

INVESTIGATION OF AN ABERRANT CELL VOLTAGE
DURING THE FILLING OF A LARGE LITHIUM THIONYL
CHLORIDE CELL

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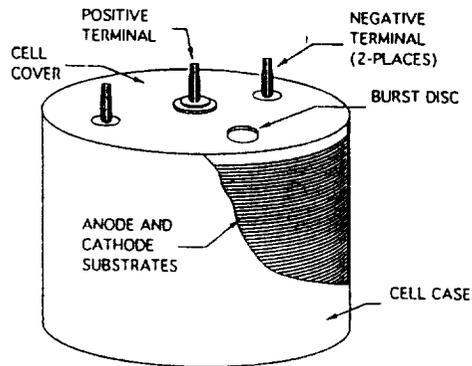
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An investigation was carried out to explain the out-of-family voltage trace associated with one of the 250 ampere hour lithium-thionyl chloride cells produced for an Air Force flight program. The voltage trace was generated during the manufacturing step where electrolyte is added to the cell while the open circuit voltage is monitored and recorded on a strip chart. Instead of recording a constant increase in cell voltage, there was a decrease in the open circuit voltage followed by a second period of increase to its expected value of greater than 3.6 volts. The intervening and unexplained drop in cell voltage was a cause of concern and an investigation into its cause was initiated. The investigation was carried out in several steps. First, discussions were held with the manufacturer. The manufacturer was able to suggest theories that were consistent with the observations that were available for review. The theories were later tested in the electrochemical laboratories of The Aerospace Corporation. Using specially constructed cells equipped with reference electrodes, the individual contributions of the anode, cathode, and cell container to the overall voltage transients associated with an interrupted cell filling process were measured. These results validated some of the manufacturers theories. What had been suggested as a minor contributor to the aberrant voltage trace was found by experimentation to be the most important one. That was the contribution of the porous carbon electrode. Our experiments added further support to the earlier conclusion that the out-of-family voltage signature seen in this cell was not indicative of a problem within the cell.

CELL DESIGN

- Manufactured by SAFT (Poitiers)
- 3.3 volts
- 250 A-hr, nominal capacity
- 300-500 Wh/kg energy density



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SAFT manufactures large, 250 ampere hour cells using the lithium-thionyl chloride system. The cylindrical cell consists of a series of anodes, cathodes, and separators which are stacked horizontally within a stainless steel can. Electrodes are attached to bus bars located near the outer periphery which connect to two anode terminals and a single, insulated, cathode feedthrough. The cell container is held at the same potential as the lithium electrodes. The electrolyte is SOCl_2 with proprietary compounds added to alleviate the voltage delay. A single burst disk protects the cell against excessive internal pressure build-up.

PROBLEM: An out-of-family voltage trace was found during the filling of a production cell

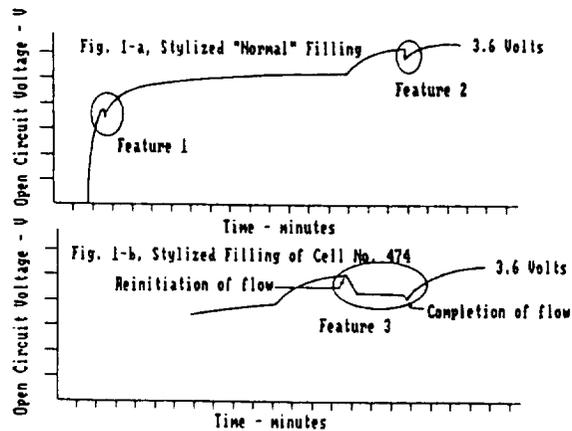
- Voltages between the positive and both of the negatives are monitored during the filling process consisting of:
 - Integrity check
 - Pull vacuum
 - Electrolyte filling (1-2 minutes)
 - Settling (15-20 minutes)
- Was the out-of-family trace caused by a short that cleared? Could the short re-establish itself?

