

CHEMICAL ANALYSIS OF CHARGED Li-SO₂ CELLS

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Summary

The origin of hazardous behaviour of Li-SO₂ cells is examined in both operational and chemical terms. The effect of charging was examined and determined to require extreme caution.

1. Introduction

For some time the U.S. Navy has been concerned about the hazards associated with charging of lithium/sulfur dioxide cells. This concern is based on earlier reports and exploratory investigations, both of which indicated that charging of these cells can result in explosion. The U.S. Navy decided to examine the charging of these cells in greater detail and initiated a joint program with the Jet Propulsion Laboratory.

The initial focus of this program was to confirm that charging can result in explosions. The results of this initial effort clearly demonstrated that cells do, indeed, explode on charge and that charging does, indeed, constitute a real and severe safety problem. These conclusions were based on numerous experimentally demonstrated explosions of sonobuoy cells that had been partially discharged and stored prior to charge at high rates [1, 2].

Subsequently this program focused on determination of the causes of the explosions. First we needed to determine if the explosions were influenced by the type and size of cell and also its operating conditions. Second we needed to determine the most likely chemical processes that were involved.

The results of investigations dealing with the impact of cell type and size, as well as charge conditions, on the explosions, were reported earlier [3], and it was shown that the occurrence of explosions is rate-dependent and appears to be generic to all lithium/sulfur dioxide cells.

The present paper describes results of work to identify the chemical reactions involved.

2. Experimental

Two types of cells were employed in this investigation. The first consisted of the commercial, spiral wound, high rate cells described previously [1, 2]. The second was a laboratory type cell installed in a glass assembly. The analytical methods were the same for both types.

The commercial cells were Duracell type LO3OSH of cylindrical configuration containing spiral wound electrodes. The cells were hermetically sealed in steel cans, and were carbon limited in design; their rated capacity was 4.2 A h at the $C/2$ discharge rate. Measured capacity was near 7 A h at the $C/30$ discharge rate.

The lab. cells consisted of small, parallel plate electrodes immersed in a commercial SO_2 solvent/electrolyte mix. These components were housed in sealed, laboratory-glass hardware. The electrode assembly consisted of two outer lithium electrodes sandwiching one inner-carbon electrode. Lengths, widths, and thicknesses of the two lithium electrodes were 0.5 in., 0.5 in., and 0.018 in., respectively. The corresponding dimensions of the carbon electrode were 0.5 in., 0.5 in., and 0.033 in. The relative sizes of the two electrodes were selected such that the cells would be carbon limited, in a manner similar to the commercial cells, and capacities were 100 mA h. The solvent/electrolyte contained 7% lithium bromide, 23% acetonitrile, and 70% sulfur dioxide by weight.

Both the laboratory and the commercial cells were operated in a similar manner in this investigation. The operation typically consisted of first discharging the cells by 20%, letting them stand, and then charging. Operating current densities were the same for both types (Table 1). The cells were disassembled in the as-received, discharged, and charged conditions.

The lab. cells permitted observations not possible with the commercial cells. With the glass hardware it was possible to observe the electrodes and color changes in the solution.

TABLE 1

Experimental conditions for cell tests

Analyzed electrodes from lab. and commercial cells in 3 states:

- Undischarged
- Discharged 20%
- Discharged 20% and then charged

Conditions for discharge/charge:

<i>Parameter</i>	<i>Lab. cell</i>	<i>Commercial cell</i>
Discharge current (mA)	10	66
Discharge duration (h)	2	24
Discharge output	20 mA h (20% DOD)	1.6 A h (22% DOD)
Charge current	100 mA (20 mA cm ⁻²)	10 A (20 mA cm ⁻²)
Charge duration (min)	8 - 15	8 - 15

Disassembly of the commercial cells in the charged condition is a potentially hazardous operation. For this reason, the procedures given below were devised and used in the disassembly of the cells. The operations should only be undertaken where proper facilities exist, because the Li-SO₂ cells may detonate during the process. It is important that each new or modified type of cell be X-rayed so that the operator will not cut through the electrode structures during the disassembly operation.

