

ADVANCES IN RECHARGEABLE LITHIUM MOLYBDENUM DISULFIDE BATTERIES

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INTRODUCTION

Considerable effort has been focused in recent years on the development of rechargeable ambient temperature lithium batteries. This effort has been spurred by the expectation that such batteries would have many of the desirable characteristics associated with non-rechargeable lithium batteries. These characteristics include high gravimetric energy density (energy per unit weight) volumetric energy density (energy per unit volume) and long charge retention times (10 years or more).

The major obstacle to overcome in the development of secondary lithium batteries has been the development of a reversible anode. A secondary obstacle has been the development of a low cost, high discharge rate cathode. Significant progress has been made in overcoming these obstacles with the development by Moli Energy Limited of the lithium molybdenum disulfide system.

The energy density of the lithium molybdenum disulfide system as manifest in practical cells is substantially higher than that of other rechargeable systems. In the first state of development the volumetric energy density of the lithium molybdenum disulfide system is approximately 50% higher than that of state-of-the-art Nicad and proportionately higher than that of sealed Pb-acid. With recent advances of the system, the energy density can be improved to the point where the volumetric energy density advantage over Nicad is greater than 100%. The charge retention capability of the system has also proven to be excellent, with a charge retention time in excess of 8 years.

The characteristics of the lithium molybdenum disulfide system are ideally matched to the power requirements of devices where light weight and low volume are of concern, particularly where they are subject to intermittent use with long interspersed standby periods when the device is not connected to a primary power source.

In this paper are presented some of the advances in the performance characteristics of 'C' size cells that have been made during the past year with a new electrolyte formulation. The characteristics of 'C' cells with the previous electrolyte formulation have been published elsewhere ¹⁾ and can be summarized as follows:

HIGH ENERGY DENSITY

The energy density of a 'C' size cell is in the range of 60 to 65 watt hours per kilogram at a discharge rate of 800 milliamperes. At rates of less than 100 milliamperes, the energy density is increased to about 70 watt hours per kilogram.

HIGH RATE CAPABILITY

Sustained drain rates of 5 amperes at a cell voltage between 2.3 volts and 1.3 volts can be obtained at 21° C.

INHERENT SAFETY BELOW 110° C

Electrical, mechanical and thermal abuse tests have shown the 'C' size cell to be resistant to venting or rupture for cell temperatures below 110° C. These tests are described in a separate article ²⁾.

WIDE AMBIENT TEMPERATURE OPERATING RANGE

Sustained drain rates of at least 1 ampere, with a cell voltage above 1.3 volts, can be maintained at temperatures from -12° C to 70° C.

CHARGE RETENTION CAPABILITY

The 'C' size cells have a charge retention time in excess of 8 years.

STATE OF CHARGE INDICATOR

The open circuit voltage of a cell decreases approximately linearly with increasing depth of discharge. This provides a simple and reliable state-of-charge indication.

HIGH ELECTRICAL EFFICIENCY

The overall round trip energy efficiency for a 'C' size cell at a discharge rate of 800 milliamperes and a charge rate of 250 milliamperes is in excess of 90%.

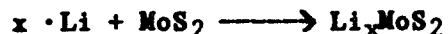
LEAKPROOF CONSTRUCTION

The 'C' size cells are hermetically sealed and no leakage or gassing should occur during either storage or normal usage. The cell contents are unpressurized.

CELL CHEMISTRY AND DESIGN

The lithium molybdenum disulfide system utilizes a lithium metal anode and a molybdenum disulfide cathode. The molybdenum disulfide, obtained

as a naturally occurring mineral is processed so as to alter its crystal structure to allow reversible intercalation, or dissolution of lithium within the crystal lattice. The discharge reaction for the system is thus represented as follows:



The ratio of lithium in the cathode material, denoted by x , can vary from about 0.2 to about 1.0.

Proprietary concepts have been developed at Moli Energy Limited which allow the recharge reaction



to proceed whereby the lithium dissolved in the cathode material is extracted and lithium is plated, in a smooth fashion, back on to the lithium metal anode. The advanced cell chemistry utilizes a new electrolyte formulation which improves lithium plating and the kinetics of discharge and charge reaction over cells with the previous electrolyte formulation.

