RELATED STUDIES IN LONG TERM LITHIUM BATTERY STABILITY

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INTRODUCTION

The continuing growth of the use of lithium electrochemical systems in a wide variety of both military and industrial applications is primarily a result of the significant benefits associated with the technology such as high energy density, wide temperature operation and long term stability. The stability or long term storage capability of a battery is a function of several factors, each important to the overall storage life and, therefore, each potentially a problem area if not addressed during the design, development and evaluation phases of the product cycle. Design (e.g., reserve vs active), inherent material thermal stability, material compatibility and self-discharge characteristics are examples of factors key to the storeability of a power source.

A significant amount of activity at Honeywell is directed toward characterizing and improving where necessary the storage affecting aspects of lithium batteries. This discussion reviews briefly, three segments of this work, the results of which are quite positive and as such, add to the confidence level associated with lithium units. These are:

o   Long term storage evaluation of electrolytes and cell systems used in Army mines batteries.

o   Material compatibility of thionyl chloride electrolyte with stainless steels used in reservoirs of reserve batteries.

o   Terminal seal glass corrosion in Li/V_2O_5 cells and TA-23 glass as a corrective measure.

RELATED MATERIAL STUDIES

ELECTROLYTES (ORGANIC AND INORGANIC)

Honeywell currently has two 10-year accelerated storage programs to assess the material compatibility and stability of both organic and inorganic electrolytes in reserve cells and ampuls. A total of 2100 cells and 10,000 ampuls comprise these extensive storage plans. The organic electrolytes: $Li/2M$ $LiAsF_6$, $0.4M$ $LiBF_4 \cdot$ Methyl Formate/V_2O_5, while the inorganic is $Li/1M$ $LiAlCl_4 \cdot$ Thionyl Chloride/$SOCl_2$. Both systems are stored at $64^{\circ}C$ ($147^{\circ}F$) to $84^{\circ}C$ ($183^{\circ}F$) environments and tested annually. Voltage monitoring for

cells occurs monthly to determine if any reserve cells have prematurely activated. For ampuls, monitoring occurs more frequently to determine the number of fractures and the physical condition of the liquid. Fracturing is monitored because gas formation is a characteristic of electrolyte deterioration. Figure 1 shows the dimensions of cell and glass ampul.

The maximum adjusted storage times for the organic electrolyte ampuls is 6.4 years at a diurnal cyclic temperature, $32/71^{\circ}C$ (90 to $160^{\circ}F$). Predictions for this cyclic environment, based on Arrhenius plots, show that these ampuls will store without fracturing for 15 to 20 years. The Army storage requirement is a minimum of 10 years at the same environment. Figure 2 demonstrates an Arrhenius plot for machine manufactured ampuls. The median time at which 50% of an ampul lot fractures is chosen as the relative point of comparison between lots. The inorganic thionyl chloride electrolyte shows excellent storage capability with no ampul fracture after 4.1 years at the maximum $84^{\circ}C$ environment.

Figure 3 compares the yearly cell test results completed for the Li/V_2O_5 cells for two lots. The effect of reserve storage time on cell output is most pronounced at the $-43^{\circ}C$ ($-45^{\circ}F$) test temperature with an apparent maximum capacity loss of 40% from the baseline value. However, the output at high temperature discharge is relatively unchanged for cells having identical storage exposure meaning a true capacity loss has not occurred. Cell impedance change as a result of anode filming with outgassing materials during high temperature storage is considered the cause of the change. This is finite and will stop once all outgassing materials have been consumed.

The reserve $Li/SOCl_2$ cell shows excellent performance at both the cold and hot test temperatures after 3-year storage. Figure 4 presents the cell life values for two lots across the storage environments and shows the small deviation from baseline performance.