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An out-of-family voltage trace was discovered during the review of the strip charts recorded during the filling of a number of the lithium-thionyl chloride cells. Two strip charts are used during production to measure the voltage response during filling and settling between the anodes and cathode of the cell. Prior to filling, the integrity of the cell is measured by checking the resistance across the electrodes and a vacuum is established inside the the case. Filling is usually accomplished on the order of a few minutes and the cell is allowed to settle for 15-20 more minutes. An unexplained voltage drop was discovered in one of the traces for a cell. Although the chart showed that the voltage recovered to an acceptable open circuit voltage 25 minutes later, there was concern as to whether or not it might have been caused by a momentary short. A fully developed short can cause venting or an explosion. A short that has burned clear might be prone to reestablishing a destructive short at a later time.

VOLTAGE TRACES DURING FILLING PROCEDURE



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The top figure is a schematic of the typical voltage changes observed during the filling of a lithium-thionyl chloride cell with electrolyte. The two characteristic voltage dips occur just after electrolyte filling commences (Feature 1) and after the vacuum is broken when filling is complete (Feature 2). The abrupt change in slope prior to Feature 2 indicates a change in strip chart speed during settling. The lower figure is a schematic of the out-of-family voltage recorded for one of the cells. It was characterized by a steep voltage drop of about 75 millivolts, followed by a linear region which lasted about five minutes, and then another short duration voltage dip. However, after these events, the cell voltage exponentially increased to an open circuit voltage of about 3.65V. Upon review of their records, the manufacturer discovered that the filling of this cell had been interrupted to clear a blockage in the filling apparatus.

THEORIES

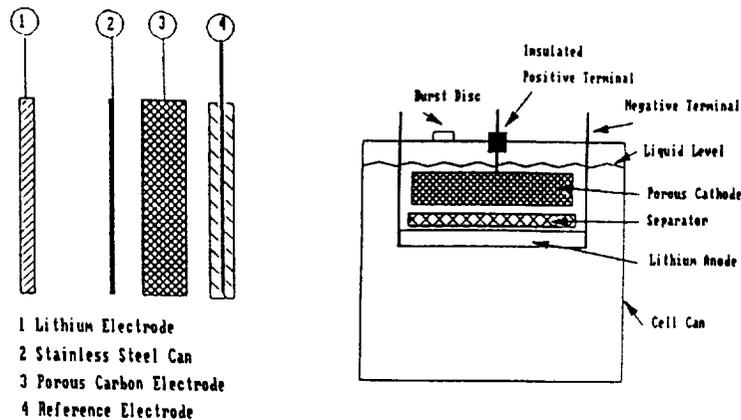
- SAFT records indicated that filling had been interrupted due to a line blockage. It was suggested that the voltage dip upon resumption could have been caused by:
 - Transient Mixed Potential of the Lithium Electrode
 - Passivation of the Stainless Steel Cell Container
 - Oxidation of the Cathode
- Aerospace initiated laboratory testing to verify which, if any, of these mechanisms were correct

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The manufacturer of the cell offered several explanations for the series of voltage dips encountered during interruption and restarting of the filling process. The lithium electrode may act as a combination lithium anode and rapidly corroding cathode as electrolyte covers its surface. During the time it takes the surface of the lithium electrode to passivate, it should display a mixed potential. The stainless steel cell case can act as a rapidly pacifying cathode when connected to the lithium electrode which might depress the open circuit voltage until passivation is complete. Finally, the porous carbon cathode could have sites which are oxidized by the thionyl chloride electrolyte upon contact. Though plausible, the magnitude of these three mechanisms, and the time scale upon which they acted, was unknown. Therefore, The Aerospace Corporation initiated a series of tests to evaluate each separately and together.

