CHARACTERIZATION OF OPEN CIRCUIT VOLTAGE AND CAPACITY AS A FUNCTION OF TIME

Paul W. Krehl and Russell C. Stinebring
Electrochem Industries
Div. of Wilson Greatbatch Ltd.

INTRODUCTION

Investigations were conducted to determine the effect of halogen/interhalogen addition on the performance characteristics of the Li/$SOCl_2$ inorganic system. As a result a high energy density battery system was developed: the Li/BrCl in $SOCl_2$ (Li/BCX) system.

The open circuit voltage (OCV) of the Li/BCX cell was found to be 3.90 ± .03V at 24 ± 3°C which is more than 0.2V higher than that of Li/$SOCl_2$ cells. One may speculate that the higher OCV is due to the presence of Cl_2 in solution resulting from a partial dissociation of BrCl. It was observed (ref. 1) that the addition of Br_2 in $SOCl_2$ also results in an increase in open circuit potential. The OCV of the Li/Br_2 in $SOCl_2$ cell was found to be 3.8V which is higher than either Li/$SOCl_2$ (3.6V) or Li/Br_2 (3.5V). It was speculated that the higher potential is due to the formation of a complex between Br_2 and $SOCl_2$. Similarly, a complex between BrCl and $SOCl_2$ should not be ruled out in the case of the Li/BCX cells.

Figure 1 shows a typical performance curve for fresh Li/BCX D cells discharged under a 10 ohm load. The cells exhibited a high voltage plateau during the initial stages of discharge and the load voltage decreased to a value of 3.5V after approximately 10% of the realized capacity of the cell was delivered.

During investigation into the discharge characteristics under pulsed load conditions it was observed that the open circuit potential of the cell changed as a function of delivered capacity. Figure 2 shows a comparison of the OCV and load voltage versus discharge time for cells subjected to a 0.25A constant current discharge at ambient temperature. The current was interrupted periodically so that the OCV could be determined. The initial OCV was 3.93V and decreased to approximately 3.67V after 12 hours of discharge. The load voltage profile is analogous to the OCV, i.e. the load voltage changes from 3.83 to 3.27V over the same period of time. The fall of the OCV closer to that of one expected for a Li/$SOCl_2$ cell suggests that in the initial few stages of discharge the concentrations of the more electroactive species are reduced.

Initial room temperature storage tests performed on twelve Li/BCX D cells showed that the OCV also varied with time. Figure 3 shows the relationship between OCV and time over a test period of 12,000 hours. The initial OCV was 3.92 ± .02V and decreased to a value of 3.75 ± 0.03V after storage for 8,000 hours at 24 ± 3°C. This corresponds to a rate of decrease in OCV of 0.02 ± .01V per thousand hours. No additional significant change in OCV was observed after 8,000 hours. For example, the values for the OCV after 12,300 hours were still approximately 3.75 ± .03V

In a separate experiment the open circuit potential of BrCl versus Li was determined. Benzonitrile was used as supporting solvent for the $LiAsF_6$ electrolyte, and BrCl was dissolved in the solution. An open circuit potential of 3.77V was observed. This corresponds well with the observed OCV for Li/BCX cell after long-term storage.

The observed behavior of the open circuit potential of the Li/BCX cell with respect to both storage time and depth of discharge suggests that there may be a relationship between the OCV and cell performance. A test program was initiated in this laboratory to observe the effects of long-term room temperature storage on both the open circuit potential and cell capacity, and to determine if there was any correlation between the two parameters.

TEST PROCEDURE

Approximately 350 Li/BCX D cells were stored under room temperature conditions. An initial OCV measurement was taken two weeks after the date of manufacture and subsequent measurements were taken on a monthly basis. At each measurement period a group of 10-12 cells representing the full distribution of observed open circuit potentials was analyzed for capacity retention. The test cells were discharged under 10 ohm loads at room temperature. The load voltage measurements were taken through the use of a timed sequential electrometer coupled with a Hewlett-Packard (HP85) computer. The realized capacities were obtained to a 2V cutoff. The OCV was measured with a Keithley (Model 177) electrometer.

