Short Communication

Thin layer activation studies of material migration during the operation of lead/acid cells

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Abstract

A thin layer activation technique was used to study the migration of material during the operation of a lead/acid cell. In theory it would be possible to observe migration of either lead or antimony. In practice only antimony was seen to move to any significant degree. The method provides a means of monitoring the migration of antimony in a quantitative fashion, without destroying the plates.

Introduction

The choice of the alloy used in the fabrication of grids for the positive plate exercises a strong influence on the performance characteristics of lead/acid batteries. In the past alloys containing a large proportion of antimony were found to give good electrochemical properties but were prone to gassing and water-loss [1]. This problem is believed to be due to leaching of antimony from the positive plate and migration to the negative where, forming a couple with the spongy lead active mass, it lowered the hydrogen overvoltage [2].

Methods of monitoring irreversible transfer of material away from either of the active masses of the cell represent a valuable means of studying degradation mechanisms. In this short paper we illlustrate the utility of the thin layer activation (TLA) technique for such investigations.

Experimental

Two formed tubular positive plates based on PbCa (0.1%) and PbSb (10%) alloy grids were irradiated using a deuteron beam in the Harwell Tandem Generator. A small circular area, 2 mm in diameter, covering an interface of the grid and the lead oxide was activated. The reactions which produced radioactive isotopes are listed in Table 1.

The antimony content was 10% in the PbSb alloy. Tin was also present in the PbCa alloys at a level of up to 0.1%, but did not give rise to any appreciable isotopes. No measurable isotopes arise from the irradiation of calcium with deuterons.

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TABLE 1

Reactions to produce radioactive isotopes

Original nucleus	Reaction (in, out)	Final nucleus	Half-life (days)
^{206}Pb	(d, 2n)	^{206}Bi	6.2
^{121}Sb	(d, 2n)	^{121}Te	17.0
^{121}Sb	(d, p)	^{122}Sb	2.7

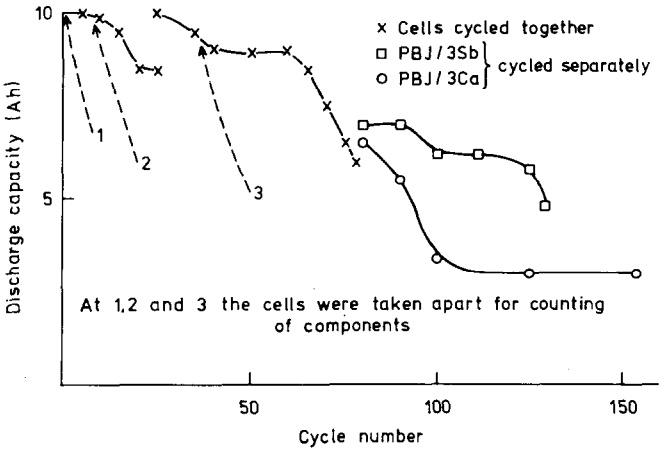

Fig. 1. Discharge capacity vs. cycle number for the cells PBJ/3Ca and PBJ/3Sb used in thin layer activation experiments. Initially the cells were cycled together and the capacity plotted is that of the cell PBJ/3Ca, with the lead/calcium positive grid. Later (on the right of the Fig.) their performance was monitored separately.

^{206}Bi and ^{122}Sb were present in a surface layer 100 μm in depth and the concentration was highest below the surface. ^{121}Te was present to a total depth of 50 μm and the greatest concentration was at the surface.

The plates were allowed to stand for 2 days in order to allow some short lived isotopes to decay.

The activity from the plates was then counted, using a germanium/lithium γ-ray spectrometer, in order to establish the initial activity of the bismuth, antimony and tellurium isotopes. They were then assembled into cells with a capacity of about 10 A h and deep discharge/charge cycled at 1 A. Figure 1 shows a plot of discharge capacity versus cycle number for the lead/calcium and lead/antimony cells denominated PBJ/3Ca and PBJ/3Sb, respectively. During the TLA experiment the cells were cycled together as a battery and the capacity recorded was that of the cell PBJ/3Ca, with the lead/calcium positive grid. The early fall in capacity and recovery at cycle 25 is an artefact that is not understood.

The cells were taken apart after 1, 9 and 37 cycles (marked 1, 2 and 3 on Fig. 1) and the activity present in the cell components was monitored so that any movement of material within the cells could be established. The counting results are shown in Table 2. Half-life corrections have been applied in order to allow for predicted decay of the radioactivity. Results obtained from measurements of three characteristic γ energy emissions from ^{206}Bi are shown.

TABLE 2

Count rates (cps: counts per second) obtained from isotopes in various cell components at intervals during 37 charge/discharge cycles

Cell	Isotope	E_γ (characteristic γ energy in keV)	Initial activity (cps)	Activity after 2.05 days 1 cycle (cps)		Activity after 12.04 days 9 cycles (cps)			Activity after 43 days 37 cycles (cps)		
				+Plate	Acid	+Plate	Acid	−Plate	+Plate	Acid	−Plate
PBJ/3Ca	^{206}Bi	803	10.23	9.91	0.0024	10.02	0.0021		8.1		
	(from Pb)	881	6.19	6.15	0.0018	6.21	0.0015		5.4		
		895	1.44	1.44	0.0003	1.45	0.0003		1.6		
PBJ/3Sb	^{206}Bi	803	13.67	13.30	0.012	13.11	0.0018		10.5	0.01	
	(from Pb)	881	8.21	8.24	0.009	8.00	0.009		6.0	0.009	
		895	1.90	1.76	0.03	1.83	0.003		2.0	0.003	
	^{122}Sb	566	8.59	8.49	0.027	9.5	0.018				
	(from Sb)										
	^{121}Te	574	3.56	3.41	0.024	3.8	0.021	0.32	5.2	0.036	0.90
	(from Sb)										

Results and discussion

No movement of irradiated material occurred from the positive plate of the cell PBJ/3Ca with the lead/calcium positive grid, apart from approximately 0.02% of the bismuth isotope arising from the lead into the electrolyte. This occurred before the end of the first cycle and it is likely that this was due to loose material being washed from the surface of the plate.

A different result was obtained in cell PBJ/3Sb with the lead/antimony positive grid. Very little movement of the ^{206}Bi arising from the lead was noticed but after 9 cycles (12 days) a ^{121}Te count was obtained from the negative plates. This indicated a level of about 10% of the initial activity on the activated spot. After 37 cycles (43 days) this had risen to between 20 and 30%. The results in Table 2 might be explained as follows. An isomer of ^{121}Te is present in small proportions. This affects the accuracy of the half-life calculations and, together with the low count rate obtained from ^{121}Te after 43 days, may account for the anomalously high count rate obtained from the PbSb positive plate after 37 cycles. However, the ^{121}Te count rate obtained from the negative plate after 43 days appears to be sensibly related to that after 10 days if steady transfer of this isotope with the parent Sb occurs from the positive grid. The absence of ^{122}Sb may be accounted for because its short half-life will have led to substantial decay by the time the negative plates were first counted. It might also be explained if transfer of Sb to the negative plates occurs only from the surface of the positive grid where the ^{121}Te is the predominant isotope.

In conclusion it seems that the only loss of material from the positive grids occurs with the transfer of antimony to the negative plates. This is a well- known phenomenon, but the effect may now be semi-quantified without destroying the plates for chemical analysis. During the first 40 or so cycles the transfer occurs to the extent of 30% of the antimony present in a 50 μm surface layer.

Acknowledgements

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References

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