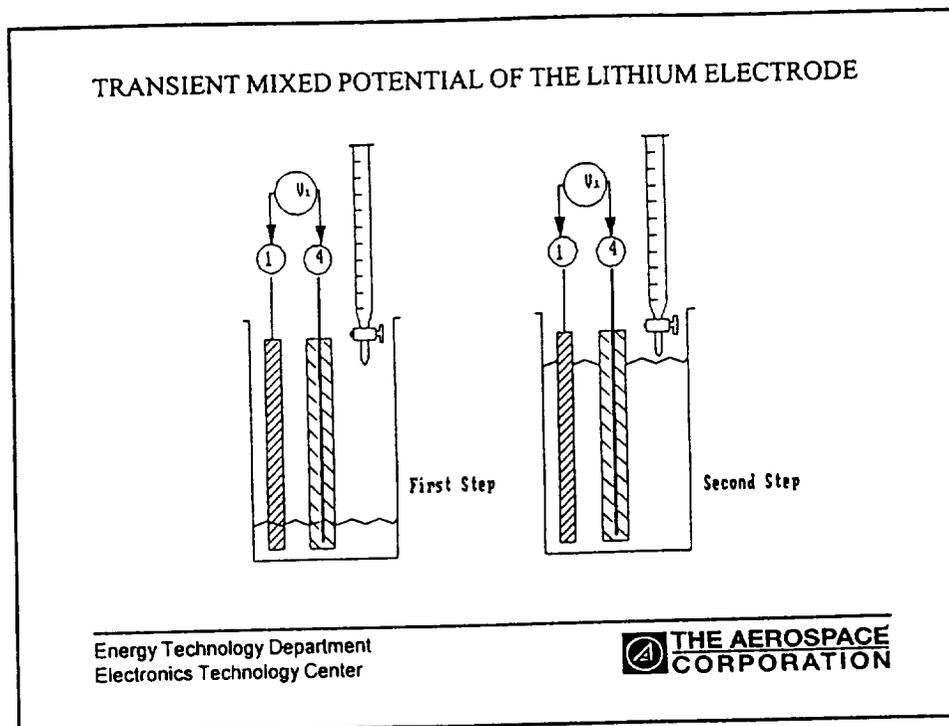
CELL PARTS USED IN ELECTRODE STUDIES



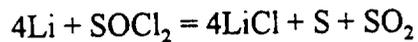
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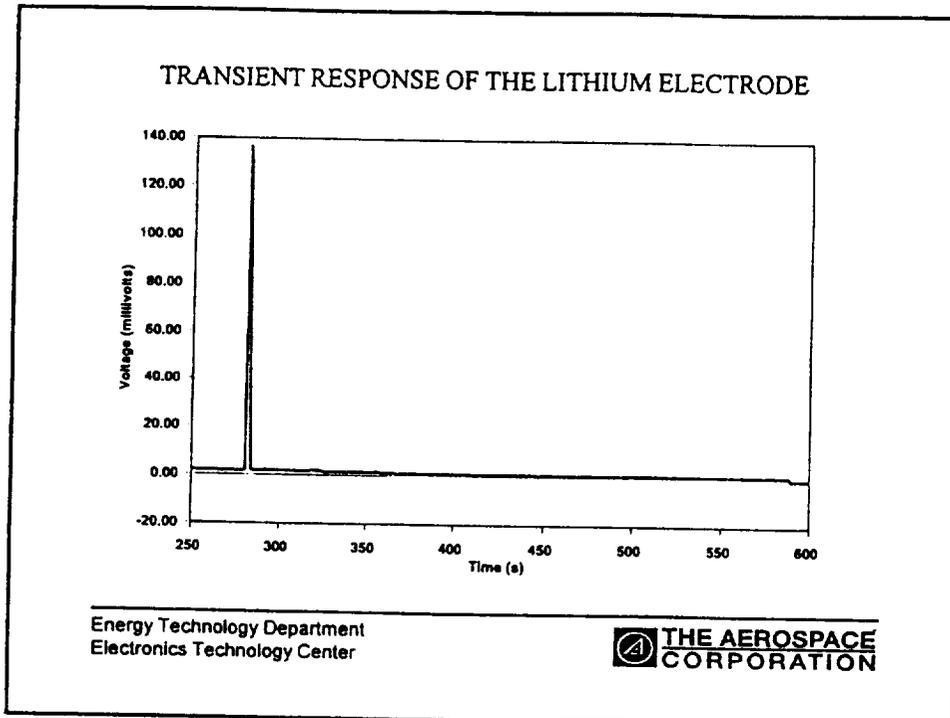
Several experiments were designed to explore the transient response of each of the three mechanisms separately. The figure above defines the schematic utilized in the following view graphs to denote the various cell structures used in the studies. The lithium was battery grade foil from Lithcoa, the electrolyte was 1.5M tetrachloroaluminate dissolved in thionyl chloride. The cathode was a mixture of carbon black and Teflon pressed and heated on a stainless steel screen. The cell container was simulated using 304L stainless steel. The reference electrode was a strip of lithium that had been equilibrated in the electrolyte for at least five minutes to render it immune from any time dependent transients. Experiments were conducted in a glass beaker. Filling commenced using a burette and interrupted after adding 10% of the electrolyte to the test cell. After a two minute pause, the rest of the electrolyte was added.