RESULTS AND DISCUSSION

A plot of the OCV versus time for approximately 350 Li/BCX D cells stored under ambient temperature conditions is presented in Figure 4. The average OCV for fresh cells (2 weeks old) was found to be 3.938. However, as the storage time increased the OCV gradually decreased until after approximately one year the average OCV was 3.783V. The results shown in Figure 4 also emphasize the variability in the open circuit potential at each specific measurement interval. Initially the open circuit voltages are grouped in a very narrow band ranging from 3.922 to 3.945 volts. However, the spread in the open circuit potential values continually increased to a range of 3.755 to 3.876 volts after one year of storage at room temperature. Comparing the data obtained from the original Li/BCX D cells stored for 12,300 hours to that obtained in this investigation, it may be speculated that the spread in the OCV values may begin to narrow as the actual open circuit potentials level at approximately 3.75 volts.

After each OCV measurement was taken, twelve samples were selected for rundown so that the original OCV distribution observed in the D cell population was not distorted. The cells were discharged under a 10 ohm load at room temperature. The results of the constant load discharge are presented in Figure 5. For fresh cells discharged under 10 ohm loads very little variability in realized capacity exists (14.45 ± 0.45 Ah). However, cells subjected to longer storage periods exhibit a lower realized capacity and a greater variability in cell performance. For example, the average realized capacity for cells stored 7 weeks was approximately 13.2 ± 1.5 Ah. The capacity for cells discharged after a storage period of 26 and 51 weeks showed a slight decrease in capacity (13.1 ± 1.4 and 12.4 ± 1.3 Ah respectively), but were not significantly different from the cells discharged after 7 weeks.

These test results show that both the cell open circuit voltage and cell capacity decrease with increasing storage duration. However, no correlation was immediately evident between the two parameters. The OCV and discharge data shown in Figures 4 and 5, respectively, were compared at individual time intervals to determine if the realized capacity was a function of the observed OCV. It was noted that cells that exhibited open circuit voltages at the extreme ends of the observed range could deliver nearly identical capacities. For example, cells stored for a period of 30 weeks showed a range in OCV of 3.914 to 3.790 volts. A particular cell that exhibited an OCV of 3.79V delivered 13.8 Ah to a 2.0V cutoff. Similarly, a cell with an OCV of 3.89V delivered 13.4 Ah.

Examination of a plot of OCV versus cell capacity (Figure 6) shows that in general cell capacity data is scattered over a wide range of open circuit potentials. It can be seen that cells with an OCV of 3.90V produced capacity values between 14.6 and 11.5 Ah. Similarly, cells with an OCV of 3.80V exhibited a range in realized capacity of 13.8 to 11.7 Ah.

SUMMARY AND CONCLUSIONS

It is noted from the data presented above that Li/BCX cells lose approximately 8% of their rated capacity in the first 2 months of storage. After this period of time, little difference is noted in the average realized capacity; however, a significant increase in the range is observed. Over the same period of time the OCV falls at a rate of 0.02V per 1,000 hours. After a period of 8,000 hours the OCV appears to stabilize at a value of approximately 3.75V. This may be related to changes in Cl_2 concentration due to self-discharge or other reactions. These data indicate that no correlation exists between the reduced open circuit voltage and the realized capacity.

REFERENCES

1. C. C. Liang, A New High Energy Density Lithium Battery System, Digest of the Combined 12th Int. Conf. on Medical and Biological Engineering and 5th Int. Conf. on Medical Physics, Part I (Aug. 1979) Paper 1.6.