(i) The cell is charged to some given point prior to venting or detonation. If the cell vents it is best to continue to charge to detonation, which usually occurs within one minute of venting.

(ii) Stop the charging current and, remotely and quickly, quench the cell with liquid argon (-189 °C: 84 K). Liquid nitrogen is not used for this purpose because it can react with lithium metal if the cell vents or detonates and create additional safety problems.

(iii) When the frozen cell voltage drops to near zero for a period of 30 min, the fill tube of the cell is opened using proper protective gear. Care should be taken with the filling tube orifice to ensure that it is open and will allow the passage of gases and liquids.

(iv) The frozen cell is stored for 2 or more days in a vacuum chamber (less than 10 mmHg) with the open fill tube pointing downward. The voltage of the cell should be 20 mV or less at this point. Any static electrical charge applied to the cell terminal may cause the cell to detonate.

(v) The cell is cut open in a dry argon atmosphere and components are stored in an argon gas environment. Care should be taken in this operation because the cell stack is quite active as is evident by crackling noises that originate at the anode. The anode materials also appear to be sensitive to any form of static electrical energy.

Because of the much smaller amounts of active material in the lab. cells, their disassembly in the charged condition was not as hazardous as that of the commercial cells. For this reason the disassembly of the latter was carried out with customary precautions and equipment for laboratory operations (safety glasses, face shield, etc.). In order to avoid contamination, the cells were disassembled in a dry room instead of a glove bag as above. Components were removed and processed into samples.

The analytical techniques employed were the same for the samples of both the lab. and the hardware cells. These techniques consisted of ultra-violet (UV), visible, Fourier Transform Infrared (FTIR) spectroscopic analyses, as well as Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS).

3. Experimental results

The lithium anodes of the undischarged, discharged, and discharged-then-charged cells were markedly different in their behavior and physical appearance, even though their chemical compositions were similar. SEM

pictures of the three types of electrodes are shown in Figs. 1 and 2. The undischarged and discharged lithium electrodes were both coated with crystalline platelets. The lithium electrodes which had been partially discharged and then charged were quite different in appearance. They were covered with rough, dull gray, non-adherent deposits which appeared to be composed of fine filaments or dendrites when studied by SEM. Upon removal from a cell and subsequent drying, these lithium electrodes were found to be very reactive. Also the charged lithium electrodes, particularly those from commercial cells, were found to sputter and yield cracking sounds when cut with scissors or hit with a hammer. Finally, charged lithium electrodes freshly removed from a cell burned when exposed to dry air. Similar behavior was not observed with uncharged electrodes.

Diffuse reflectance FTIR spectroscopy [4] was used to study the surface films on the three types of lithium electrodes. This technique was chosen to minimize disturbance of the anode surface films. As is clear from Fig. 3, the surfaces were chemically similar. The major component was $\text{Li}_2\text{S}_2\text{O}_4$ (peaks at 1075, 1025, and 910 cm^{-1}) with traces of Li_2SO_3 or Li_2SO_4 (peaks at 975 and 655 cm^{-1}). Peaks in the 1150 - 1250 cm^{-1} region are assigned to traces of lithium polythionates [5, 6].