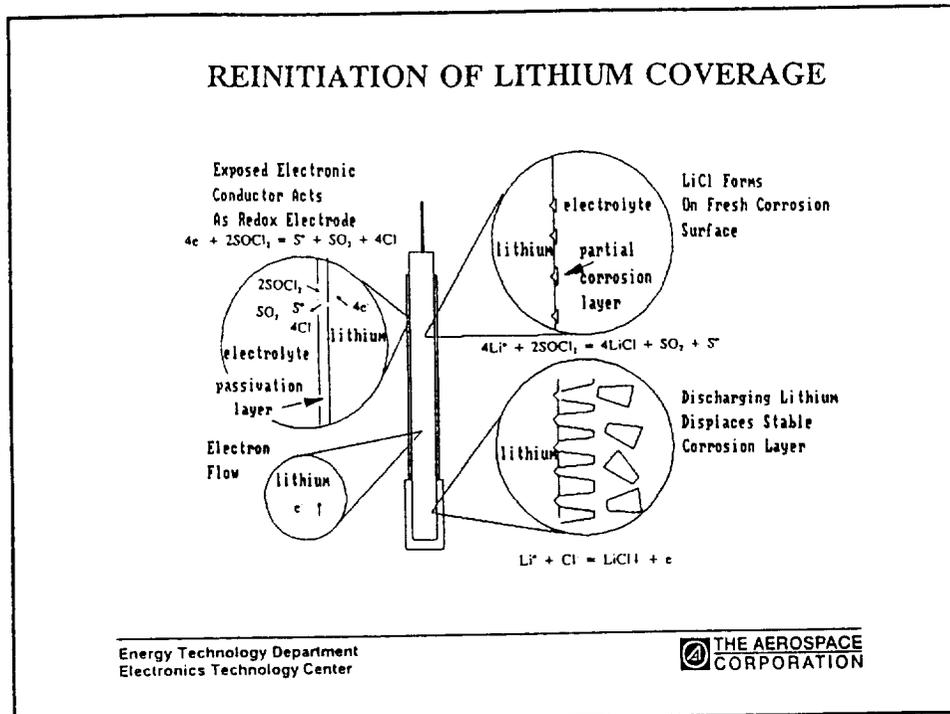
This schematic shows the arrangement used to measure the transient voltage of the lithium electrode. When a fresh lithium surface is exposed to the oxidizing thionyl chloride, the surface is rapidly corroded as it forms a protective layer of lithium chloride.



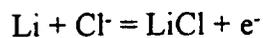
When the second portion of electrolyte is added, the upper portion of the lithium will function as a redox cathode for a short period of time until it too has become passivated. Although most of the reaction occurs within seconds, the lithium chloride layer can continue to grow for days which contributes to the voltage delay.



