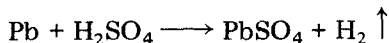Water loss in service is a result of:

(i) the chemical reaction of PbO_2 and Pb with the electrolyte, from thermodynamic considerations at the anode:

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*Author to whom all correspondence should be addressed.

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2 \uparrow$$

and at the cathode:

$$Pb + H_2SO_4 \longrightarrow PbSO_4 + H_2 \uparrow$$

(ii) the related electrochemical decomposition of water during charge and overcharge.

Assuming a constant potential charge, the rate of gas evolution, particularly hydrogen on the cathode, is largely governed by the concentration of metal ion impurities which can be plated out on the negative electrode and show a lower hydrogen overpotential than lead.

Various methods have been used to measure the effects of metallic impurities. Vinal [1] quotes results in which specific impurities were added to the electrolyte and their effects measured by the gain in weight of the negative plate. Pierson [2] similarly doped the electrolyte with known impurities but assessed the effects by measuring the total gas evolved, both oxygen and hydrogen, from the cell. More recently [3 - 6] the hydrogen evolution reaction on a plain lead surface in which the impurity of interest was added as an integral part of the alloy was investigated. Based on observations such as these, specifications for the lead used in M.F. batteries have been developed. The basis for these specifications is questionable for the following reasons:

(i) The effect of any impurity is strongly dependent on the battery component, *e.g.*, impurities in the positive active material would be expected to be more readily leached out into solution than the same impurity in the grid lead.

(ii) It is uncertain how much of each impurity will be leached out into solution and how this varies as a function of time.

(iii) The effect of any impurity could be strongly dependent on the other impurities present and on their respective concentrations. Copper and antimony have been reported to show synergism [1].

(iv) Specifications often quote values of a few parts per million (ppm) for some impurities but accurate analysis of these low levels is difficult.

A range of analytical results on primary and secondary lead and resultant oxide has highlighted some of the problems and led us to develop a simple gassing test which measures the combined effect of the impurities on the hydrogen evolution rate.

Experimental

Samples of lead feedstock and the resultant oxide were analysed for impurities. Samples were analysed under contract using atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), inductively coupled plasma (ICP), and emission spectroscopy. Two sources of lead were used, primary lead, chosen because of its high degree of purity, and secondary lead as a source with higher expected levels of impurities.

Linear sweep voltammetry (LSV) was carried out using a single compartment, beaker-type cell which contained the working electrode and a pure lead sheet (BDH AnalaR) counter electrode. The working electrode was a small section of negative plate, dimensions 2×3 cm, containing approximately 5 g of negative active material; the electrolyte was 1.280 S.G. AnalaR sulphuric acid, and the reference electrode was $Hg/Hg_2SO_4/H_2SO_4$ 1.280 S.G. The working electrode was potentiostatically controlled and the LSV traces were recorded at a sweep rate of 0.5 mV s^{-1}.

Gassing rates for periods of up to 70 days were measured by collecting the evolved hydrogen from a known weight (7.6 g) of negative active material (at 20 °C) in an upturned burette, using a filter funnel to direct the gas into the burette. A large excess of electrolyte was used to ensure a constant composition during the experiment.

These experiments led to the development of a gassing test method using the gas collector shown in Fig. 1. This was filled with 90 cm^3 of 1.280 S.G. AnalaR sulphuric acid and held at 40 °C. 5 g of negative active material, washed and vacuum dried, was introduced into the main tube. After allowing 5 min for gas evolution to subside (due to trapped air and carbonate), the tube was inverted to remove all gas and gas collection was started. The quantity of hydrogen evolved was monitored from the length of the gas space in the 5 mm dia. tube. Each tube was calibrated prior to use. It was found that for comparative purposes, the gas evolved over a 20 h period was a convenient measure of the active material gassing rate. Calculation shows that during this period the change of acid concentration due to reaction was negligible (<0.1%).
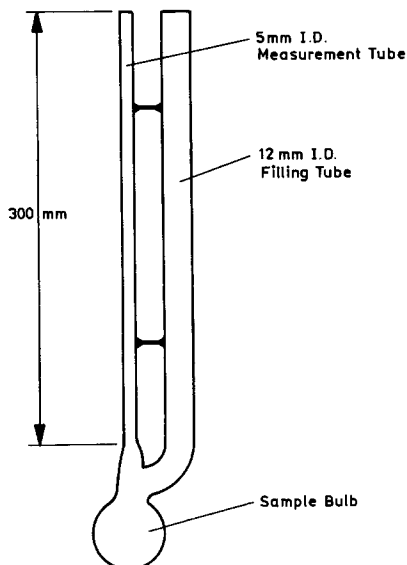