The 'C' size lithium molybdenum disulfide cell is constructed in a spirally wound format. The cathode is electrically connected to a central mandrel which in turn is attached to the centre terminal of the cell. The electrodes are separated by a microporous polymeric separator. The total geometrical surface area of each electrode is about 750 square centimeters.

The cell is hermetically sealed utilizing welded construction and a glass-to-metal seal. Two safety vents are incorporated into the cell to allow for the controlled release of excessive pressure should the cell be subject to extreme abusive conditions. The vents are coined at both ends of the cell case.

DYNAMIC PERFORMANCE OF 'C' CELLS

A number of standard tests have been devised to evaluate the performance of the 'C' size and other molybdenum disulfide cells. These include a charge and discharge profile test, standard cycling tests and discharge rate capability tests. Test results of advanced 'C' cells are given in this paper.

A typical charge/discharge voltage profile is shown in Figure 1. In this case the 'C' cell was discharged at 840 milliamperes to a voltage cutoff of 1.3 volts and charged immediately following the discharge at 280 milliamperes to a voltage cutoff of 2.4 volts. This charge/discharge sequence defines one standard cycle. The profile

given is for the tenth such cell cycle. Under these conditions the voltage profile is independent of the two electrolyte formulations used. The round trip energy efficiency as calculated from the results shown in Figure 1 is about 92%.

A standard cycling test is defined by a sequence of standard cycles which are performed without time lag. This test is continued until the cell capacity falls to a preselected capacity value.

Generally the delivered capacity falls gradually with increasing number of cycles: there is no precipitous loss in capacity which defines end of life. The failure mode of the cells is a gradual increase in cell impedance with an increasing number of cycles. The capacity of a typical 'C' cell as a function of cycle number under the standard test conditions is shown in Figure 2. The cycle life of cells with advanced electrolyte formulation is twice or more that of cells with the previous electrolyte formulation.

Figure 3 shows the capacity of 'C' cells as a function of cycle number for two different depths of discharge. The depth of discharge is reduced by narrowing the voltage range on cycling. Data presented here are of cycling tests which are still in progress.

The standard discharge rate capability test is conducted as follows. A cell is charged at 280 milliamperes until the cell voltage reaches 2.4 volts. The cell is then discharged at the highest discharge rate at which the delivered capacity of the cell is to be measured. The discharge is terminated when the cell voltage on discharge falls to 1.3 volts. The cell is then rested on open circuit for a time equal to that of the just completed discharge. The cell is then further discharged at a discharge rate, equal to one half of the rate on the previous discharge again until the cell voltage falls to 1.3 volts. The delivered cell capacity at this lower rate is then taken to be the sum of the discharge capacities for the two discharges. The cell is then rested again for a period of time equal to the total elapsed time from the beginning of the first discharge, and the cell is discharged at one quarter of the initial discharge rate. The delivered cell capacity at this rate is then taken to be the sum of the capacities of the cells for all discharges undertaken since the cell was charged. The process is repeated until the discharge rate has been reduced successively by one half until the realized capacity at the lowest rate desired has been measured. This procedure has been found to give equivalent results to those obtained when the cell is fully charged before each discharge at the desired rates or to those obtained when matched fully charged cells are discharged at different rates. The deliverable 'C' cell capacity as a function of drain rate for environmental temperatures of 22°C, -20°C, and -30°C is shown in Figure 4. The cell is capable for sustained discharge currents in excess of 5

amperes at room temperature, in excess of 1 ampere at -20°C , and .5 amperes at -30°C , respectively. This represents a substantial increase in low temperature rate capability over cells using the previous electrolyte formulation.