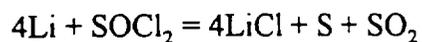
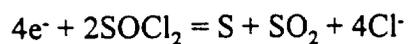
The above voltage response was measured during the final addition of the electrolyte in a cell containing just the lithium electrode. The voltage rose very sharply, about 135 millivolts above the reference electrode of passivated lithium. The transient only lasted about 5 seconds before returning very close to the potential of the reference electrode.



The chemical and electrochemical reactions taking place in the lithium electrode during the transient are shown schematically. Once a stable passivation layer is formed in areas that have been exposed to the thionyl chloride electrolyte, and new areas are subsequently exposed, the newly exposed areas function as an electrode for the discharge of thionyl chloride while the previously exposed areas are discharged. Electrons from the previously passivated portion of the lithium are supplied to the portion that is discharging thionyl chloride. As the passivation process progresses, the amount of current flowing between the two portions of the lithium diminishes. The reaction taking place at the lower portion of the the electrode is:

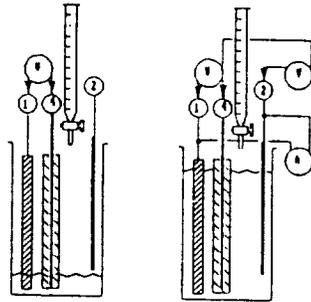


Thus the lithium electrode is acting as a redox electrode, and the surface functions only to interchange electrons to soluble species in the electrolyte. The reactions occurring on the newly exposed surface as it corrodes are:

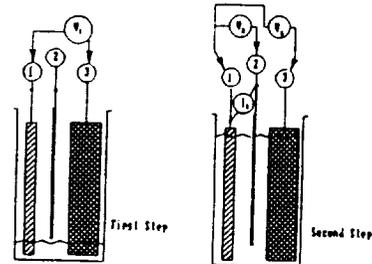


SHORTING OF THE STAINLESS STEEL CELL CONTAINER

CAN SHORTS OUT TO THE LITHIUM



DELATED TOUCHING OF THE CAN

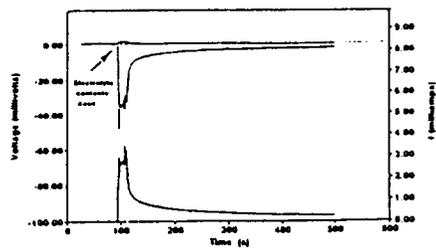


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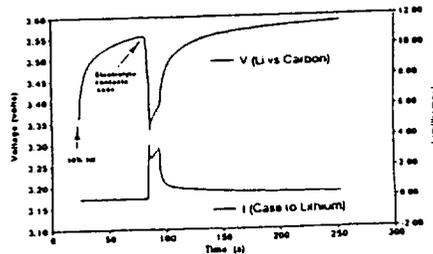
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The influence of the stainless steel cell container was investigated using two different scenarios. In the first, the can is shorted to the lithium and the current measured while the stainless steel acts as a redox electrode for the the reduction of thionyl chloride until it is passivated. In the second configuration, the electrolyte does not contact the stainless steel can until after both the lithium anode and carbon cathode are wetted. When filling is resumed, both the lithium and the stainless steel act as rapidly passivating redox cathodes.

TRANSIENT RESPONSES DUE TO THE CELL CONTAINER



CAN SHORTS



BELATED CONTACT

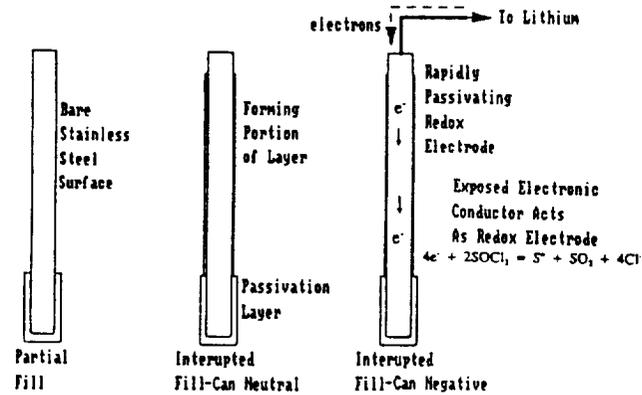
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The figure on the left shows the transient of the current and voltages measured against the reference electrodes of the stainless steel shorted to the lithium electrode. The top curve shows a small voltage rise measured between the stainless steel and the lithium anode. The middle curve depicts the voltage drop as measured between the lithium anode and the reference electrode. The bottom curve is the measured current between the case and the lithium anode.