Fig. 1. Gas collector. 300 mm; 5 mm i.d. measurement tube; 12 mm i.d. filling tube; sample bulb.

Results

Trace analysis

A summary of the main analytical results is shown in Table 1. The main purpose of the analysis at this stage was to identify any major differences between impurity levels in the two types of lead feedstock, primary and secondary, but this, it generally failed to do. AAS (company 2), however, did show small amounts of Cu in the secondary lead, while Sb levels were higher in the secondary than in the primary lead, which would be expected — although the value of 32 ppm Sb for primary lead was also high. The high level of Bi in secondary lead (90 ppm) is in agreement with that found by emission spectroscopy. The AAS analysis from company 1 on the leady oxide failed to detect any impurity in primary or secondary based oxide.

Emission spectroscopy gave Bi and Cu levels similar to that found by AAS, but also lower Sb levels and much higher Ag levels.

ICP results (not listed in Table 1) failed to detect any impurity except for small traces of Ni and Fe.

XRF appears unsuitable for this type of analysis, the detection limits being too high. The quoted values of 200 ppm Ni and 100 ppm Ca are difficult to explain as is the 1% Ca and Si levels on the oxide. This method failed to detect any differences between primary and secondary lead.

The main differences detected were between the different instrumental methods. Only AAS and emission spectroscopy detected differences between primary and secondary lead and these were not consistent between themselves.

Linear sweep voltammetry

Figure 2 shows a typical sweep for negative active material obtained from primary and secondary lead oxide. The flat portion of the curve, up to 1.2 V, is a 'charging current', a residual current from the normal reduction of $PbSO_4$ to spongy lead. For a freshly-formed electrode, particularly one that has been partially oxidised or sulphated due to poor drying, this residual current can be very large — up to 50 mA for the electrode size used in this work. Potentiostatting the electrode at -1.4 V overnight reduces this current to 1 - 2 mA, enabling it to be separated from the hydrogen evolution current, which is represented by the Tafel slopes from -1.2 V upwards. These slopes readily show the effects of impurities, the gassing rate for the secondary lead-based oxide being typically two orders of magnitude higher than that for the primary. The effect of impurities is to reduce the hydrogen evolution potential, the example in Fig. 2, by 88 mV, the slopes themselves being parallel. It is perhaps unwise to attempt to interpret these curves in any detail in terms of the a and b constants of the Tafel equation because of the non-ideal nature of the electrode under investigation.

TABLE 1

Analysis of results (all figures ppm unless stated, ND = not detected)