MATERIALS OF CONSTRUCTION

Metal Reservoir (Thionyl Chloride)

Stainless steel reservoirs are used in reserve $Li/SOCl_2$ batteries. Specific types of stainless steel most commonly utilized are 321 S.S. and 316L S.S. Presented below are evidences for the corrosion resistance of these materials to neutral (1.5M $LiAlCl_4/SOCl_2$) electrolyte when subjected to long term storage at elevated temperature ($71^{\circ}C$).

Electrolyte analysis for iron concentration by U.V. absorption techniques showed only a slight increase after 12-month storage at $71^{\circ}C$. SEM photomicrographs of the steel surfaces revealed the formation of a protective film which can either eliminate or reduce further material corrosion. The existence of this film is shown in Figure 5 for both 316L S.S. and 321 S.S. Additional SEM observations of the surfaces indicated film formation to be

more rapid during their initial period of storage and with the 321 S.S. exhibiting higher degree of corrosion (based on Fe analysis) than 316L S.S. Metallographic analysis of the specimens showed no visible corrosion into the specimens, thus rendering additional support to the presence of a protective film on the 321 and 316L stainless steel's surfaces when exposed to $SOCl_2$.

Glass-To-Metal Seal (TA-23 Glass)

Glass corrosion has been clearly identified as a failure mode in Li/SO_2 system but also exists in other systems such as Li/V_2O_5 and $Li/SOCl_2$ in varying degrees. The corrosion mechanism was found to involve underpotential disposition of lithium metal onto the glass initiating at the glass/metal interface maintained at the lithium potential. The corrosion process causes the glass to become conductive so that once the glass is traversed, a conductive path will cause the cell to self-discharge and deplete the remaining capacity. The path presented in this section will focus only on the Li/V_2O_5 system.

The magnitude of corrosion in Li/V_2O_5 system with 9013 glass has been estimated using the radial corrosion distance outward from the pin across the glass surface. Corrosion rates, based on the measured corrosion distance and the age of the cell, were calculated and correlated to the integrated average temperature over the life of the cell using an Arrhenius-type relationship. This is shown in Figure 6. Fitted equation was obtained using the least squares method. This equation can be used for predicting time to failure for existing cells. Non-accelerated cells noted in Figure 6 were cells stored between $4^\circ C$ and $57^\circ C$ for varied periods of time. Radial corrosion distance has been shown to be a viable means of quantitizing the magnitude of glass corrosion in Li/V_2O_5 cells.

An approach to resolving the glass corrosion in Li/V_2O_5 cells is to change the glass from 9013 to TA-23 developed by Sandia National Laboratories. Hardware with TA-23 glass was submitted to an accelerated test plan ($+71^\circ C$ storage); with cells removed weekly for a 7-week period. Each cell, after storage, was discharged and postmortemed. Results of the postmortems showed no sign of corrosion (Figure 7).

SUMMARY

A key benefit of lithium based battery systems is the capability to store over a wide temperature range for very long periods of time. There are many factors important to this capability and a major portion of research and development resources have and continue to be dedicated to the characterization and improvement of the long term stability of lithium systems. The three examples discussed herein offer positive consideration to this area.

o   Mine system cells and electrolytes in a 10-year scheduled program are providing good storage data after 4 and 3 years, respectively, so far.

o   Thionyl chloride electrolytes have been shown to be compatible with the stainless steels most often used in reserve battery reservoirs.

o   Glass corrosion can occur in Li/V_2O_5 systems with slightly less rapidit than in Li/SO_2 units. Sandia's TA-23 glass appears to be equally effective in solving the problem.