The figure on the right depicts the voltage measured following belated contact of the stainless steel to the wetted lithium and carbon electrodes. The traces shown are the voltage between the lithium anode and carbon cathode, and the current measured between the stainless steel and the lithium anode. The transients from both scenarios are rapid and last about 10-20 seconds.

DIFFERENT STAINLESS CONDITIONS

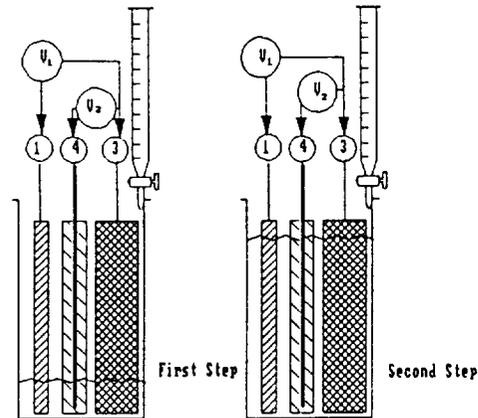


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The stainless steel portions of the cell are protected by a passivation layer of chloride as a result of being oxidized by the thionyl chloride (left-hand side figure). When connected to the lithium anode, a complete electrochemical cell is formed which discharges active material until a passivation layer is formed on the stainless steel at which time the reaction falls to a negligible rate. In this case, the stainless steel acts as a redox electrode as shown in the right-hand side figure. In the case neutral position (center figure), the stainless steel still reacts with the thionyl chloride to form a passivation layer which protects the metal against further oxidation by the thionyl chloride.

SEARCH FOR CATHODE TRANSIENT

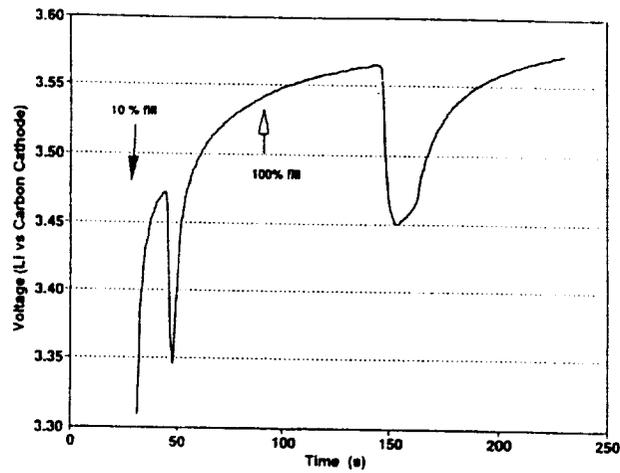


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The porous carbon electrode is a candidate for the lowered voltage transients seen because it is formed in a reducing atmosphere and thus may have oxidizable surface sites that react upon exposure to the thionyl chloride. Also, the carbon electrode is partially non-wetting which could affect the rate of oxidation by the electrolyte. The above schematic shows the configuration used to measure the relative contributions of voltages from the lithium anode and carbon cathode in an interrupted filling process.

