

CHEMICAL ANALYSIS OF CHARGED Li-SO₂ CELLS

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1. Introduction

For some time the Navy has been concerned about the hazards associated with charging of lithium/sulfur dioxide cells. This concern is based on earlier verbal reports and also exploratory investigations both of which indicated that charging of these cells can result in explosion.

Based on these initial inputs the Navy deemed it important to examine the charging of these cells in greater detail. For this reason the Navy initiated a joint program with the Jet Propulsion Laboratory to study the charging of these cells.

Initial focus of this program was to confirm that charging can indeed result in explosions and thereby constitute a significant safety problem. 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].

Subsequent efforts of this program were focused on determination of the causes for the observed explosions. In particular, it was desired to resolve two major issues. The first of these was to determine if the explosions were

influenced by the type and size of cell and also its operating conditions. The second was to determine the most likely chemical processes that are involved and could explain the origin of the explosions.

A report is in preparation on results of investigations dealing with the impact of cell type and size as well as charge conditions on the explosions (3). Therein it will be shown that the occurrence of explosions is rate dependent and appears to be generic for lithium/sulfur dioxide cells.

This paper describes results of the second effort to identify the chemical reactions involved in and responsible for the observed behaviors.

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. This section contains a brief description of these cells as well as the procedures employed in handling and disassembling them for analyses. The analytical methods were the same for both types and are also described herein.

The commercial cells were Duracell type L030SH with the cylindrical configuration and contained spiral wound electrodes. The cells were hermetically sealed in steel cans, and were carbon limited in design; rated capacity of these was 4.2 amp-hr at the C/2 discharge rate.

The lab cells consisted of small parallel plate electrodes immersed in a commercial SO₂ solvent/electrolyte mix. These components were housed in sealed laboratory glass hardware. The electrode assembly consisted of two outer lithium electrodes that sandwiched 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. Corresponding dimensions of the carbon electrode were 0.5 in., 0.5 in., and 0.033 in. Relative sizes of the two electrodes were selected so that the cells would be carbon limited, like the commercial cells, and capacities were 100 mah. The solvent/electrolyte contained 7% lithium bromide, 23% acetonitrile, and 70% sulfur dioxide by weight.

Both the lab and commercial cells were operated in a similar manner in this investigation. The operation typically consisted of first discharging them 20%, then letting them stand, and then placing them on charge. Operating current densities were the same for both types, and specifics are shown in Table I. The cells were disassembled in the fresh, discharged, and charged conditions.

The lab cells provided a great deal of versatility to this investigation and permitted controlled and visual operations not possible with the commercial cells. With the glass hardware it was possible to observe the electrodes and color changes in the solution as described herein.

Disassembly of the commercial cells in the charged condition was not treated lightly in that this is a potentially hazardous operation. For this reason, the following procedures were devised and used in disassembly of these cells in the charged condition.

These operations should only be done in proper facilities 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.

- A. The cell is charged to some given point prior to venting or detonation. If the cell vents it is best to continue the charging to detonation which usually occurs in less than a minute after venting.
- B. 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 added safety problems.
- C. When the frozen cell voltage drops to near zero for a period of 30 minutes, the fill tube of the cell is then opened by an operator using proper protective gear. Care should be used that the filling tube orifice is open and will allow the passage of gases and liquids.

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

- E. 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 in that the cell stack is quite active as evidenced by some crackling noises that originate at the anode. Also the anode materials appear to be sensitive to any form of static electrical energy.

Because of the much smaller amounts of active materials in the lab cells, the disassembly of these in the charged condition was not deemed as hazardous as that of the commercial cells. For this reason the disassembly of these 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 samples of lab and hardware cells. These techniques consisted of ultraviolet (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 anode of the undischarged, discharged, and discharged-then-charged cells were markedly different in their behavior and physical appearance even though their chemical analyses were similar. SEM pictures of the three types of electrodes are shown in Figures 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 these charged lithium electrodes, particularly those from commercial cells, were found to sputter and yield cracking sounds when cut with a scissors or hit with a hammer. Finally the charged lithium electrodes that were freshly removed from a cell were observed to burn when exposed to dry air. No similar behavior was 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 Figure 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].

