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THE EFFECT OF WATER ON INCINERATED LITHIUM–SULFUR DIOXIDE BATTERIES

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Summary

Incinerated lithium batteries were found to release enough gases upon the addition of water to account for all of the lithium of the anode and part of the aluminium used in the cathode collector, *i.e.*, most of the lithium was not released from the cells upon incineration. The major gas released was found to be acetylene indicating that a portion of the lithium had reacted with carbon from the cathode and formed lithium carbide.

Introduction

What happens to the lithium metal of an electrochemical cell involved in a fire ? We have often measured temperatures as high as 1090 °C in our firebox using JP-5 as a fuel. At these temperatures lithium metal has a reported vapor pressure of 100 Torr [1] and could consequently be expected to rapidly escape from the cell. The results from this study indicate that this is not the case since the lithium reacts with cell components forming water reactive materials. In addition, the battery vents appear to be plugged with the products formed from the reactions of lithium with oxygen and nitrogen, so that lithium is often sealed inside cells that have previously vented their more volatile components.

Experimental

We measured the volume and nature of the gases released from water-soaked Duracell L0-26SH and L0-30SH cells that had been incinerated for periods of 30 - 60 min at firebox temperatures averaging 1000 °C. Both propane gas and JP-5 were used as sources of fuel to heat the firebox. Water was used to quickly cool the firebox at the conclusion of a burn. The

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batteries were placed in plastic bags for storage on the following day.

Just prior to testing, one end of each cell was cut off with a tubing cutter. Up to 3% of the cells showed evidence of air-reactive, glowing granules at this point. Each cell was then placed into an air-tight container and sufficient water was slowly added so as to allow complete reaction. The volumes of gases released were measured by a series of inverted cylinders filled with water. The pressures of these volumes were corrected for the height of water remaining in the cylinders. The volume was converted to the standard temperature and pressure (STP) of one atmosphere at 0 °C. Corrections were not made for the amount of gases dissolved in the water, so the resulting volumes represent minimum values. For ease of analysis, the apparatus was often preflushed with helium prior to the addition of water. The nominal weight of the incinerated L0-26SH cells was 47 g and that of the L0-30SH cells was 37 g. Some of these cells already had large holes in their sides and most of their "vents" appeared to have resealed (by products of air-reactive lithium vapor?).

Figure 1 shows the volume of gases measured from the L0-26SH cells. The smaller L0-30SH cells produced proportionately smaller volumes. We have analyzed the gases evolved from the reaction of water with the contents of 25 Duracell L0-26SH and L0-30SH cells. The results of the tests using gas chromatography (GC) are shown in Table 1. We detected primarily acetylene,

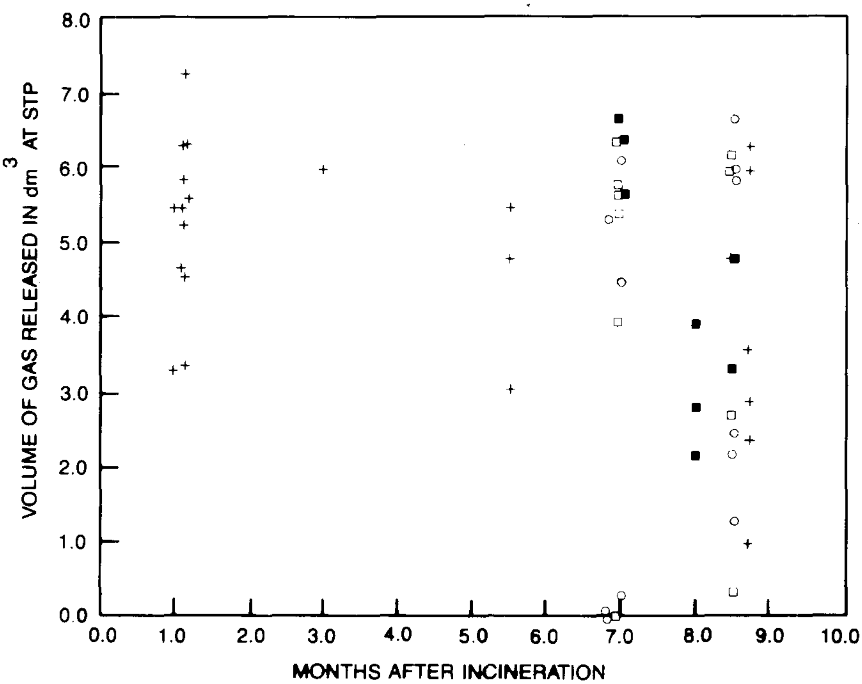

Fig. 1. Volume of gas released from water-soaked incinerated Duracell L0-26SH cells after storage for various periods of time. Different symbols indicate different burns.