The advanced electrolyte formulation enables a larger capacity to be realized from the 'C' cells because the cells can be charged to a higher voltage, and discharged to a lower voltage than can cells with the previous electrolyte. This is possible because of the improved kinetic stability of the electrolyte. During discharge, the open circuit voltage varies between 2.5 volts for a fully charged cell and 1.1 volts for a fully discharged cell. The 'C' cell will deliver 3 ampere hours on its initial cycle when cycled in this way, and will deliver in excess of 2 ampere hours even after 150 deep cycles. A modified cycle life test similar to the standard cycle life test was performed on these cells, but where the voltage for termination of charging is 2.6 volts rather than 2.4 volts as it is for the standard test, and the voltage for termination of discharge is 1.1 volts rather than 1.3 volts as it is for the standard tests. The charge and discharge currents used were identical to those used in the standard test. The realized capacity of a cell as a function of cycle number for the modified test is shown in Figure 6. The energy density of the 'C' cell with improved electrolyte using the extended voltage range is about 90 watt hours per kilogram.

The effect of environmental temperature on discharge voltage profiles for cells cycled over the extended voltage range is shown in Figure 7. At a temperature of -10°C , a capacity in excess of 2 ampere hours can be achieved when the cell voltage is allowed to drop to .9 volts.

The effect of various discharge currents on the cell voltage profile is shown in Figure 8. Discharge currents of 10 amperes can be sustained for more than 9 minutes corresponding to a cell capacity of 1.6 ampere hours before the cell voltage drops to .9 volts. This increased rate capability is due to the change in electrolyte which has caused the a.c. impedance of the cell measured at a frequency of 1 Hertz to drop from a value of 80 milliohms to about 60 milliohms.

OTHER PERFORMANCE ATTRIBUTES

The lithium molybdenum disulfide cells with the improved electrolyte formulation have proven to be very stable on open circuit stand. Although direct measurements of charge retention times have not yet been completed, microcalorimetric techniques have been used to compare charge loss rates of cells with the advanced electrolyte formulation with cells of the previous chemistry. The charge loss rate is projected to be less than 8% per year.

Electrical, mechanical, and thermal abuse tests, are being performed to establish the range of safe operation for cells with the advanced electrolyte formulation and the improved vent system. Experiments conducted so far show improved safety characteristics.

CONCLUSION

The lithium molybdenum disulfide system as demonstrated in a 'C' size cell, offers attractive performance characteristics for applications where light weight and low volume are important. A gravimetric energy density of 90 watt hours per kilogram can be achieved in a 'C' size cell package. The combination of excellent charge retention capabilities, high energy density and a state-of-charge indicator in a rechargeable cell provides an ideal power package for a wide range of devices. The system overcomes the 'memory' effect in Nicads where the full capacity of the battery cannot be utilized unless the full capacity of the battery was utilized on previous cycles. The development of cells with an advanced electrolyte formulation has led to an improved rate capability especially at low temperatures and to a significantly improved cycle life.

REFERENCES

- 1) J.A.R. Stiles, Lithium - Molybdenum Sulfide Secondary Cells, Progress in Batteries and Solar Cells, Volume 5, 1984, page 52.
- 2) K. Brandt, D. Fouchard, J.A.R. Stiles, Safety Aspects of a Rechargeable Lithium C Cell, Proc. 31st Power Sources Symposium, May 1984, Cherry Hill, N.J. (in press)

FIGURE CAPTIONS

- Figure 1 - Charge/discharge profile for a 'C' cell cycled in the standard voltage range. Charge current 280 mA, discharge current 840 mA. Cell at cycle number 10.
- Figure 2 - Capacity vs. cycle number for a 'C' cell cycled in the standard voltage range. Charge current 280 mA, discharge current 840 mA.
- Figure 3 - Capacity vs. cycle number for 'C' cells cycled to different depths of discharge.
1: Cell cycled between 2.2V and 1.6V
2: Cell cycled between 2.2V and 1.8V
- Figure 4 - Capacity vs. discharge current for three different temperatures. 'C' cell at cycle number 10.
- Figure 5 - Charge/discharge profile for a 'C' cell cycled over the extended voltage range. Charge current 280 mA, discharge current 840 mA. Cell at cycle number 1.
- Figure 6 - Capacity vs. cycle number for a 'C' cell cycled in the extended voltage range. Charge current 280 mA, discharge current 840 mA.
- Figure 7 - Discharge profiles for 'C' cells at three different temperatures at a current of 840 mA. Charged at 280 mA to 2.6 V. Cell at cycle number 1.
- Figure 8 - Discharge profiles for 'C' cells for various discharge currents. Charged at 280 mA to 2.6 V. Cell at cycle number 1.