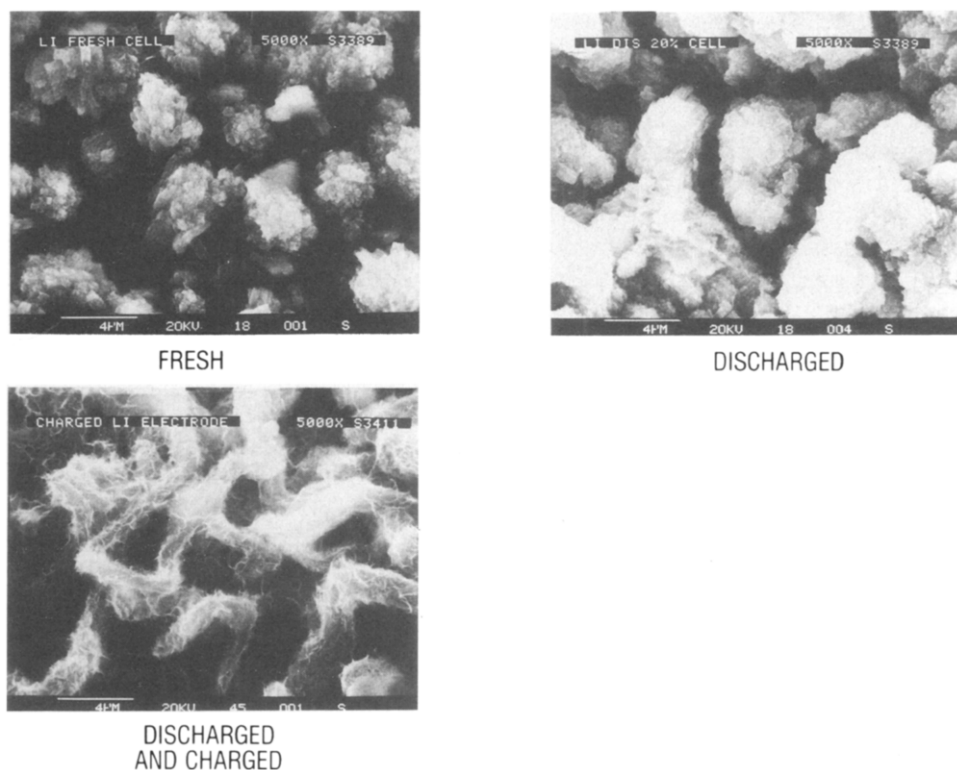
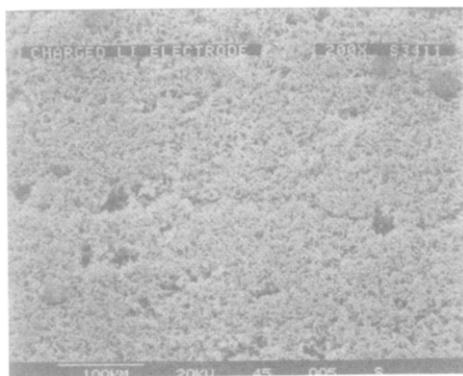
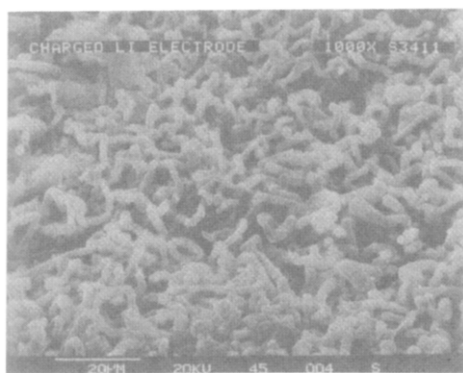


Fig. 1. Scanning-electron micrographs of lithium electrodes I.



CHARGED (200X)



CHARGED (1000X)

Fig. 2. Scanning electron micrographs of lithium electrodes II.

The deposit/film on the lithium electrode was examined by EDS and found to contain Li, S, and O in the ratio of approximately 2:2:4. This result supports the assignment of $\text{Li}_2\text{S}_2\text{O}_4$.

The carbon cathodes were examined in a manner similar to that described above. They were quite benign on removal from the cells, and did not sputter and crack as did the lithium electrodes. Diffuse reflectance FTIR measurements were made on the carbon cathodes from fresh, discharged, and charged cells. Spectra for each of these cathodes were found to be quite similar and are shown in Fig. 4. The peaks are assigned to $\text{Li}_2\text{S}_2\text{O}_4$ (1043, 1027, and 921 cm^{-1}) [7]. These results indicate that $\text{Li}_2\text{S}_2\text{O}_4$ is the predominant species in all three types of cells (the smaller peaks at 1237 cm^{-1} are attributed to traces of polythionates). This finding is not unexpected in the case of the discharged cells in that $\text{Li}_2\text{S}_2\text{O}_4$ has been reported as the end product of the cell reaction. The presence of some $\text{Li}_2\text{S}_2\text{O}_4$ in the fresh cell may be attributed to short duration test discharges applied by the cell or sonobuoy manufacturer before delivery of the units.