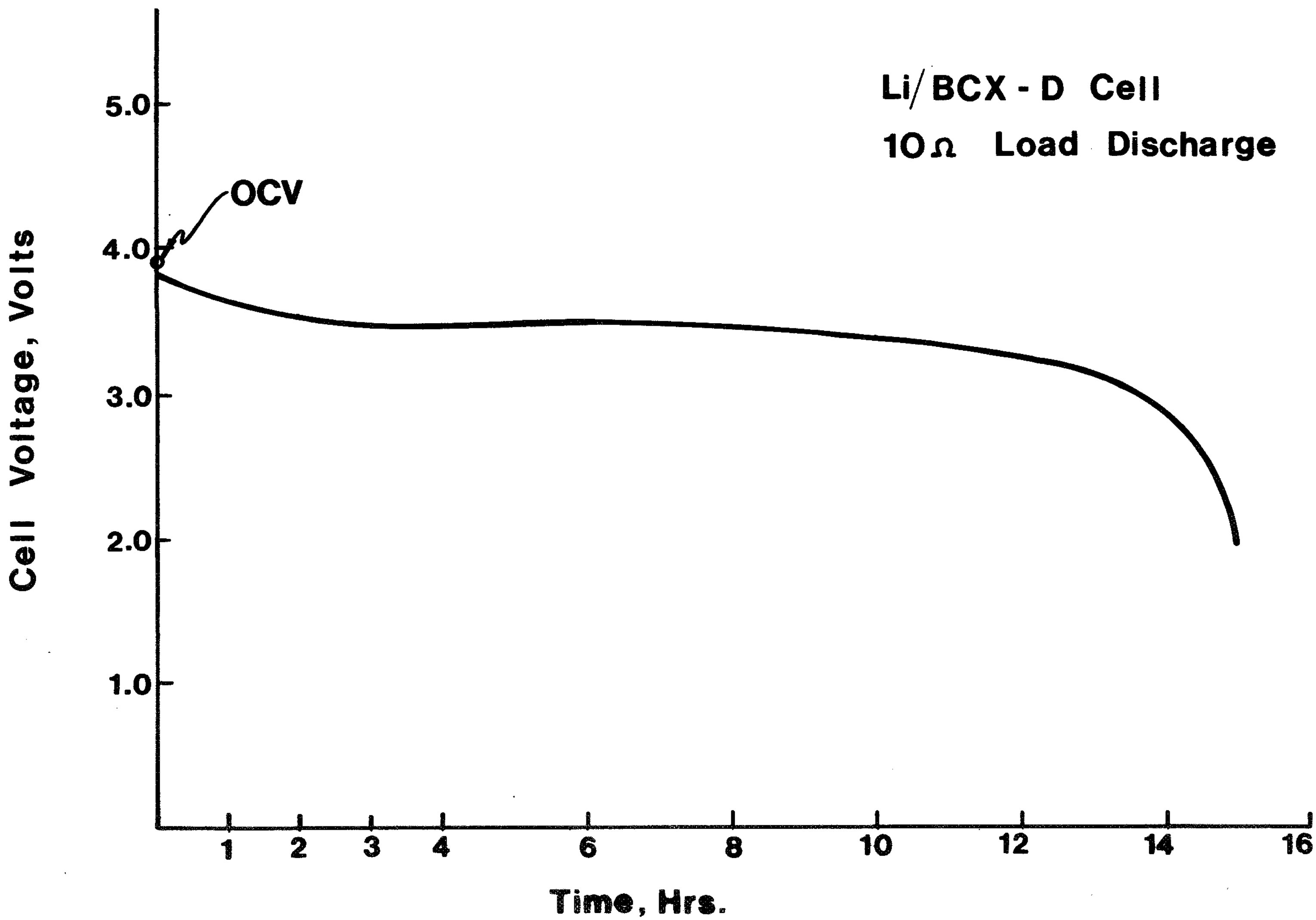

Figure 1. Typical constant load discharge characteristics for fresh Li/BCX D cells at room temperature.