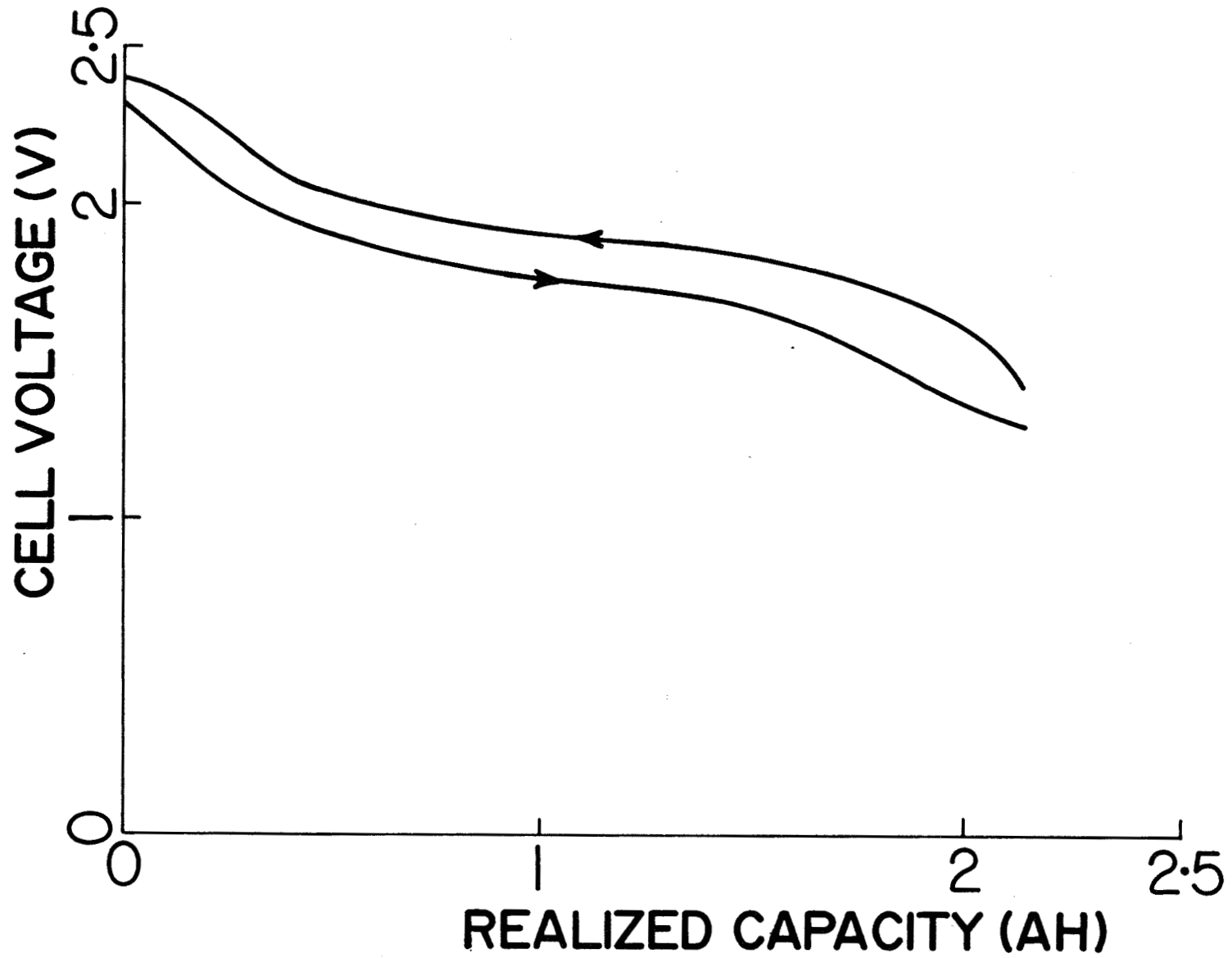


Figure 1 - Charge/discharge profile for a 'C' cell cycled in the standard voltage range.
Charge current 280 mA, discharge current 840 mA. Cell at cycle number 10.