TABLE 1

Gas analysis, weight, and volume measurements

Test no.	Date tested	Burn no.	Batt. wt. (g)	$Vol._{STP}$ (l)[a]	Percentage measured by GC: O_2 (%)	N_2 (%)	H_2 (%)	C_2H_2 (%)	CH_4 (%)	O_2/N_2	H_2/C_2H_2	$CH_4/H_2 + C_2H_2$
8	6/12/85	6	46.0	4.52	7.30	25.80	8.20	50.20	...[b]	0.2829	0.1633	0.0000
13	6/14/85	6	47.5	5.60	6.00	21.30	10.90	42.90	...[b]	0.2817	0.2541	0.0000
22	10/15/85	6	38.5	1.73[c]	4.97	18.20	3.92	26.55	1.13	0.2731	0.1476	0.0371
25	10/15/85	6	47.5	4.78	3.06	11.40	11.01	36.02	6.55	0.2684	0.3057	0.1393
27	10/16/85	6	48.0	3.03	4.58	17.08	10.31	28.67	6.53	0.2681	0.3596	0.1675
30	12/10/85	7	47.5	5.77	6.60	23.80	13.30	33.70	5.20	0.2773	0.3947	0.1106
39[d]	12/12/85	7	48.5	5.64	17.20	65.20	0.70	1.60	0.70	0.2638	0.4375	0.3043
42	12/13/85	8	51.0	5.27	6.40	22.90	10.60	45.60	5.70	0.2795	0.2325	0.1014
48	12/16/85	8	37.5	0.93[c]	5.10	18.20	11.10	30.40	5.50	0.2802	0.3651	0.1325
51[d]	12/19/85	8	48.5	6.08	18.10	69.60	6.80	4.00	1.60	0.2601	1.7000	0.1481
54	12/19/85	9	47.0	6.76	5.30	19.00	13.40	39.50	6.00	0.2789	0.3392	0.1134
59	1/16/86	9	37.0	3.00[c]	11.70	43.20	7.90	29.80	3.30	0.2708	0.2651	0.0875
62	1/16/86	9	45.5	2.80	11.30	41.60	7.90	28.10	3.70	0.2716	0.2811	0.1028
65	1/27/86	6	49.0	5.98	6.60	24.00	9.00	23.40	4.30	0.2750	0.3846	0.1327
68	1/27/86	6	47.5	0.98	15.60	57.60	2.10	8.40	1.20	0.2708	0.2500	0.1143
73	1/28/86	6	36.0	1.78[c]	12.60	45.00	9.70	10.90	1.40	0.2800	0.8899	0.0680
79	1/30/86	7	37.5	2.10[c]	12.80	47.20	2.60	26.20	2.40	0.2712	0.0992	0.0833
83	1/31/86	7	48.0	6.62	6.70	24.50	11.50	29.40	6.00	0.2735	0.3912	0.1467
86	2/ 3/86	7	50.0	2.18	11.80	43.60	5.80	14.80	7.40	0.2706	0.3919	0.3592
89	2/ 5/86	8	51.5	2.07	14.00	52.40	8.40	14.20	1.90	0.2672	0.5915	0.0841
91	2/ 6/86	8	50.0	2.70	12.80	45.90	11.40	10.20	6.50	0.2789	1.1176	0.3009
95	2/ 7/86	8	37.0	2.54[c]	10.40	36.50	10.40	21.40	1.80	0.2849	0.4860	0.0566
96	2/ 7/86	9	38.5	0.56[c]	16.00	58.90	3.30	0.07	1.10	0.2716	4.7143	0.2750
97	2/ 7/86	9	49.0	3.33	8.60	30.80	13.20	18.40	6.70	0.2792	0.7174	0.2120
98	2/ 7/86	9	48.0	4.80	7.20	26.50	12.40	32.40	8.80	0.2717	0.3827	0.1964

[a]Volume standard temperature pressure. [b]CH_4 was not tested for. [c]L0-30SH cell. [d]Helium not used.

hydrogen, and methane. Infrared spectroscopy, mass spectroscopy, and gas chromatography techniques were used. Using GC, the ratios of the amounts of hydrogen divided by the acetylene varied from 0.1 to 4.7 with an average ratio of 0.6. The ratio of methane to total acetylene and hydrogen varied from 0.04 to 0.4 with an average value of 0.15.

Discussion

Since acetylene can be generated from lithium carbide, and methane from aluminum carbide [2], the following reactions are suggested as having occurred inside the lithium–sulfur dioxide battery during incineration:

$$2Li + 2C \longrightarrow Li_2C_2 \quad (1)$$

$$4Al + 3C \longrightarrow Al_4C_3 \quad (2)$$

and when soaked with water:

$$Li_2C_2 + 2H_2O \longrightarrow C_2H_2 + 2LiOH \quad (3)$$

$$2Li + 2H_2O \longrightarrow H_2 + 2LiOH \quad (4)$$

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3 \quad (5)$$

Since two moles of lithium are required to produce one mole of either acetylene or hydrogen, six dm^3 of hydrogen and acetylene gas at STP would be equivalent to 3.7 g of lithium, very close to the 3.5 g indicated as being present in the anode of an L0-26SH cell by Duracell [3].

Conclusions

In conclusion, almost all of the lithium of the anode can remain inside an incinerated cell, primarily in the form of both lithium and lithium carbide formed through the reaction of metallic lithium with the carbon of the current collector. More gas from water reactive chemicals is released than can be accounted for by just the lithium used as the anode. Since methane is also found in appreciable amounts, it is suggestive that this gas comes from a water-reactive aluminum compound such as aluminum carbide. The water reactive materials inside an incinerated battery cell are stable for months with a small decrease in reactivity with increased time. This decreased reactivity is no doubt due to the reaction of the cell contents with moisture from the air; cells showing no water-reactive materials were found to be much heavier than the others. Incinerated L0-26SH cells that did not release gas upon the addition of water usually weighed around 60 g as opposed to the usual 46 - 48 grams.

We feel that these results are of importance to anyone considering using incineration as a means of disposal of lithium–sulfur dioxide batteries, because the slow introduction of water into incinerated cells would, in turn, release large quantities of flammable and explosive gases. Another area where these findings would be of value is in the extinguishment of fires where lithium–sulfur dioxide batteries are present. If most of the initial lithium metal can be accounted for within the cell, then the amount that escapes the cell in a fire should be minimal. We have applied Halon 1211, AFFF, water, and carbon dioxide to fires containing Duracell L0-26SH and L0-30SH lithium–sulfur dioxide cells and did not observe anything that could be attributed to a reaction of the fire extinguishment agent with the lithium of the cells.

Acknowledgements

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