| Element	Feedstock lead Primary AAS Company 2	Feedstock lead Primary Emission spec.	Feedstock lead Primary XRF Company 1	Feedstock lead Secondary AAS Company 2	Feedstock lead Secondary Emission spec.	Feedstock lead Secondary XRF Company 1	PbO powder AAS Company 1 Primary	PbO powder AAS Company 1 Secondary	PbO powder XRF Company 2 Primary	PbO powder XRF Company 2 Secondary
Cu	<0.04	1	<100	4	4	<100	<2	<2	20	20
Sb	32	<10	<800	60	<10	<800	<2	<2	ND	ND
Ag	0.8	9	<600	1.4	15	<600	—	—	ND	ND
Ni	—	1	200	—	3	200	<1	<1	ND	ND
Cd	—	—	<700	—	—	<700	<1	<1	ND	ND
As	—	1	<200	—	1	<200	<10	<10	ND	ND
Ca	—	<10	100	—	<10	100	—	—	~1%	~1%
Zn	—	<10	<100	—	<10	<100	—	—	ND	ND
Bi	8	<10	<900	90	90	<900	—	—	ND	ND
S	—	—	<900	—	30	<900	—	—	ND	ND
Se	<6	1	<300	<6	—	<300	<10	<10	ND	ND
Fe	—	<10	<100	—	<10	<100	<5	<5	ND	ND
Mn	—	—	<100	—	—	<100	<1	<1	ND	ND
Te	—	<10	<100	—	<10	<100	<2	<2	ND	ND
Co	—	—	<100	—	—	<100	<1	<1	ND	ND
Cr	—	—	<100	—	—	<100	<1	<1	ND	ND
Others	Pd <0.1 Sn <0.5 Pt <1 V <2	Sn <10		Pd <0.1 Sn <0.5 Pt <1 V <2	Sn <10				Si 1% Ti 100 K 100 Al 100	Si 1% Ti 100 K 100 Al 100
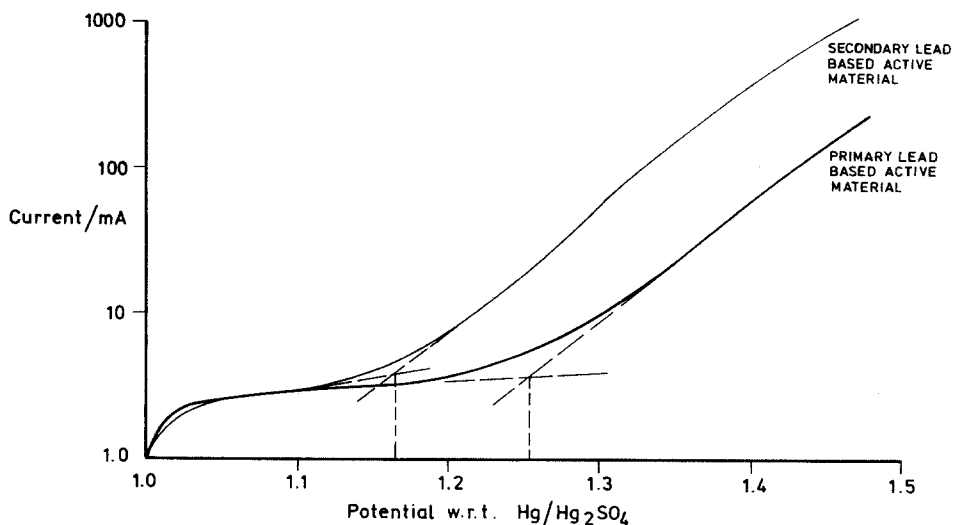
Fig. 2. Tafel plots on negative active material.

Gassing tests

Gassing test results using upturned burettes for hydrogen collection are shown in Fig. 3. The differences between primary and secondary lead are readily seen, with the latter gassing at 6 times the rate of the former. For both primary and secondary lead the gassing rate decreased as a function of time. This was thought to be due to lead sulphate passivating the lead surface. With a sample weight of 7.6 g, however, the maximum volume collected, 36 cm^3 after 70 days, corresponds to a reaction of 4% of the total lead present. It is difficult to believe that the observed reduction in gassing rate could result from a 4% decrease in Pb active material. The primary lead, which gassed at a much lower rate, also showed the same effect. It seems more likely that the lead sulphate preferentially passivates the active sites for hydrogen evolution, these sites being associated with the impurity metals responsible for increased hydrogen generation.