ACKNOWLEDGEMENTS

2.09 cm (.825")

.254 cm (.1")

.051 cm (.02")

1.65 cm (.65")

1.41 cm (.555")

1.27 cm (.50")

.878 cm (.346")

CELL

AMPUL

Figure 1. Cell and ampul used for long term storage
evaluations.
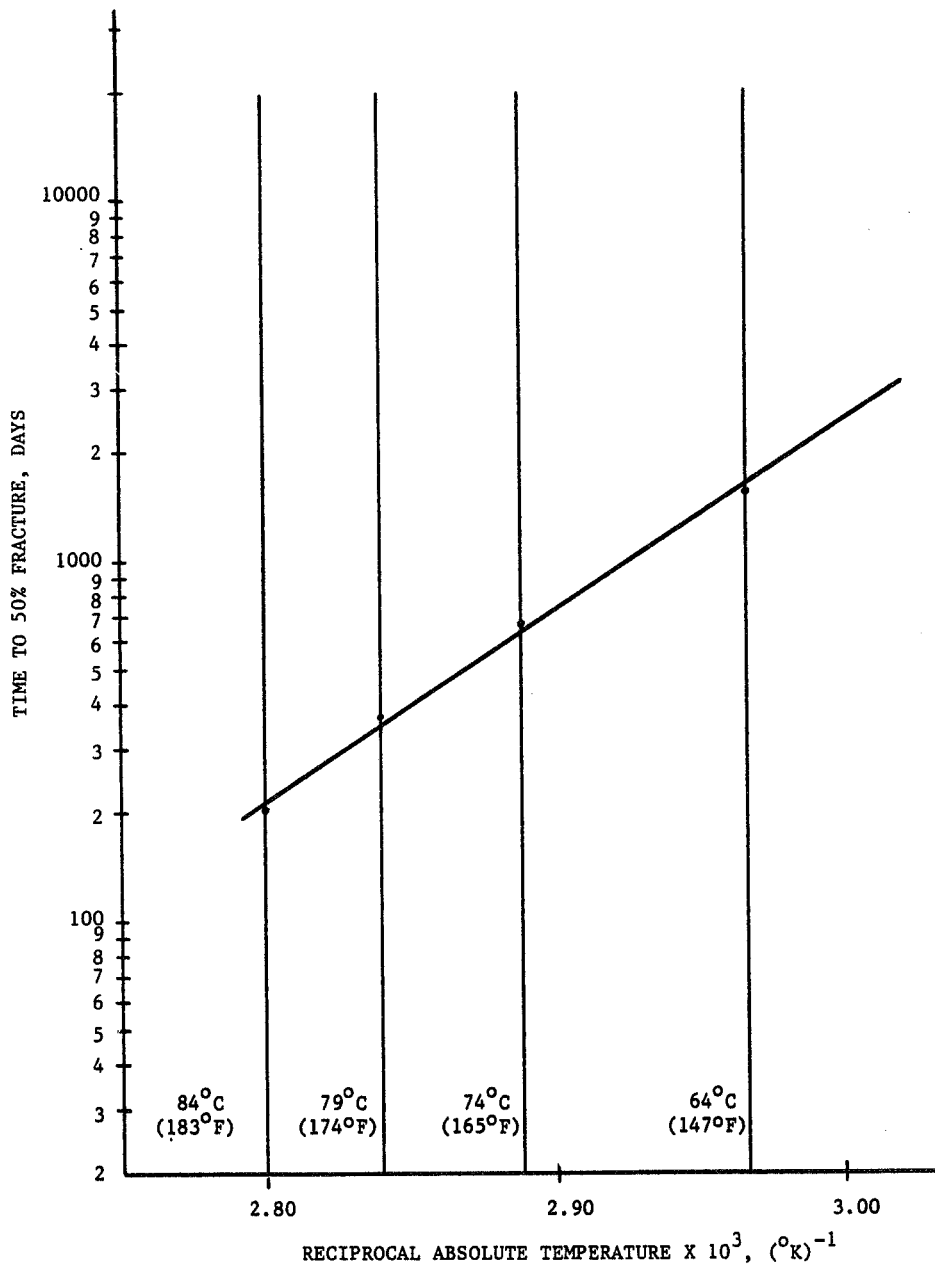
Figure 2. Arrhenius plot for machine
manufactured ampuls.