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 similar manner to that described above. Upon removal from the cells, these cathodes were quite benign and did not sputter and crack like 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 Figure 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.

Figure 5 illustrates the effect of charging on the aluminum grid current collectors of the carbon cathodes. Shown therein are the grids from three cells subjected to varying amounts of charge. The grids on the left designated

as "discharged" were from cells that received no charge. These appear quite smooth. The grids in the middle designated as "discharged and charged" were from cells that were discharged 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 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 oxidation of bromide ions at the carbon electrodes during charge.

The laboratory cells were used in another series of runs 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 Figure 6, reveal a difference in the voltage behavior of the two types. At the start of the stand period, both cell voltages were noted to be near 3.6 volts. After a few minutes, the voltage of the partially discharged cell was noted to decline to 3.0 volts while voltage of the fresh cell remained at 3.6 volts. Color changes were also noted for the solvent/electrolyte of these cells. After the start of charging, the color of 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 after a few minutes of standing 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 volts which corresponds to that of the Li- Br_2 couple and also the reddish color which is associated with bromine. Support for the 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 the intimate contact of these two 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 $\text{Li}_2\text{S}_2\text{O}_4$ in that this cell was not discharged. Finally it should be pointed out that after about 10 hrs the solution color in the freshly charged cells had

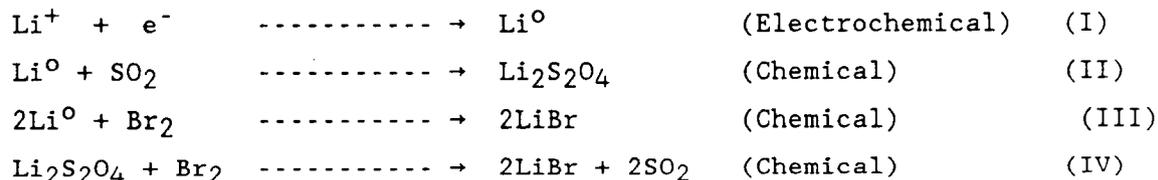
faded and cell voltage returned to 3.0 volts. This observation is explained by the slow diffusion of bromine to the lithium electrode and consumption of bromine by the Li-Br₂ reaction.

6. Conclusion

The finely divided particles on the surface of the lithium electrodes after charging are believed to be comprised of a mixture of Li₂S₂O₄ (as shown by FTIR & EDS) and metallic lithium. The Li₂S₂O₄ 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 SO₂ in the electrolyte.

The pyrophoric behavior of the charged lithium electrodes is attributed to the reaction between the Li and Li₂S₂O₄. Support for this explanation is based on the work of Kilroy who showed that the mixture of these two reacts quite readily and exothermically [8]. The rapid and highly exothermal nature of the reaction for these particular samples is attributed to the fact that the mixture is very finely divided.

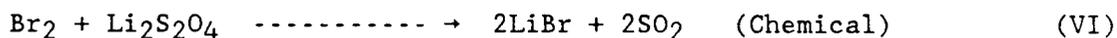
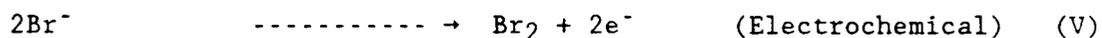
Based on our experimental observations the following reactions are deemed possible at the lithium electrode during charge:



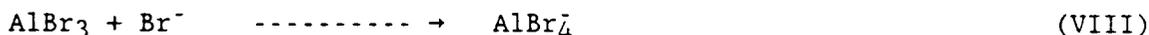
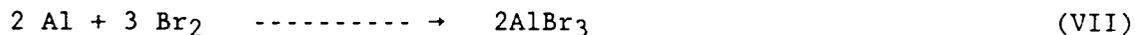
Equations I-IV give reactions at the lithium electrode. Equation I describes the predominant electrochemical reaction which is the reduction of lithium ions to form lithium metal. Equations II and III give two overall chemical reactions in which the lithium can be consumed. Equation II gives the reaction for oxidation of the lithium by the SO₂ which is part of the solvent/electrolyte. Equation III gives the reaction for oxidation of the lithium by Br₂ which diffuses from the cathode, where it is formed, to the anode. Equation IV describes another chemical reaction of the evolved Br₂. This consists of oxidation of the Li₂S₂O₄ film on the anode. In a partially

discharged cell, Equations III and IV will be relatively minor in that most of the Br₂ will be consumed by reaction with Li₂S₂O₄ at the carbon electrode.

Equations V and VI give reactions at the carbon electrode. Equation V describes the predominant electrochemical reaction; the oxidation of Br⁻ ion in the electrolyte to form elemental Br₂ as suggested above. Equation VI represents the chemical oxidation of Li₂S₂O₄ by the Br₂. The only difference between this and Equation IV is that in Equation VI the Li₂S₂O₄ is on the carbon electrode where the Br₂ is formed and there is no diffusion required for contact of the two.



Equations VII and VIII give reactions at the aluminum grid portion of the carbon electrode. Equation VII describes the oxidation of the grid by the evolved Br₂. Equation VIII represents the subsequent chemical reaction of AlBr₃ with Br⁻ from the electrolyte to form AlBr₄⁻ ion.



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 SO₂ in the electrolyte to cover each dendrite with a layer of Li₂S₂O₄. An explosion may then be caused by a run-away reaction involving the finely divided particles of lithium, Li₂S₂O₄, SO₂, 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 SO₂, Br₂ and Li₂S₂O₄, as well as Li and Br₂, and Al and Br₂. Additional heating is caused by the cells' resistance to the flow of current (I²R 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 for "normal" charging.

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 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 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.

TABLE I. 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

<u>Parameter</u>	<u>Lab Cell</u>	<u>Commercial Cell</u>
Discharge current	10 mA	66 mA
Discharge duration	2 hrs.	24 hrs.
Discharge output	20 mAh (20% DOD)	1.6 Ah (20% DOD)
Charge current	100 mA (20 mA/cm ²)	10 A (20 mA/cm ²)
Charge duration	8 - 15 min.	8 - 15 min.