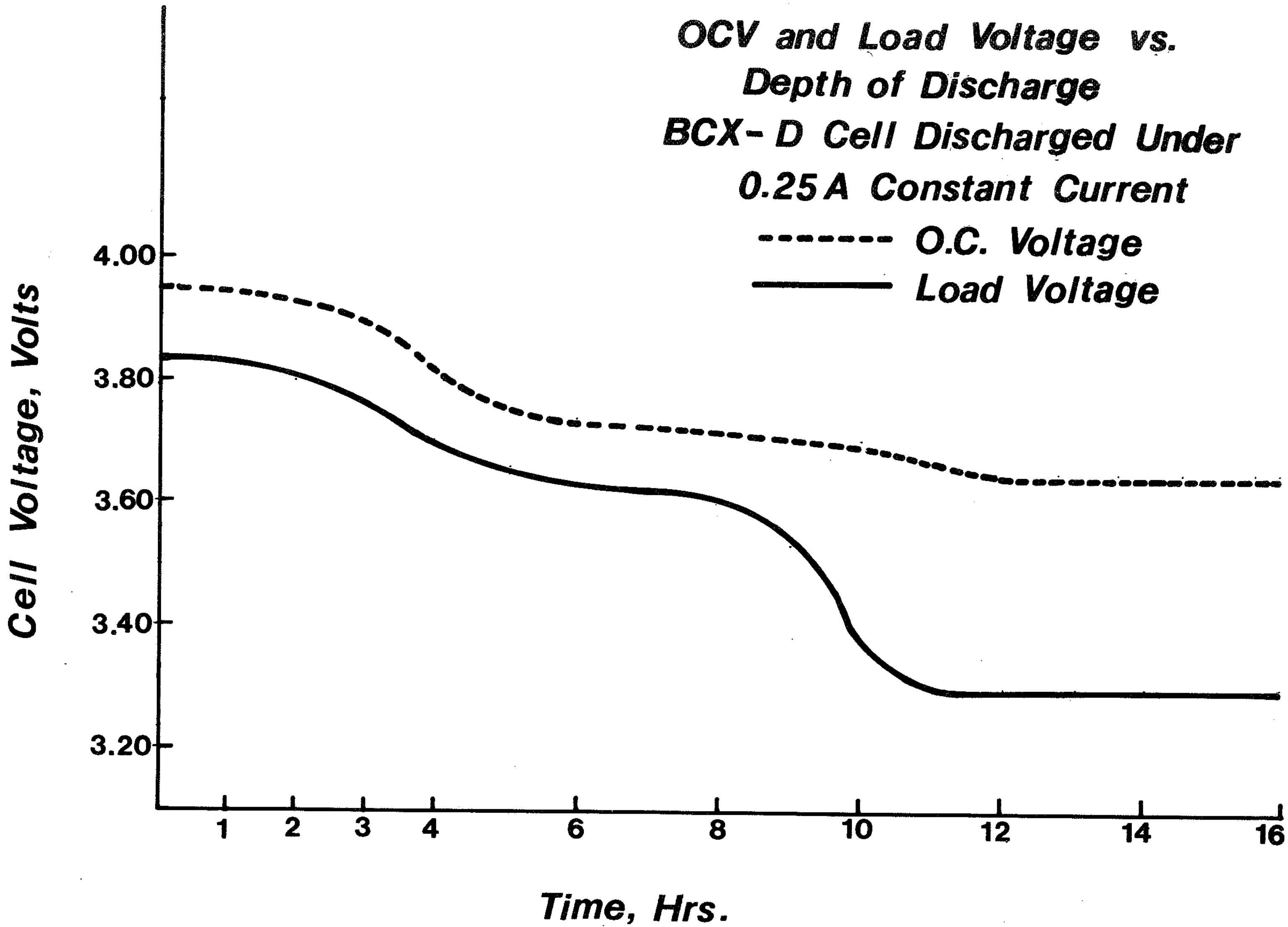

Figure 2. Comparison of the OCV and load voltage to discharge time under 0.25A constant current conditions.