CATHODE VOLTAGE TRANSIENTS (FRESH CATHODE)

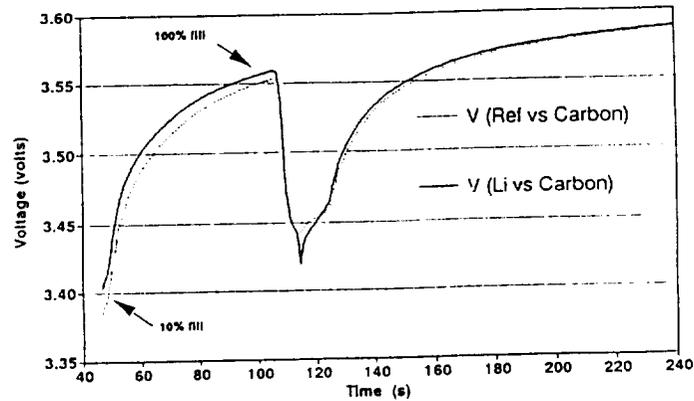


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This expanded voltage transient was measured between the reference electrode and the carbon electrode. It shows the characteristic initial dip (Feature 1) common to the normal filling process as well as the final dip at the end of filling.

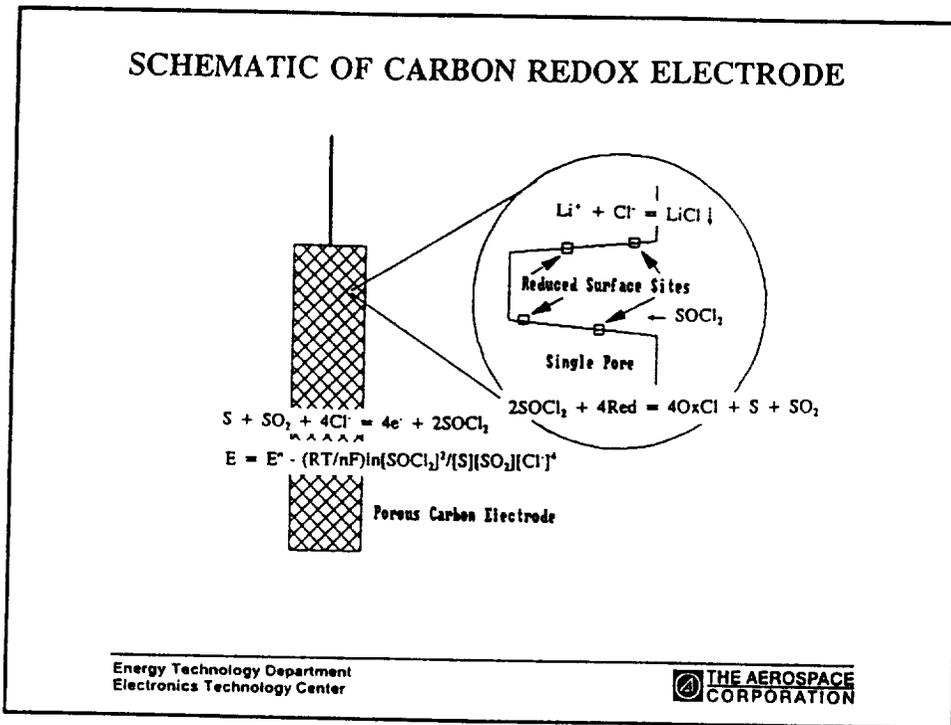
VOLTAGE TRANSIENTS FROM REFERENCE ELECTRODES



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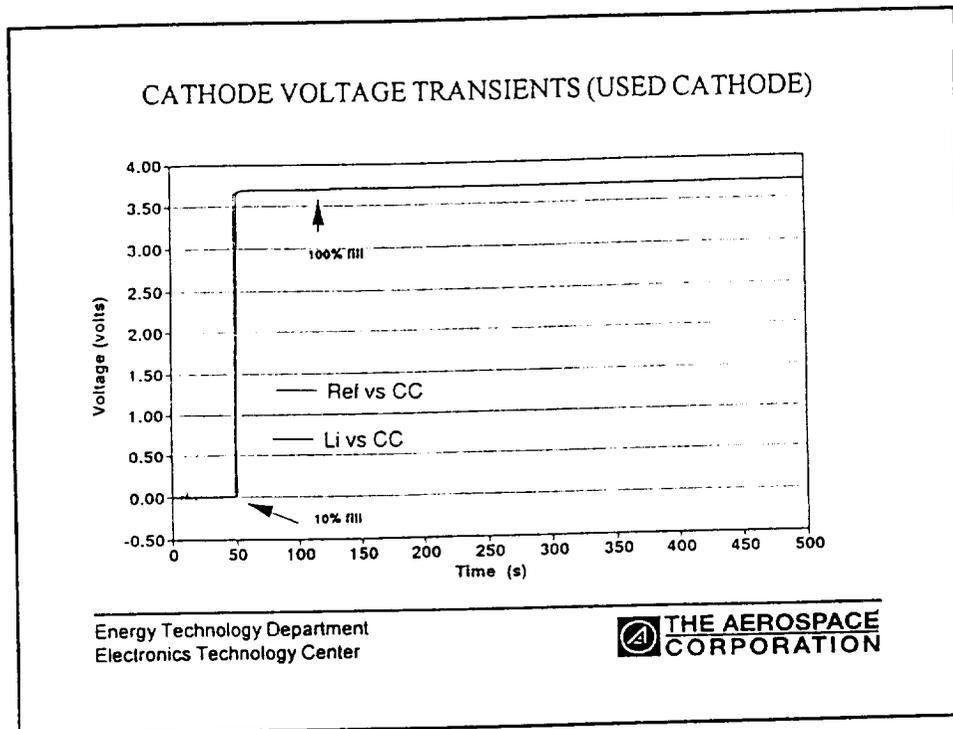
This figure shows the relative contributions of both the lithium and the carbon electrodes to the second filling transient shown on the last figure. It is evident that the majority of the response is due to the oxidation of the porous carbon electrode. Note that this voltage transient is much longer than the transients associated with the passivation of the lithium anode and the stainless steel can.



The figure above depicts the internal oxidation reaction by the thionyl chloride on the porous carbon electrode. The oxidation reaction can be described by the Nernst equation where the voltage is a function of the concentrations of species present. :

$$E = E^\circ - (nF/RT) \ln \frac{[SOCl_2]^2}{[S][SO_2][Cl^-]^4}$$

When new portions of the carbon cathode are exposed, there is a rapid drop in voltage (Feature 1), but not all interior sites are immediately oxidized. There is a slow recovery as reaction products diffuse out of the carbon electrode into the bulk electrolyte, and as a result, the voltage exponentially approaches the open circuit value. Porosity and wetting behavior also affect the rate of the oxidation of the cathode. Many of pores are at a higher pressure than the rest cell during the vacuum-filling process, and once vacuum is broken at the end of filling and the cell is exposed to atmospheric pressure, the electrolyte quickly penetrates these regions causing the final, short voltage dip identified as Feature 2 in the normal filling process.