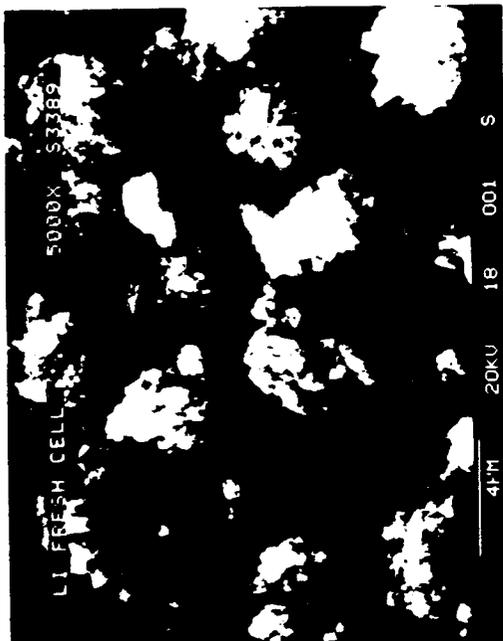
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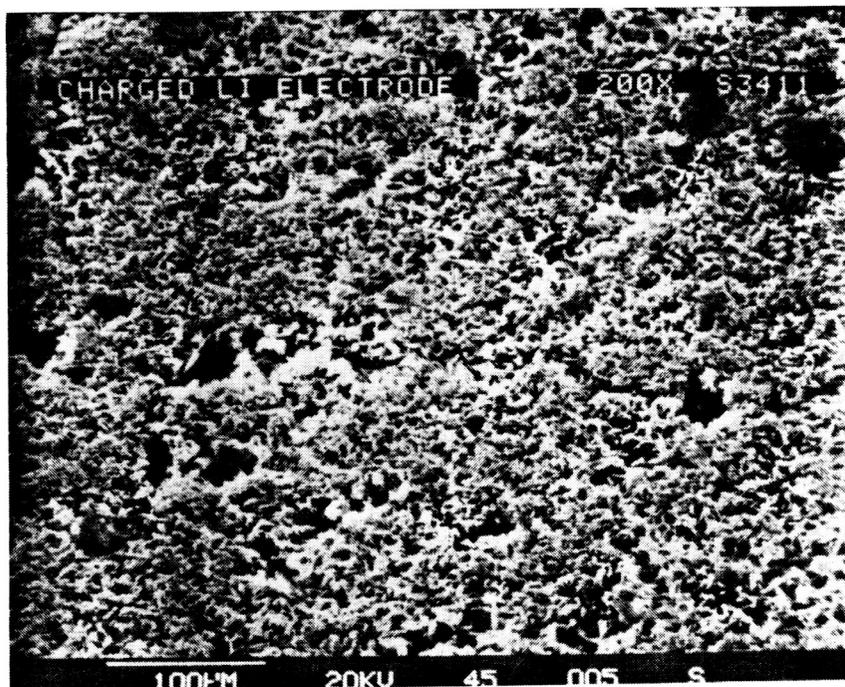
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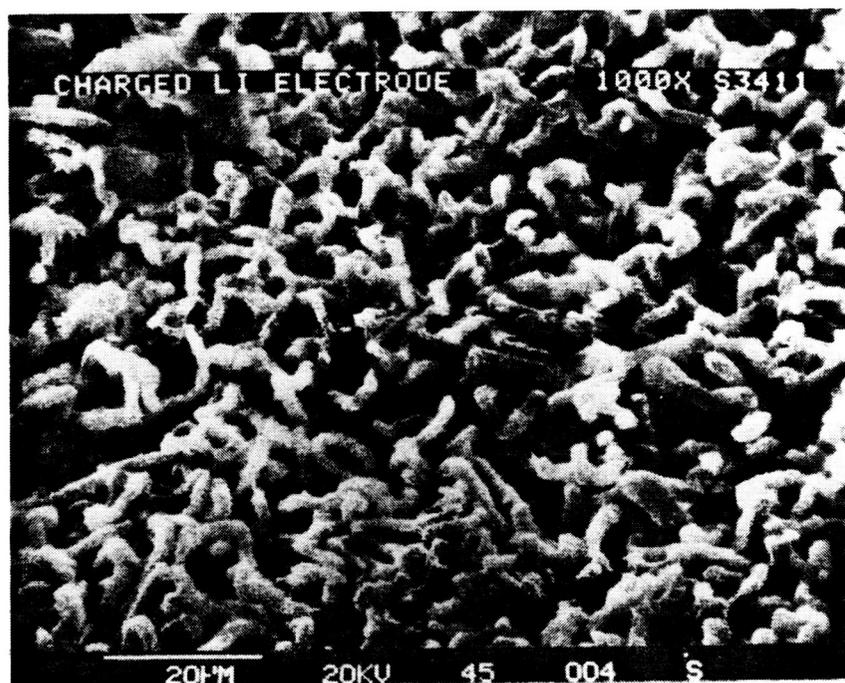
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Figure 1. Sem of Lithium Electrodes I.

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Figure 2. Sem of Lithium Electrodes II.