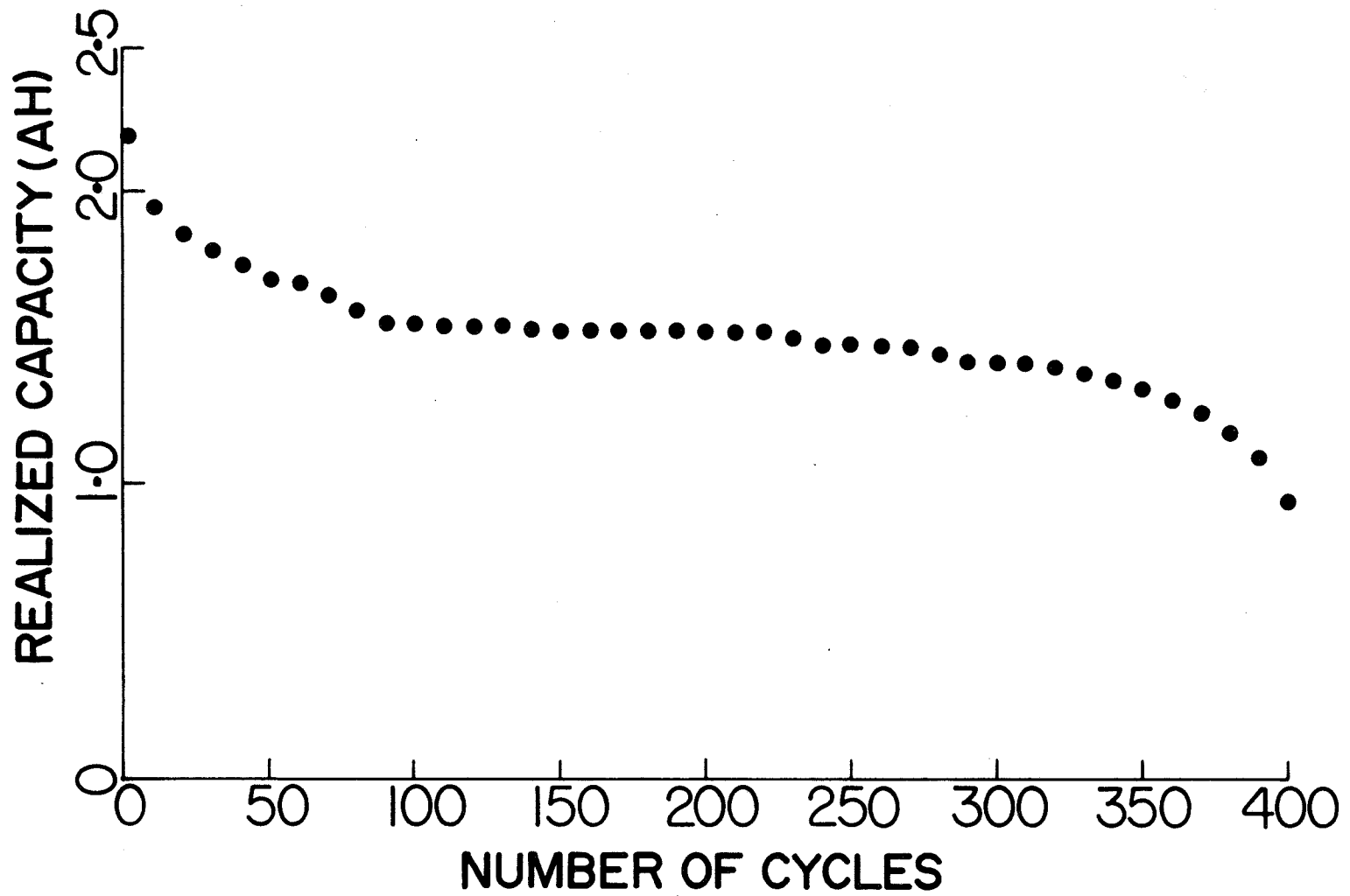


Figure 2 - Capacity vs. cycle number for a 'C' cell cycled in the standard voltage range.
Charge current 280 mA, discharge current 840 mA.