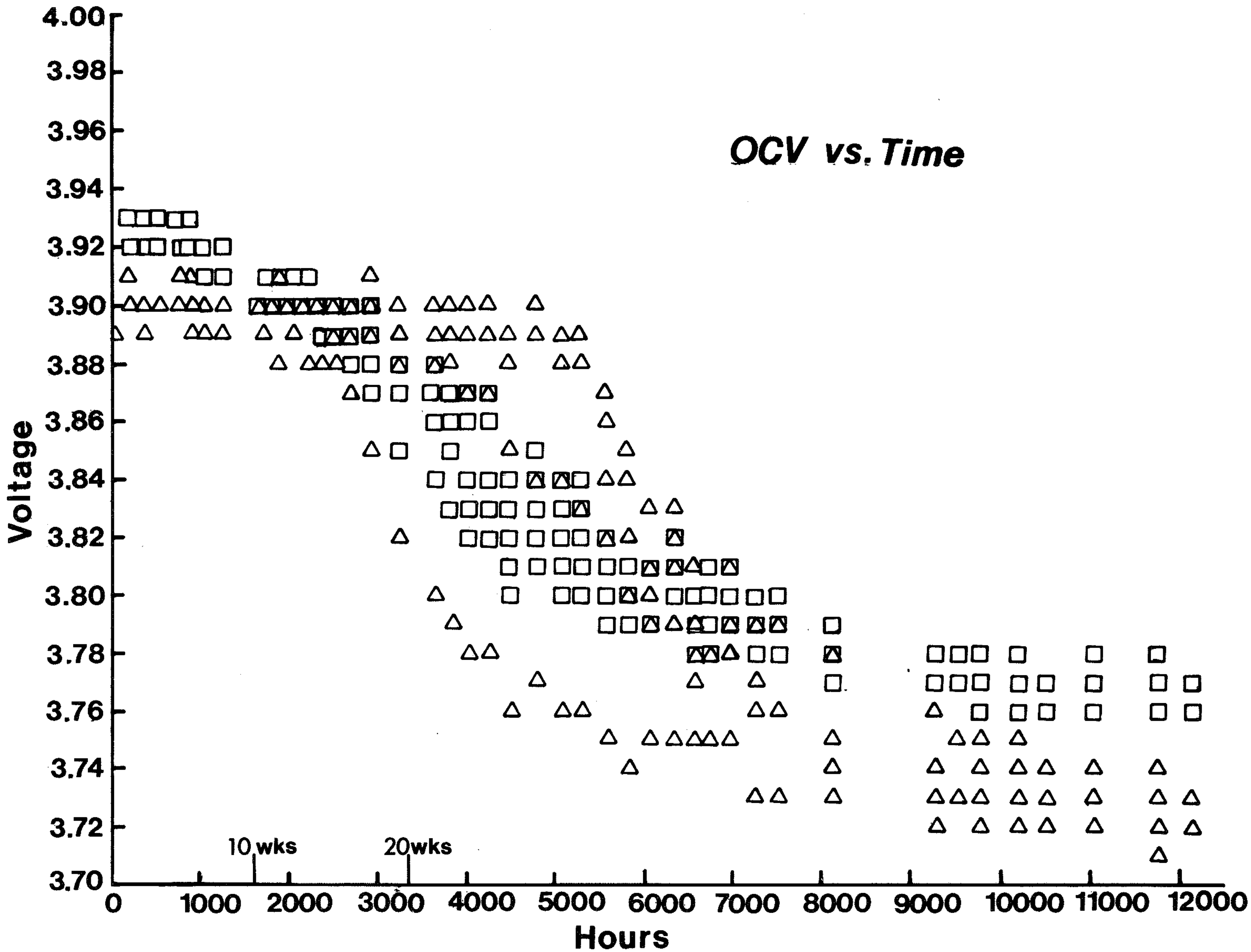

Figure 3. Comparison of the OCV to time under room temperature storage conditions.