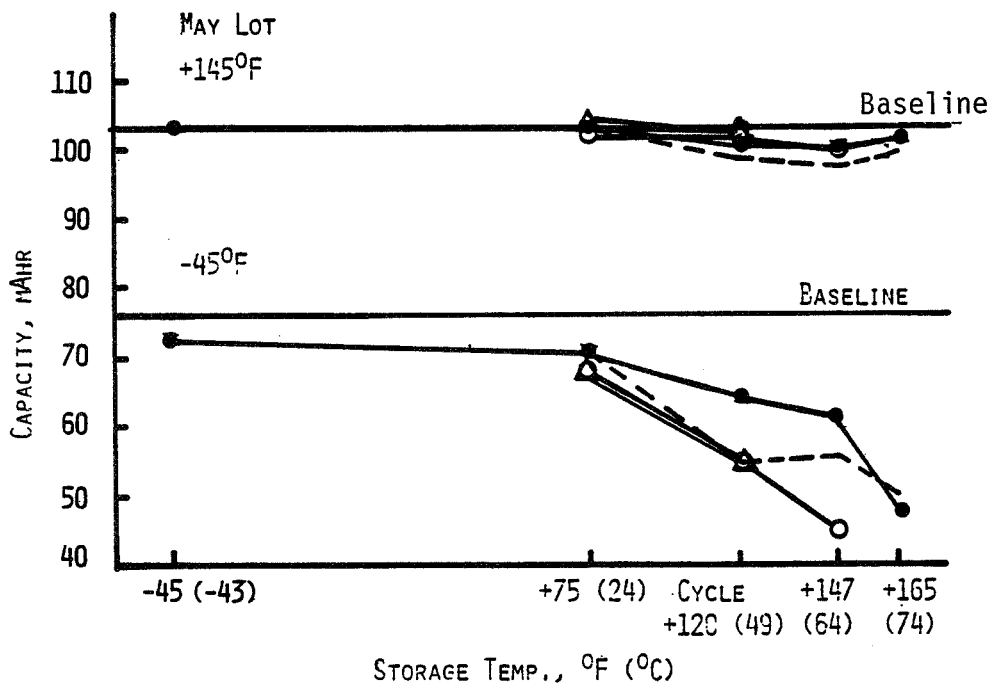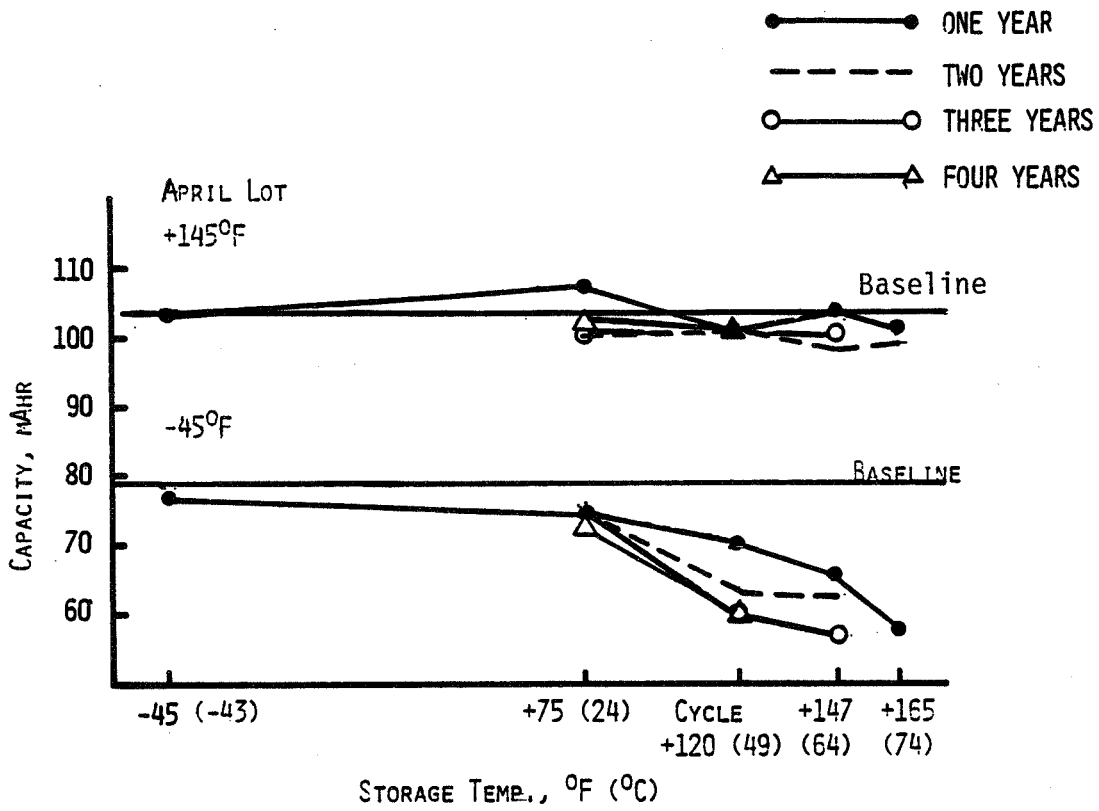Figure 3. Capacity vs. storage temperature for Li/V$_2$O$_5$ cells.