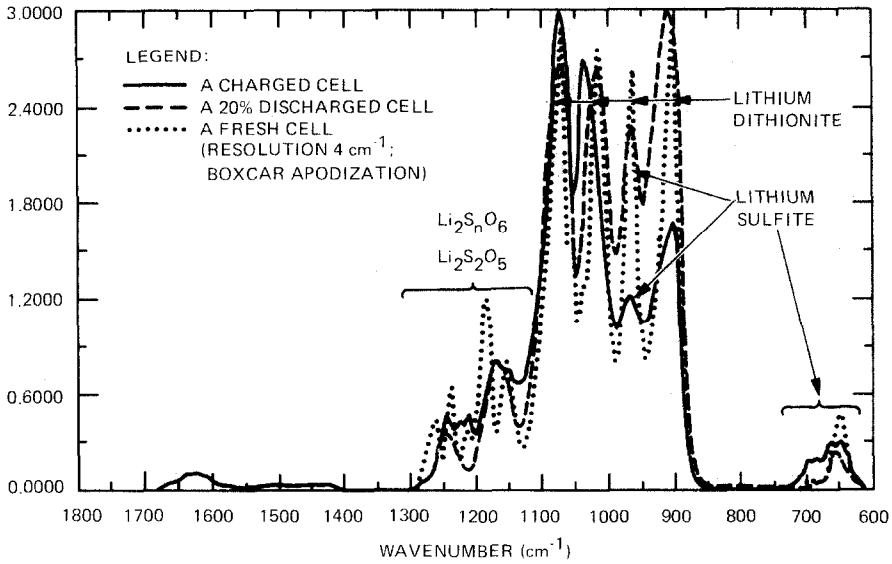


Fig. 3. Infrared spectra of lithium electrodes.

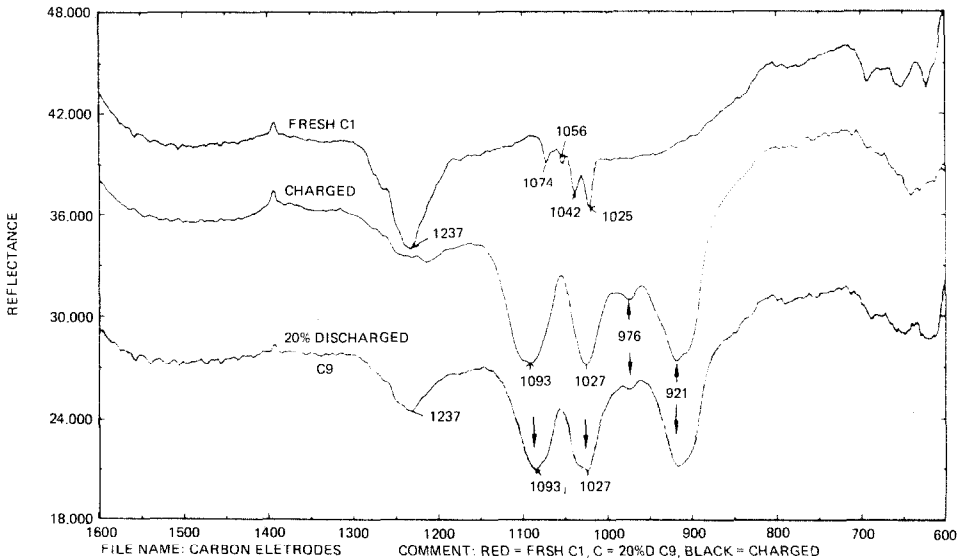


Fig. 4. Infrared spectra of carbon cathodes.