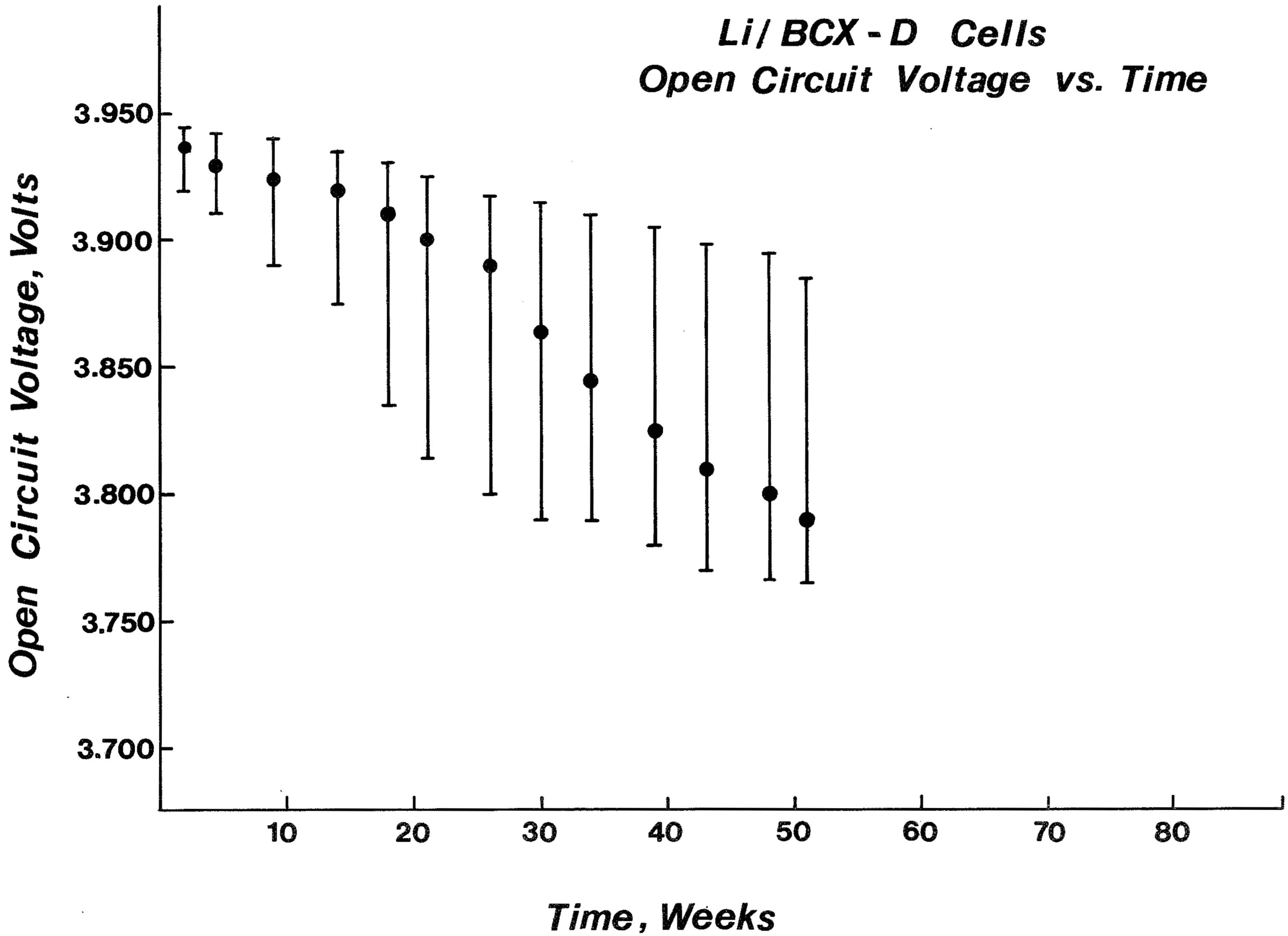

Figure 4. The average and range of measured open circuit potentials as a function of storage time.