DISCHARGE LOAD 3.3K OHMS
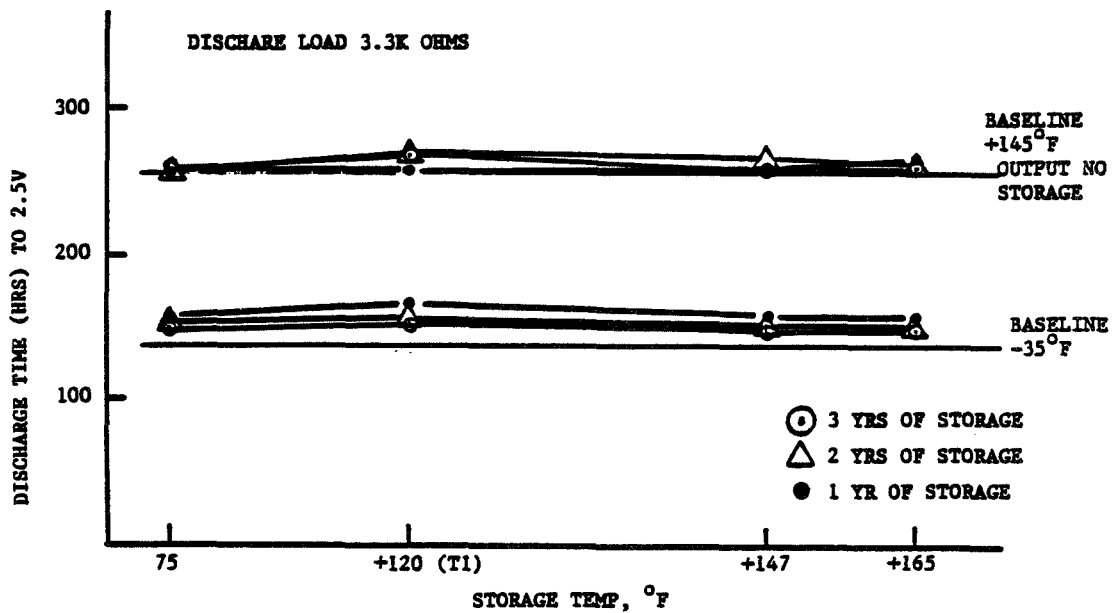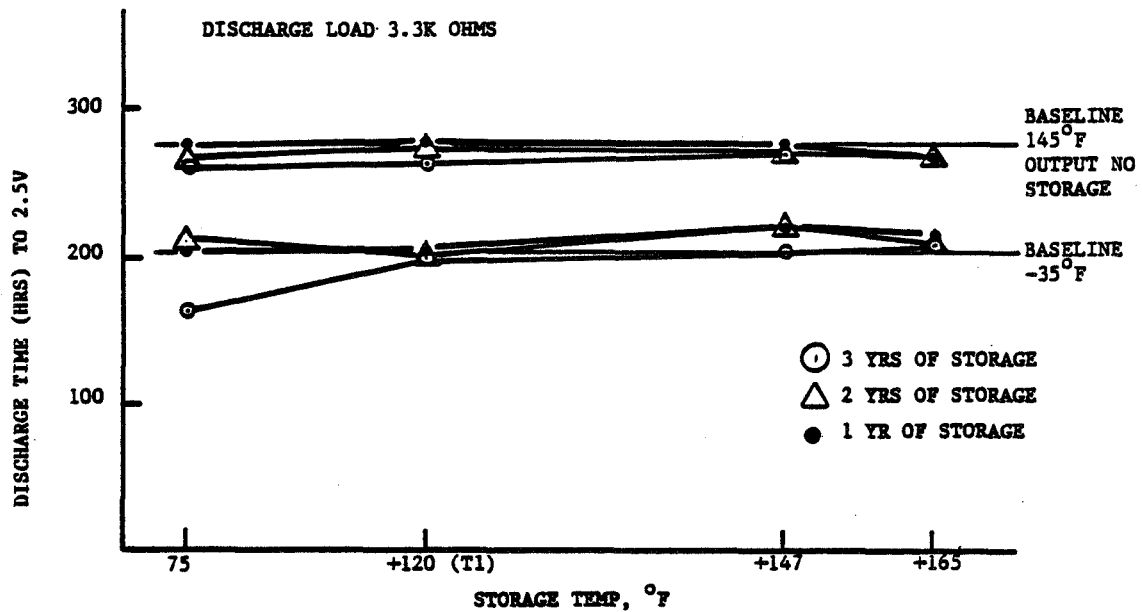
300