The gassing tests showed a major difference between primary and secondary lead, and this was confirmed using the gas collector shown in Fig. 1. The results in Fig. 4 are expressed as a bar chart, summarising a total of 50 lead samples, 25 each from primary and secondary lead. They illustrate not only the increased gassing from secondary lead active material but also the much wider spread of results. This would be expected due to the poorer control on impurity levels and variation in impurity metals. There is some overlap in distribution, an indication that secondary lead can have a similar gassing performance to primary lead-based active material.

The effect of specific impurities can be evaluated with this apparatus. One approach is to dope the electrolyte used for the gassing test, and some results using this technique are shown in Fig. 5. In each test the lead active material used was from primary lead, and in AnalaR sulphuric acid gave a
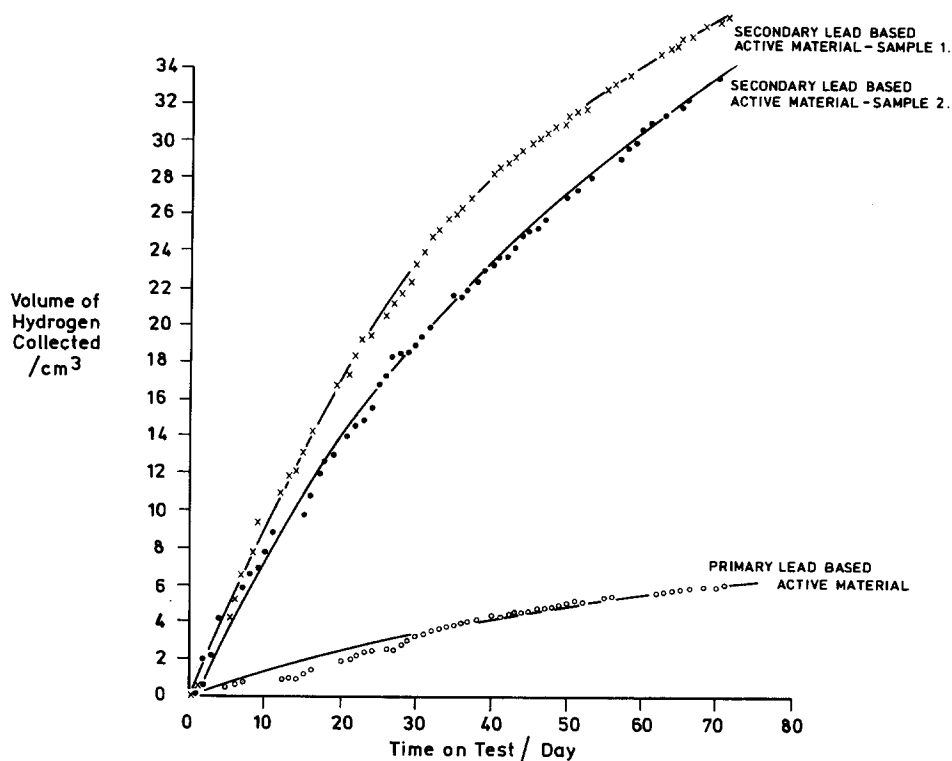
Fig. 3. Hydrogen generation as a function of time.

gassing rate of 0.1 cm^3 per 20 h period. The impurities were Spectrosol A.A standards (potassium antimony tartrate, copper nitrate, tellurium fluoride). It was assumed that the anion in each case had a negligible affect on the gassing behaviour. The effect of the antimony content on the gassing rate is readily seen, but the suggested synergism of Sb and Cu [1] is not evident. Tellurium is a particular problem with some secondary lead supplies, and the effect of doping the electrolyte is shown in Fig. 6. The two sample sizes show an approximate doubling of the gassing rate from a 10 g sample of active material as from a 5 g sample (as might be expected).

A further approach is to form the negative plates in an electrolyte containing the impurity. This is illustrated in Fig. 7 for low-gassing active material formed in electrolyte containing 5 and 10 ppm Sb. The equivalent data for similar active material, with antimony at the same levels, added to the test electrolyte is also shown in Fig. 7.