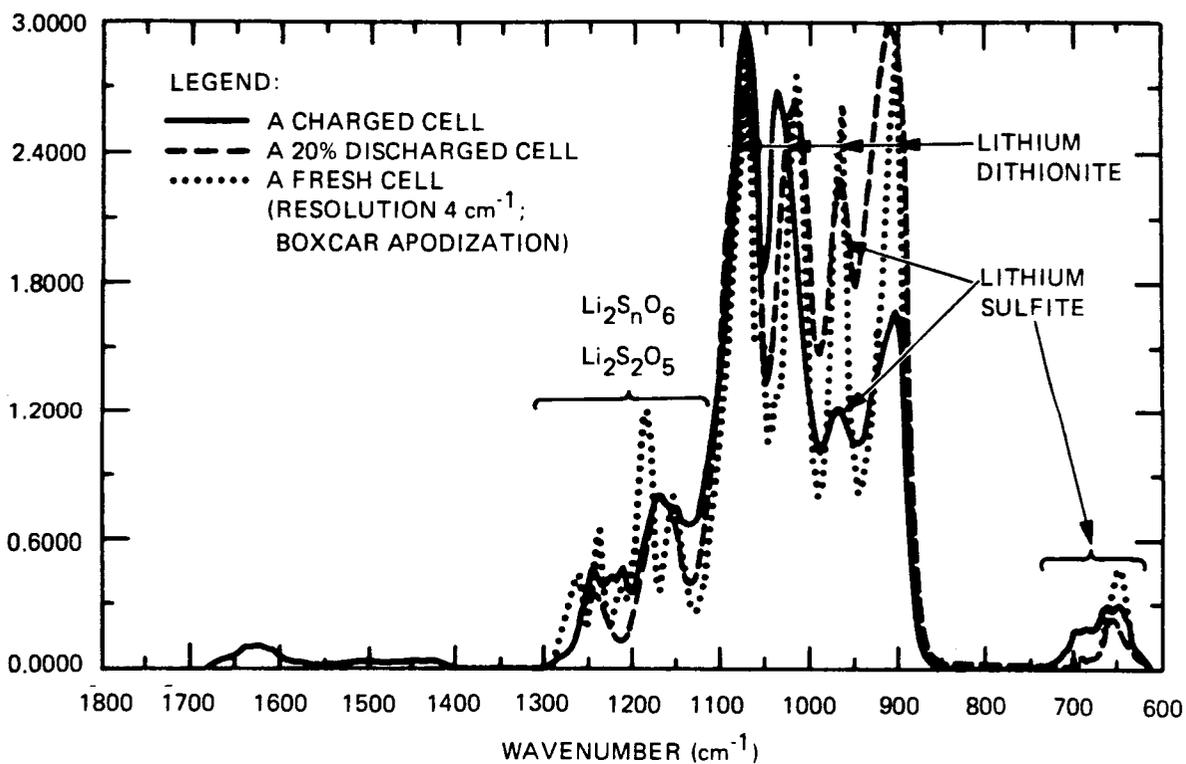


Figure 3. Infrared Spectra of Lithium Electrodes.