DISCHARGE TIME (HRS) TO 2.5V

200

100

75   +120 (T1)   +147   +165

STORAGE TEMP, °F

BASELINE
145°F
OUTPUT NO
STORAGE

BASELINE
-35°F

⊙ 3 YRS OF STORAGE
△ 2 YRS OF STORAGE
● 1 YR OF STORAGE

DISCHARE LOAD 3.3K OHMS

300

DISCHARGE TIME (HRS) TO 2.5V

200

100

75   +120 (T1)   +147   +165

STORAGE TEMP, °F

BASELINE
+145°F
OUTPUT NO
STORAGE

BASELINE
-35°F

⊙ 3 YRS OF STORAGE
△ 2 YRS OF STORAGE
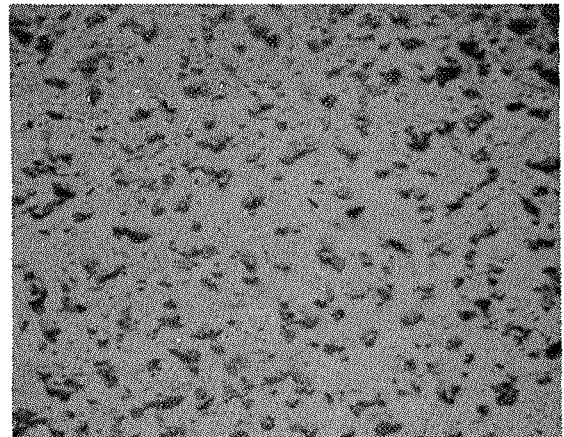● 1 YR OF STORAGE

Figure 4. Reserve cell run time to 2.5 volts vs. storage time and temperature (Li/SOCl$_2$ system).