The effect of Sb is to increase the gassing rate but the affect is more pronounced when it is added to the test electrolyte (by a factor of about 3). As the ratio of Pb to solution was roughly the same in each case, the total Sb impurity present on the lead was similar. It is concluded that the Sb present in the formation electrolyte is largely trapped in the active material during the formation process, and consequently is not as accessible to the electrolyte during the gassing test.
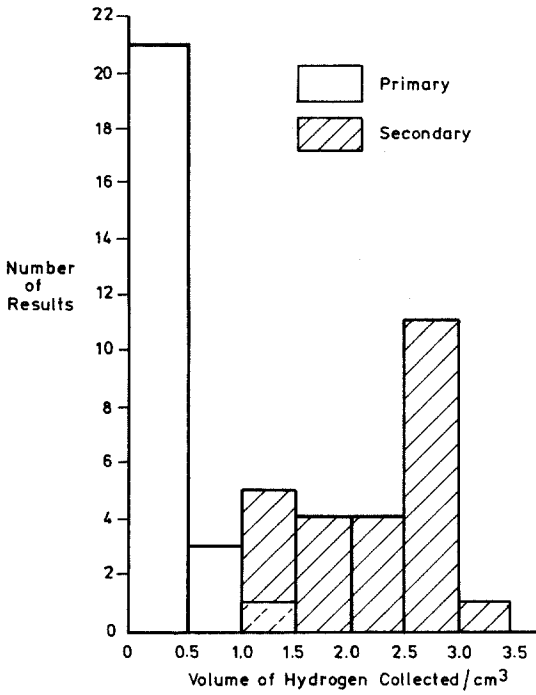
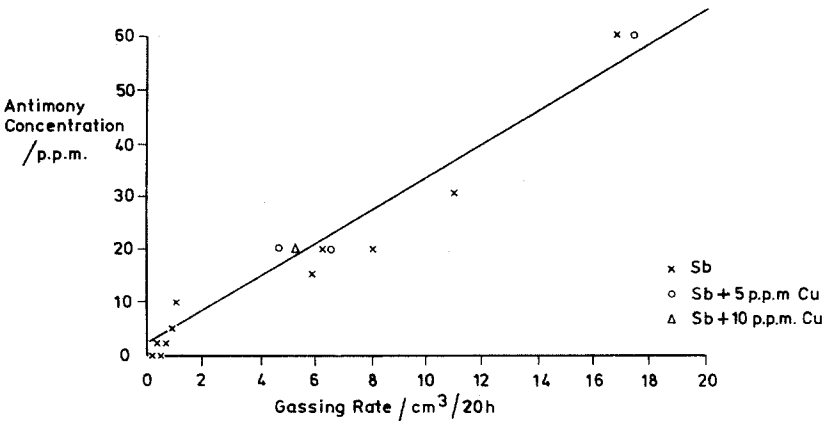Fig. 4. Gassing test — comparison of primary and secondary lead based active material.

Fig. 5. Effect of antimony on gassing rate. ×, Sb; ○, Sb + 5 ppm Cu; △, Sb + 10 ppm Cu.