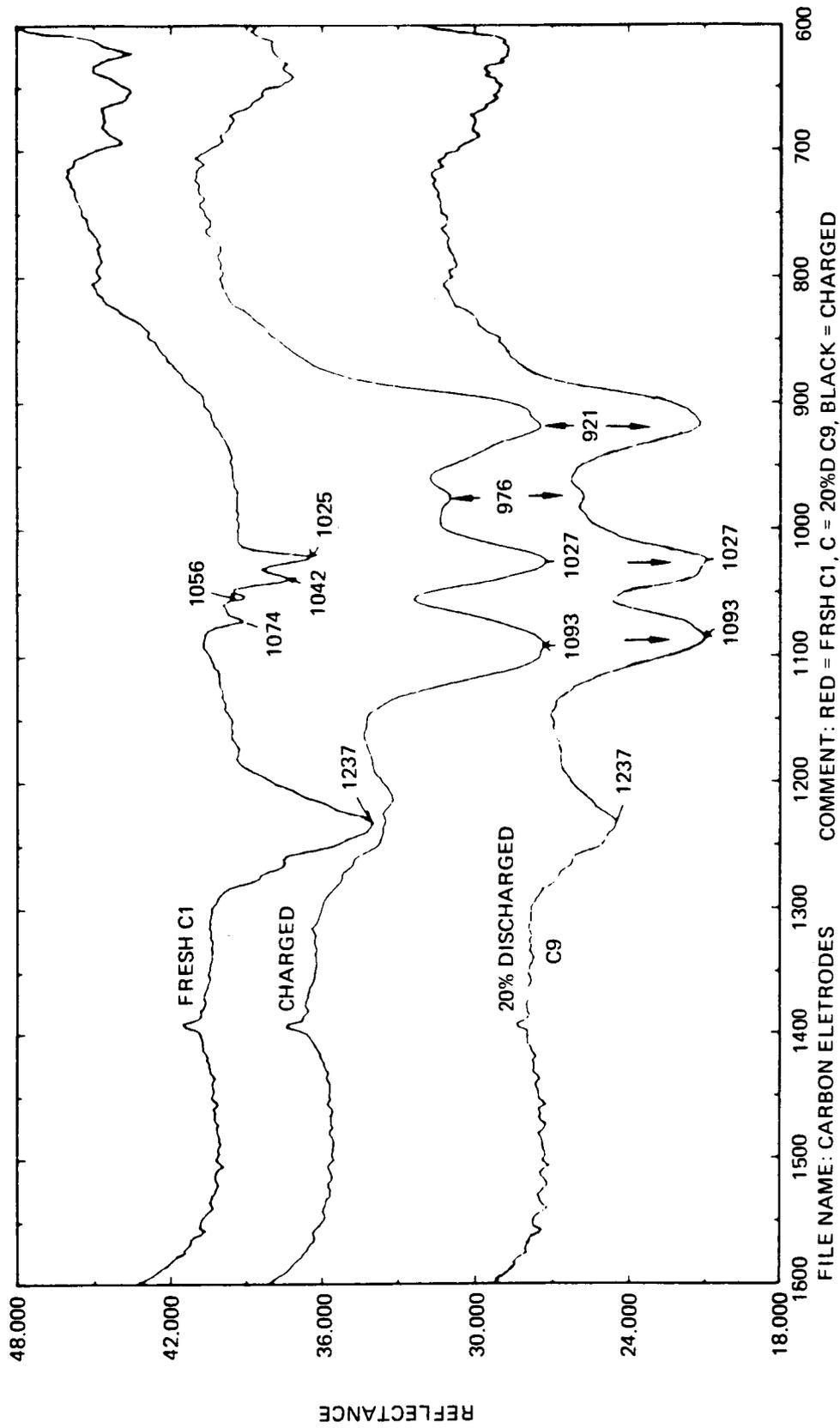


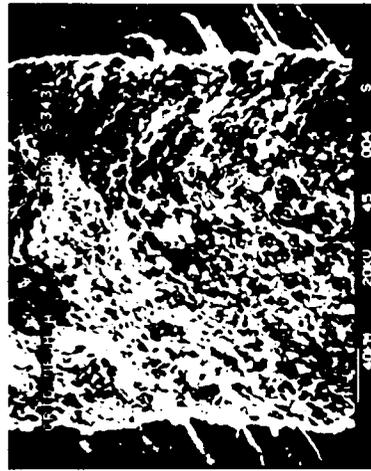
Figure 4. Infrared Spectra of Carbon Cathodes.

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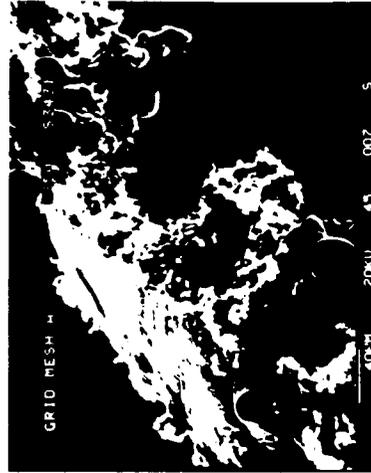


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Figure 5. Effect of Charge on Aluminum Cathode Grid.