321 S.S.   316L S.S.
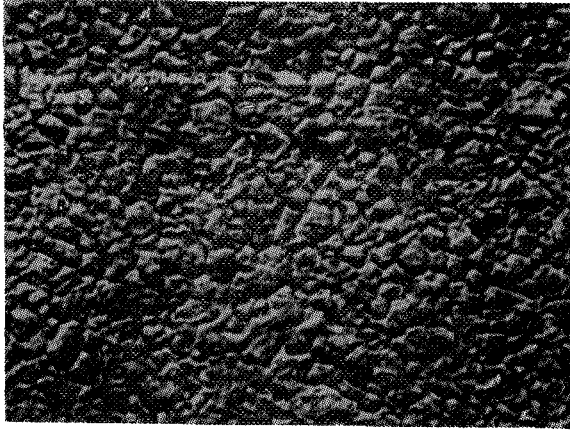
Before exposure to electrolyte

After exposure to electrolyte for 12 months at 71°C

Figure 5. SEM photomicrographs of the surfaces of 321 S.S. and 316L S.S. before and after exposure to the neutral electrolyte solution (1.5M LiAlCl$_4$/SOCl$_2$).

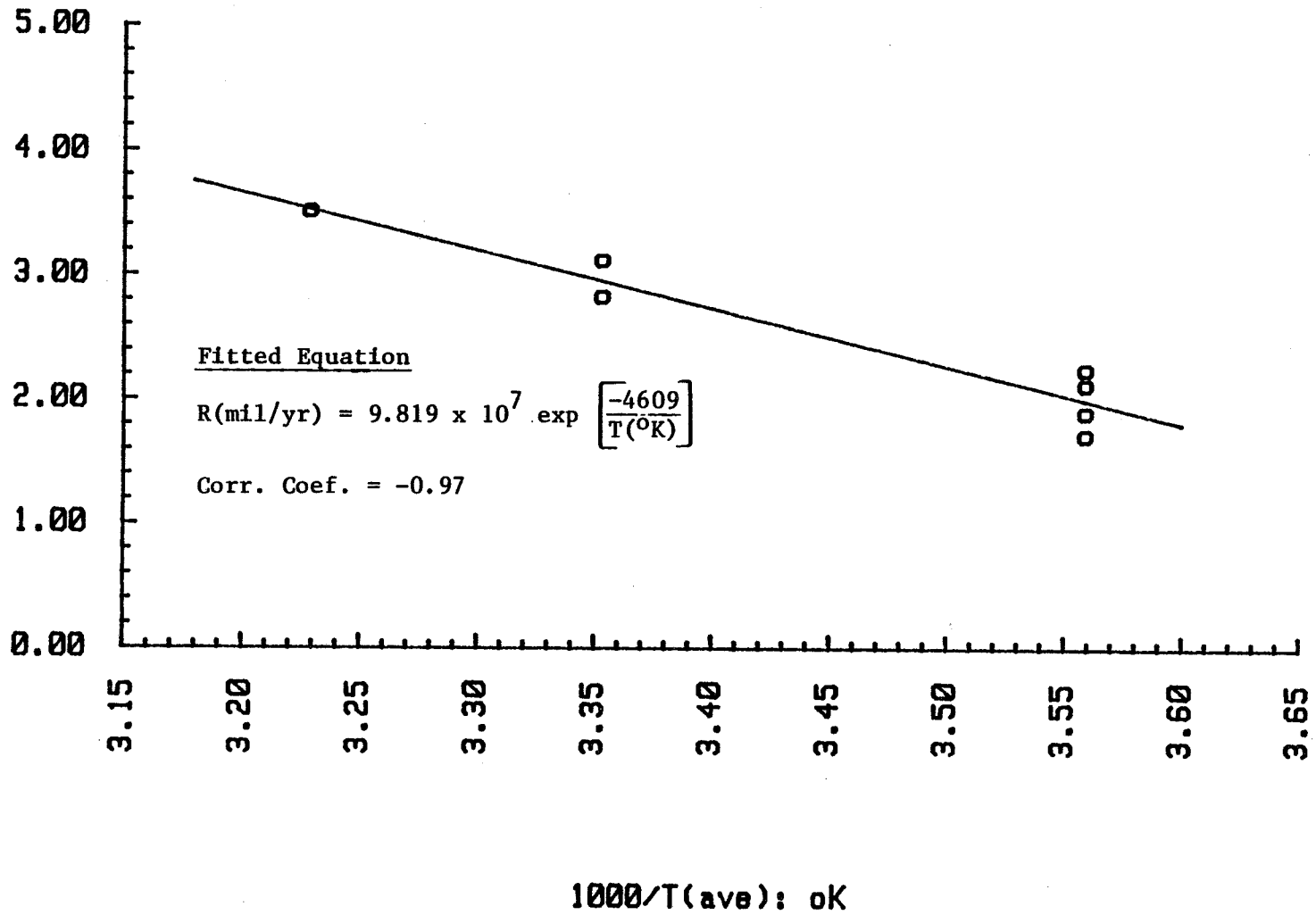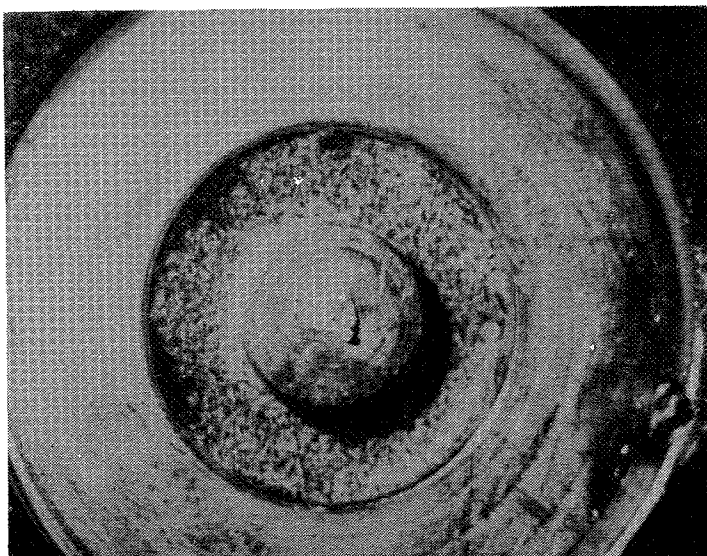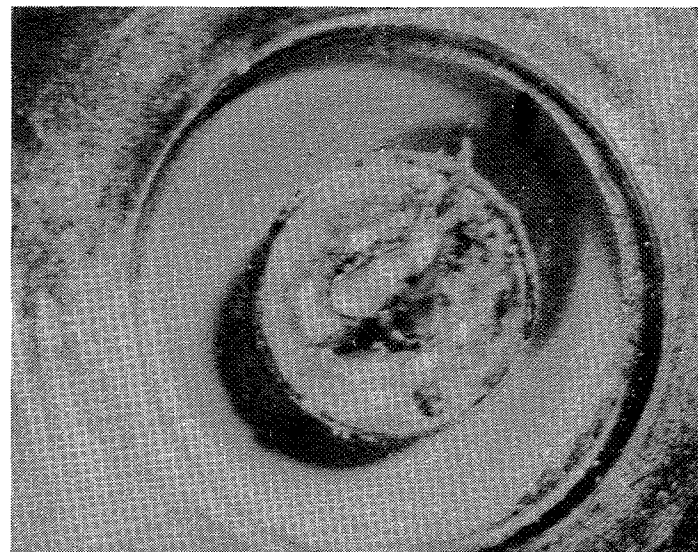Figure 6.   Arrhenius plot of corrosion data for nonaccelerated storage
cells incorporating type 9013 glass seals.

9013 Glass   TA23 Glass

Full Glass Corrosion   No Corrosion

Figure 7.   Comparison of 9013 glass and TA-23 glass after accelerated test for
            seven weeks at 71°C.   Li/V$_2$O$_5$ system.

Q. Barnes, NSWC: In your work with the ampules, you talk about no breakage. Is that on passive storage or is that after a period of vibration?

A. Chua, Honeywell: That's on passive storage. I should, however, mention that, as part of the analysis of the storage we also, once a month, withdraw a sample for ACM analysis.