Figure 5 illustrates the effect of charging on the aluminum grid current collectors of the carbon cathodes. Grids from three cells subjected to varying amounts of charge are shown. The grids on the left, designated as "discharged", were from cells that received no charge. These appear quite

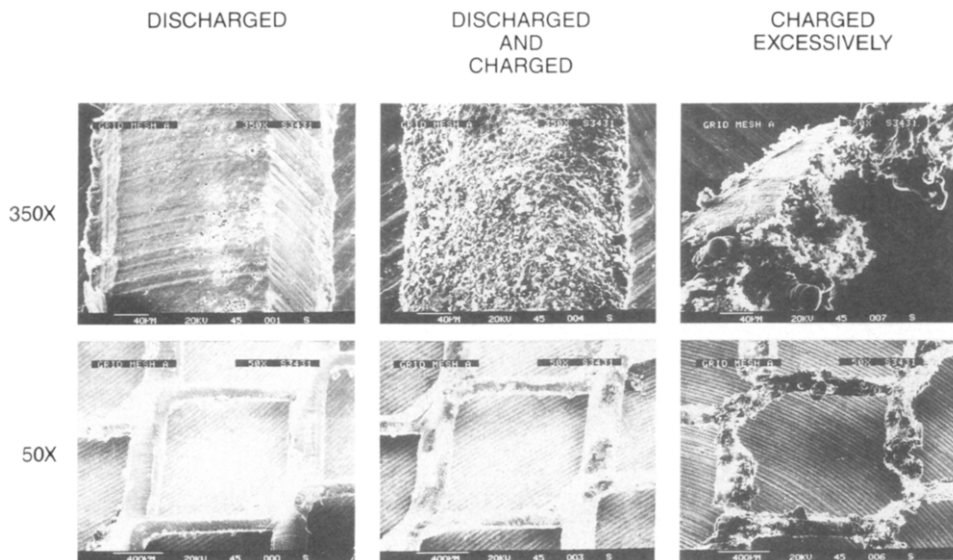


Fig. 5. Effect of charge on aluminum cathode grid.

smooth. The grids in the middle, designated as “discharged and charged”, were from cells that were discharged by 20% of capacity and then recharged back to full capacity. These appear to be slightly corroded. The grids on the right, designated as “charged excessively”, were from previously discharged cells that were charged to approximately 300% of capacity. Comparison of these grids indicates that charging causes corrosion, which is dependent upon the amount of applied charge. The corrosion is believed to be caused by bromine (Br_2) which is formed by the oxidation of bromide ions at the carbon electrodes during charge.

The laboratory cells were used in another series of tests to examine the time-dependence of cell open circuit voltage after charging. The procedure consisted of charging both fresh and partially-discharged cells and then terminating charge and monitoring cell voltages. Results, shown in Fig. 6, reveal a difference in the voltage behavior of the two types. At the start of the stand period, both cell voltages were near 3.6 V. After a few minutes, the voltage of the partially-discharged cell declined to 3.0 V while the voltage of the fresh cell remained at 3.6 V. Color changes were also noted for the solvent/electrolyte of these cells. After the start of charging, both solutions changed from colorless to a dull red. After termination of charge, the solution of the fresh cell remained red while the color of the partially-discharged cell began to fade. The fading of the latter solution occurred a few minutes after being set aside and corresponded to the decline of cell voltage. These results were attributed to the formation of bromine during charge, and subsequent rapid reaction of the Br_2 with $\text{Li}_2\text{S}_2\text{O}_4$ in the case of the partially-discharged cell. Support for the formation of bromine is given by the observed voltage of 3.6 V, which corresponds to that of the Li-Br_2