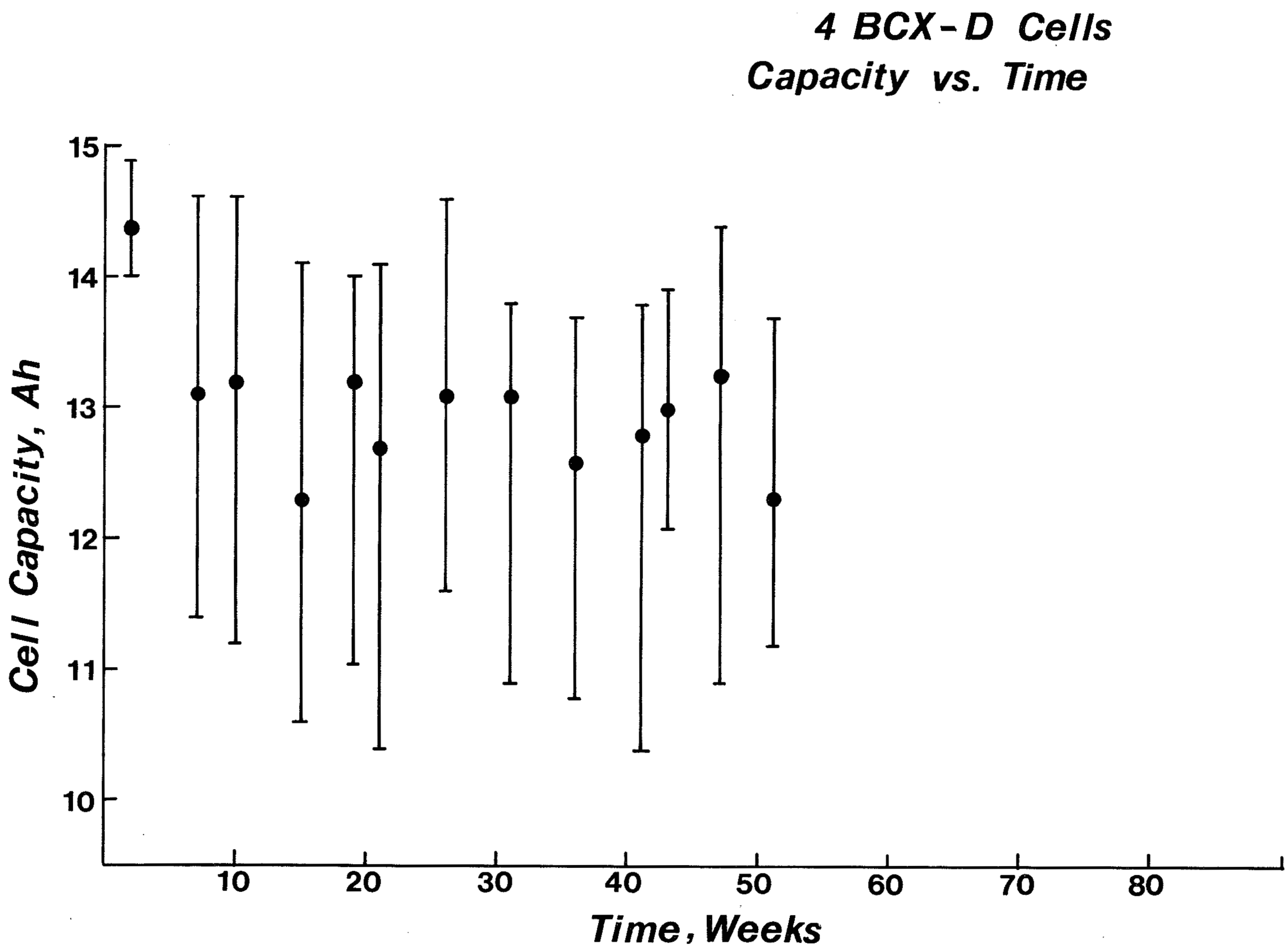

Figure 5. The average and range of realized capacities of cells discharged under 10 ohm loads as a function of storage time.