Discussion

The analytical results from the impurity analysis on feedstock lead and resultant oxide were disappointing in that the correlation of results from different analytical methods/sources was difficult. Emission spectroscopy and
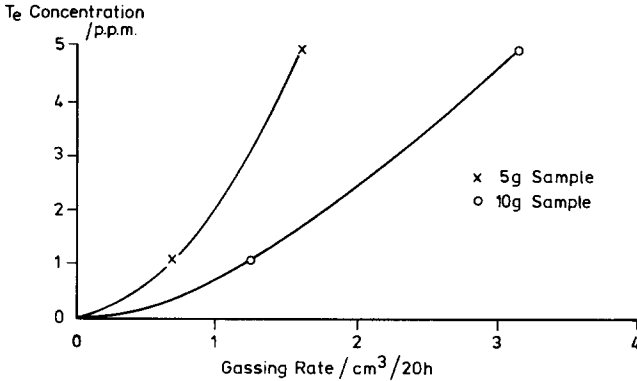
Fig. 6. Effect of tellurium on gassing rate. ×, 5 g sample; ○, 10 g sample.
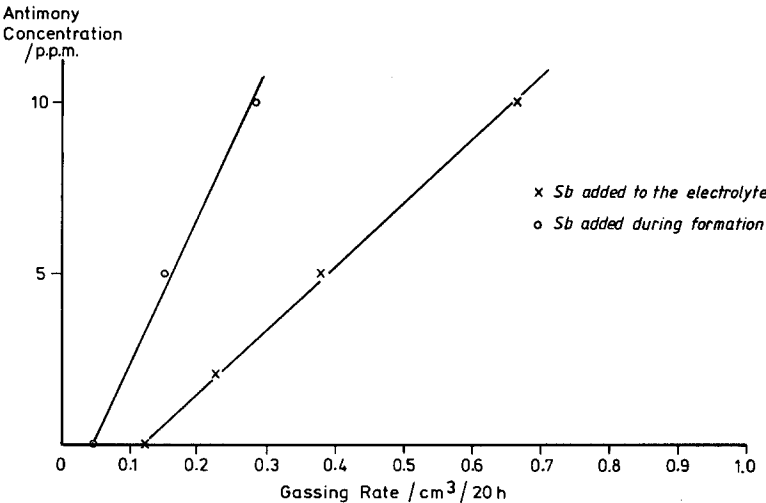

Fig. 7. Effect of antimony in formation electrolyte.

AAS appeared to be the most reliable methods although emission spectro-scopy can only be used on metallic samples. With further effort it is possible that the other methods tried would yield better results. Two analytical tech-niques which could be useful for trace analysis are ion chromatography and polarography [7, 8]. Ion chromatography looks particularly attractive as a rapid method of impurity determination and could prove to be a useful tool for quality control.

Whichever analytical technique is used, however, the problem of equat-ing impurity levels with effects on batteries remains. The gassing test devel-oped here offers a rapid and cheap route to quantifying the total affect of the impurities. For instance, the difference between active material based on primary and secondary lead is graphically illustrated in Fig. 5 (a difference not found by analysis), and offers a ready technique for evaluation of lead supplies. This technique is now in use in some of our operating companies

for quality control. By sampling the active material from formed batteries on a regular basis, any sudden increase in gassing rate can be pinpointed, and the same test can be used to identify the cause, for example, changes of lead or acid supply, contaminated battery boxes and separators.

The gassing test can be used to determine the effects of specific impurities. Results are shown in Figs. 5 - 7, but these results also illustrate that care is required in choosing how the impurity is to be added to the system. Adding the impurity ion to the gassing test electrolyte gives a gassing rate 10 times that of when the impurity is added to the formation electrolyte. Consequently it is difficult to specify the levels of impurity that can be tolerated in a battery system, as the level depends strongly on how accessible the impurity is to the electrolyte. One would expect, for instance, that an impurity in the electrolyte would have a greater affect on gassing than the same level in the oxide as it is more accessible. By carrying out the gassing test using acid and active material from a battery one has a quantitative test for the total affect of the available impurities in the system. As such, it must be considered as a valuable tool in production quality control.

Conclusions

Although it is conventional in the industry to use analytical techniques such as emission spectroscopy and atomic absorption spectroscopy to analyse for impurity levels in lead supplies, it was observed that different analytical techniques gave widely different results. In particular, the analytical results could not clearly differentiate between primary and secondary lead. The gassing test developed measured directly the affect which impurities had on the rate of hydrogen production on the lead active material of the negative plate, and proved a simple and cheap method of quantifying the purity of lead supplies. By using the test with active material and acid from the same battery a quantitative measure of the battery gassing rate can readily be obtained — an important criterion for maintenance free batteries.

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