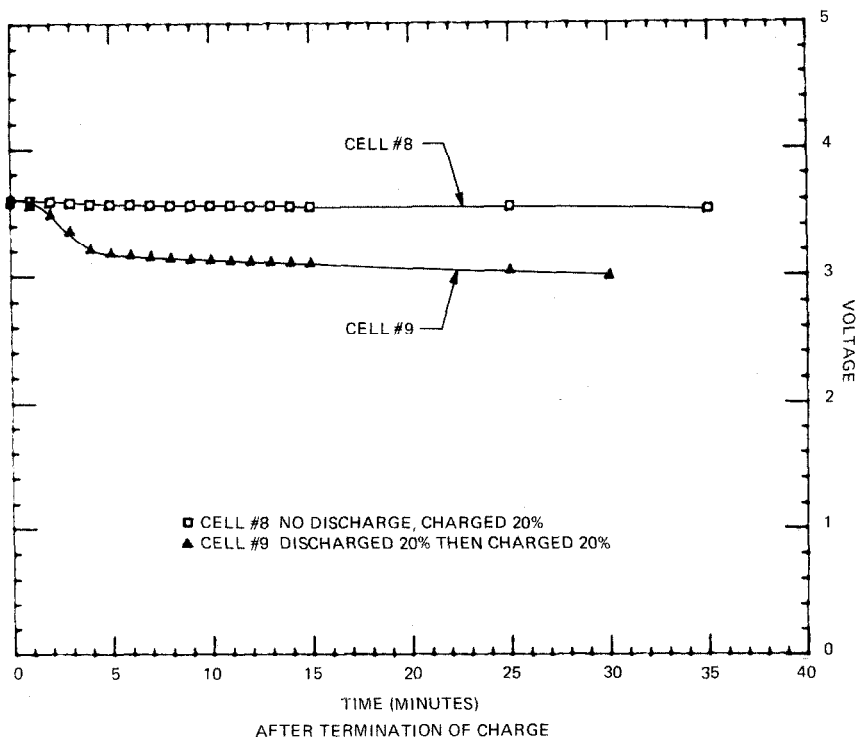


Fig. 6. Voltage decay after charging.

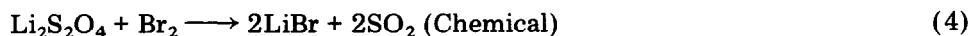
couple, and also the reddish color which is associated with bromine. Support for the proposed reaction of bromine with $\text{Li}_2\text{S}_2\text{O}_4$ is based on favorable thermodynamics, the known reaction of the two, and their intimate contact at the carbon electrode during charge. The persistence of the red color in the solution of the fresh cell is explained by the absence of significant amounts of $\text{Li}_2\text{S}_2\text{O}_4$ because the cell was not discharged. Finally, it should be pointed out that after about 10 h the solution color in the freshly charged cells had faded and the cell voltage had returned to 3.0 V. This observation is explained by the slow diffusion of bromine to the lithium electrode and the consumption of bromine by the $\text{Li}-\text{Br}_2$ reaction.

4. Conclusion

The finely-divided particles on the surface of the lithium electrodes after charging are believed to comprise a mixture of $\text{Li}_2\text{S}_2\text{O}_4$ (as shown by FTIR & EDS) and metallic lithium. The $\text{Li}_2\text{S}_2\text{O}_4$ may be in the form of a layer that encapsulates the lithium. This mixture would be expected to form, as freshly reduced lithium reacts with SO_2 in the electrolyte.

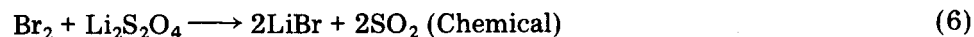
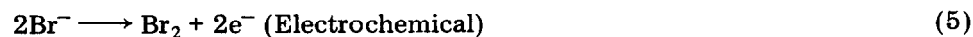
The pyrophoric behavior of the charged lithium electrodes is attributed to the reaction between the Li and $\text{Li}_2\text{S}_2\text{O}_4$. Support for this explanation comes from the work of Kilroy who showed that a mixture of the two reacts quite readily and exothermically [8]. The rapid and highly exothermic nature of the reaction for these particular samples is attributed to the fact that the mixture is very finely divided.