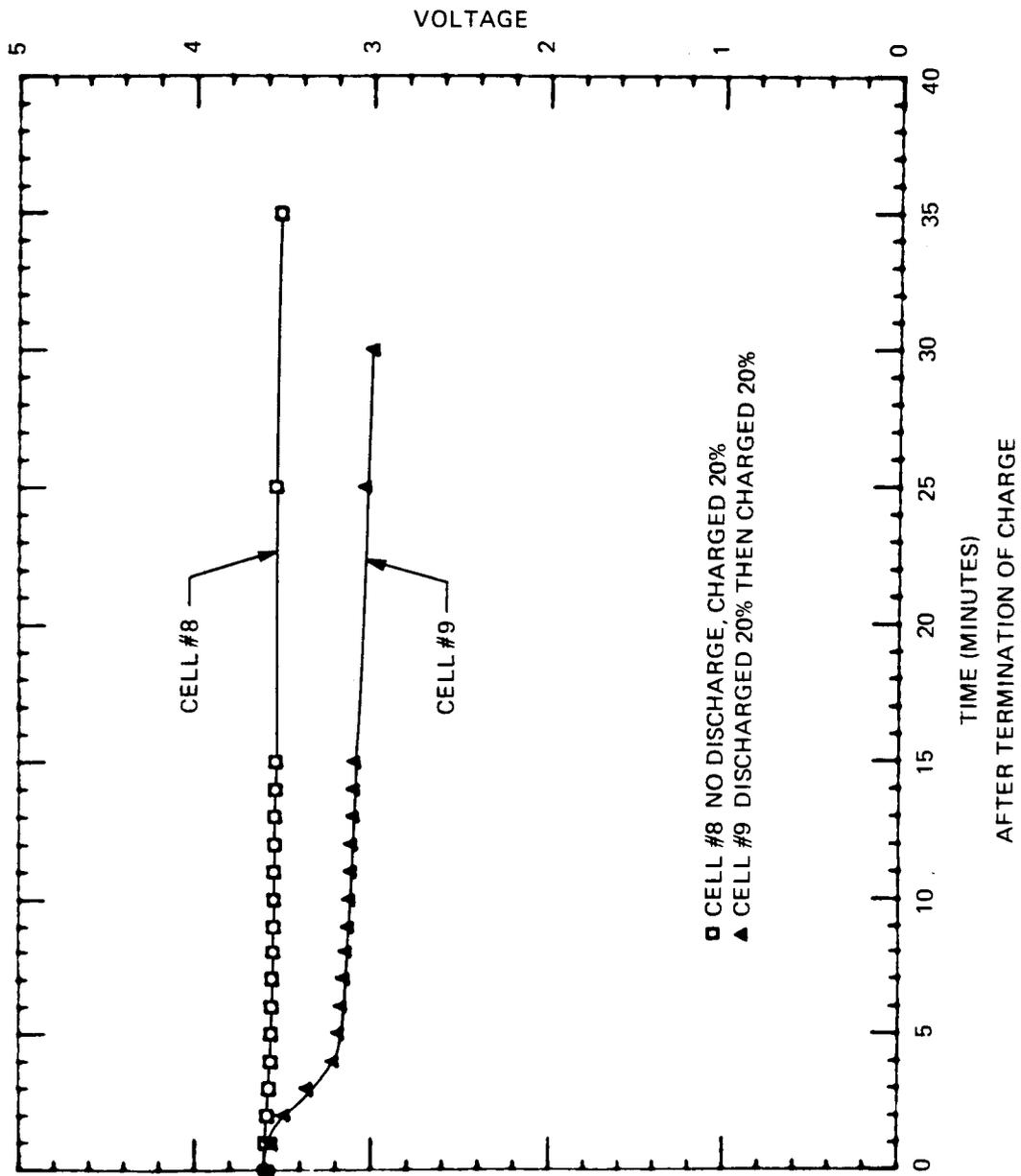


Figure 6. Voltage Decay After Charging.