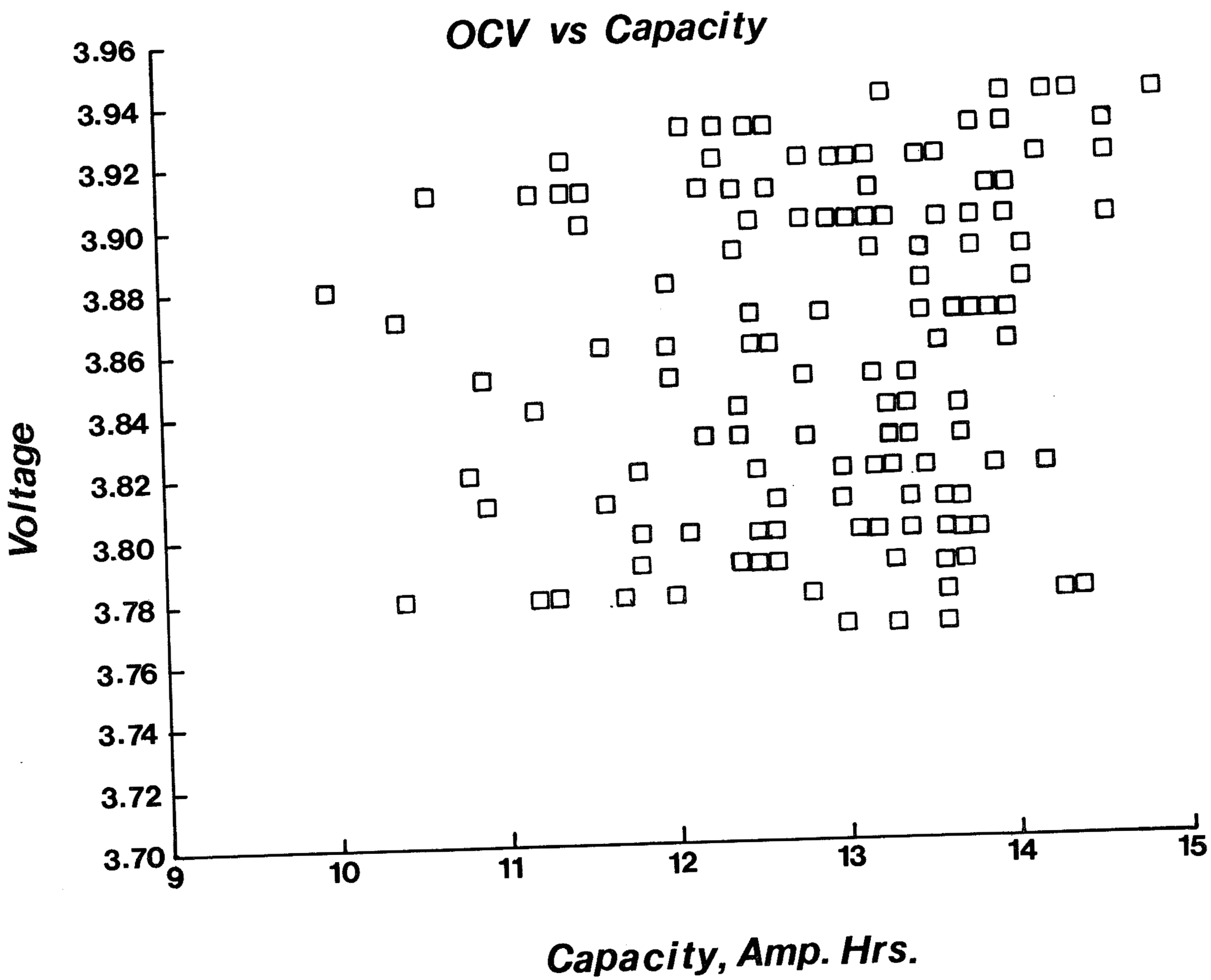

Figure 6. Comparison of OCV to realized capacity for cells stored for various periods of time under room temperature conditions.

Q. Kunigahalli, Bowie State College: Would you please tell me the mechanism that is causing the plateau? Is it the anode or the cathode or what may be the reaction?

A. Krehl, Wilson Greatbatch Ltd.: The high voltage plateau?

Q. Kunigahalli, Bowie State College: The low voltage plateau. I saw in one of the viewgrafts you showed the discharge curve showing the plateau - lower voltage plateau?

A. Krehl, Wilson Greatbatch Ltd.: Well, we think that's just the base solvent after any of the dissociation products are depleted and we get to the actual load voltage that the cell is going to see. The cell actually is cathode limited.

Q. Yen, JPL: You mentioned about the high open circuit voltage of over 3.9 volts due to the addition of PCX. Okay, over the standing and the cell voltage decline. Have you done any post-mortum analysis correlating the PCX content - the voltage decline and the capacity decline. Do you know anything about the chemistry?

A. Krehl, Wilson Greatbatch Ltd.: I'm sorry to say we really haven't done too many studies with respect to that. Some of our work was done with the cell. And the BRCL actually showed a peak I think it was actually 3.85 and as the cell discharged we could see that peak gradually decrease and we got a increase in a peak at about 4.15 which corresponded to bromine - free bromine. So it appeared that, if there was some dissociation there and giving free chlorine, we are depleting that and shifting things down to bromine, but we really haven't done too much in the way of studies there.

Q. Yen, JPL: Have you done any measurement about the dissociation constant of PCX and the correlation of the concentration of PCX use related to the voltage decline?

A. Krehl, Wilson Greatbatch Ltd.: We got a dissociation constant from now. It was in a non-polar solvent and it was .38. That, when we calculated out how much free chlorine and free bromine would be in a cell. We came up with the discharge curve showing about 70% of that capacity would be under those initial high voltage plateaus and then the rest would discharge under the lower plateau.