Based on our experimental observations the following reactions are deemed possible at the lithium electrode during charge:



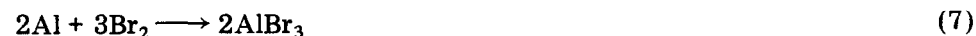
Equations (1) - (4) give reactions at the lithium electrode. Equation (1) describes the predominant electrochemical reaction which is the reduction of lithium ions to form lithium metal. Equations (2) and (3) give two overall chemical reactions in which the lithium can be consumed. Equation (2) gives the reaction for oxidation of the lithium by the SO_2 which is part of the solvent/electrolyte. Equation (3) gives the reaction for oxidation of the lithium by Br_2 which diffuses from the cathode, where it is formed, to the anode. Equation (4) describes another chemical reaction of the evolved Br_2 . This consists of oxidation of the $\text{Li}_2\text{S}_2\text{O}_4$ film on the anode. In a partially discharged cell, eqns. (3) and (4) will be relatively minor since most of the Br_2 will be consumed by reaction with $\text{Li}_2\text{S}_2\text{O}_4$ at the carbon electrode.

Equations (5) and (6), below, give reactions at the carbon electrode:



Equation (5) describes the predominant electrochemical reaction; the oxidation of Br^- ion in the electrolyte to form elemental Br_2 as suggested above. Equation (6) represents the chemical oxidation of $\text{Li}_2\text{S}_2\text{O}_4$ by the Br_2 . The only difference between this and eqn. (4) is that in eqn. (4) the $\text{Li}_2\text{S}_2\text{O}_4$ is on the carbon electrode where the Br_2 is formed and diffusion is not required for their contact.

Equations (7) and (8) give reactions at the aluminum grid portion of the carbon electrode.



Equation (7) describes the oxidation of the grid by the evolved Br_2 . Equation (8) represents the subsequent chemical reaction of AlBr_3 with Br^- from the electrolyte to form AlBr_4^- ion.

The results suggest that the explosion which can occur when a lithium/sulfur dioxide cell is charged may result from a combination of events. First, very reactive lithium metal, in the form of high-surface area dendrites, is deposited on the lithium electrode. This metal then reacts with the SO_2 in the electrolyte to cover each dendrite with a layer of $\text{Li}_2\text{S}_2\text{O}_4$. An explosion may then be caused by a run-away reaction involving the finely-divided particles of lithium, $\text{Li}_2\text{S}_2\text{O}_4$, SO_2 , and other cell components. This run-away reaction can be initiated in a variety of ways. It is believed that in a high-rate charging experiment, the reaction is most likely initiated by thermal means. The required initiation temperatures are produced by the heat released from a variety of reactions including those between Li and SO_2 , Br_2 and $\text{Li}_2\text{S}_2\text{O}_4$, as well as Li and Br_2 , and Al and Br_2 . Additional heating is caused by the cells' resistance to the flow of current (I^2R heating). Monitoring of cell temperature during charging, and theoretical studies of cell heat balance (calculations involving heat added, heat lost, and cell heat capacity), support this hypothesis.

Although the thermal explanation for initiation is quite straightforward and can account for most of the observed behaviors, it should be pointed out that other possible explanations exist. For example, the explosions can sometimes occur in charged cells by the application of a physical blow. In this case the initiation could be attributed to mechanical shock.

It is the goal of this study to gain a quantitative understanding of the relationship between charging and subsequent hazardous reactions or explosions of lithium/sulfur dioxide cells. Some progress has been made in reaching this goal in the work described herein, and from additional results of electrical tests to be reported in a forthcoming document [3]. Although results to date have not been shown to be entirely reproducible, the variations which can and do occur are most likely related to differences in cell design and history. Until this matter is completely resolved there remains a degree of uncertainty between "probably safe" and "clearly dangerous" cells under conditions of charging. For this reason, extreme care should be taken to avoid charging lithium/sulfur dioxide cells.

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