To test the hypothesis that the voltage transients were indeed caused by the oxidation of the carbon cathode by the thionyl chloride, the previous experiment was repeated with a fresh lithium anode and a used porous carbon electrode. The above voltage transients between the reference electrode and the carbon cathode, and between the lithium anode and the carbon cathode, were measured during the interrupted filling procedure. Note that there are no voltage dips, and Features 1 and 2 are absent.

SUMMARY STATEMENTS

- An aberrant voltage trace was noted during the review of cell filling data
- Incident was traced to an interruption during filling
- Experimentation suggested oxidizable sites within the carbon electrode were responsible for the drop in voltage
- The voltage anomaly could be reproduced by interrupting the filling of similar cells
- Anomalous voltage dip was not due to a short
- The battery containing this cell is scheduled for flight

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The out-of-family voltage signatures seen in the filling of the 250 ampere hour lithium thionyl chloride cell can be attributed to the response of the carbon electrode to interrupted filling. It is controlled by the rate of oxidation of the carbon cathode by the thionyl chloride. Both the magnitude and the time duration of the response, which were experimentally measured, were in accordance with the initial anomaly. Other interrupted filling tests of lithium-thionyl chloride batteries by the manufacturer reproduced the signature on similar cells. These studies showed that the response of the production cell was appropriate for an interrupted filling procedure and not indicative of a temporary short. The cell is now part of a nine-cell battery scheduled for flight.