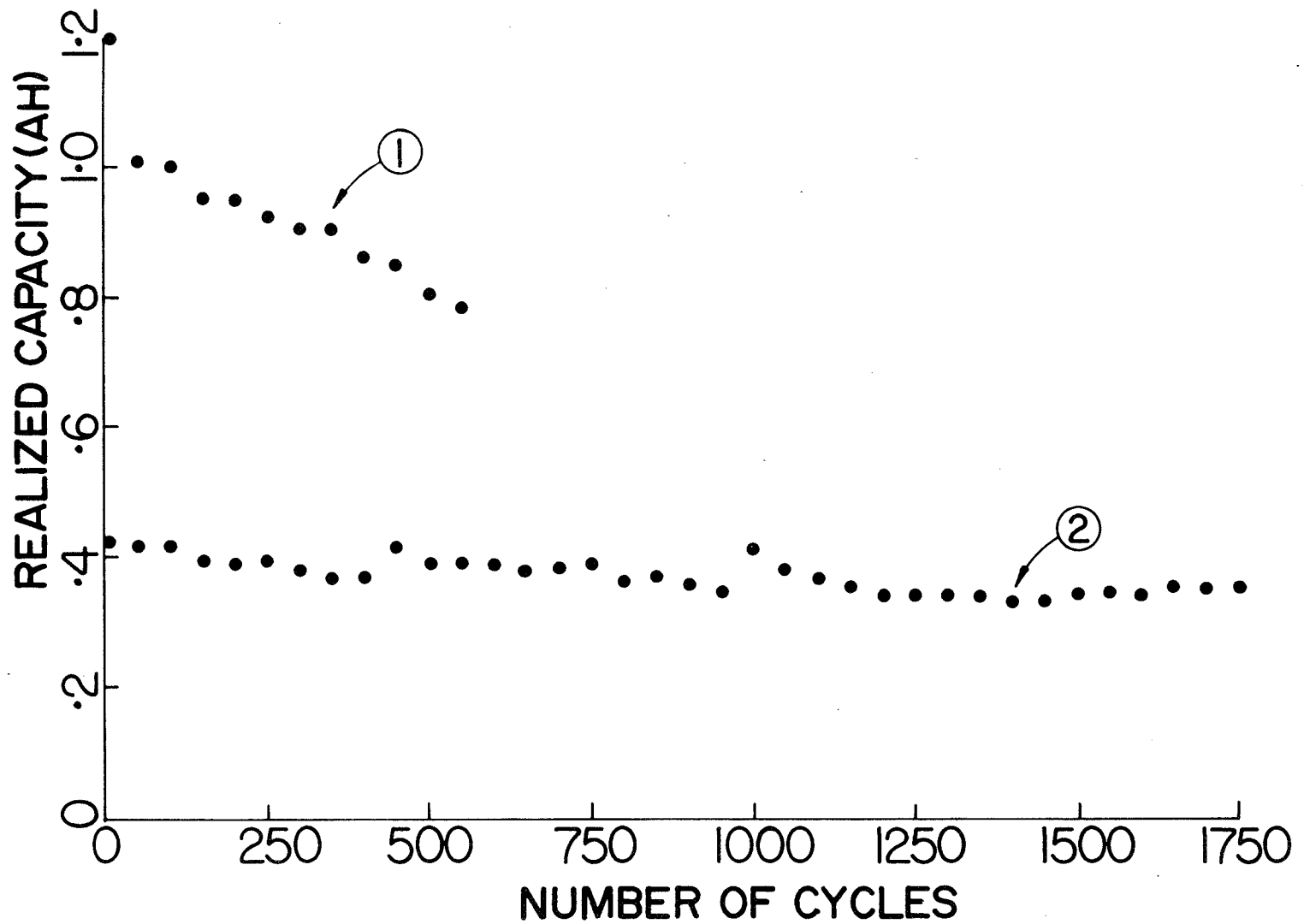


Figure 3 - Capacity vs. cycle number for 'C' cells cycled to different depths of discharge.
1: Cell cycled between 2.2V and 1.6V
2: Cell cycled between 2.2V and 1.8V

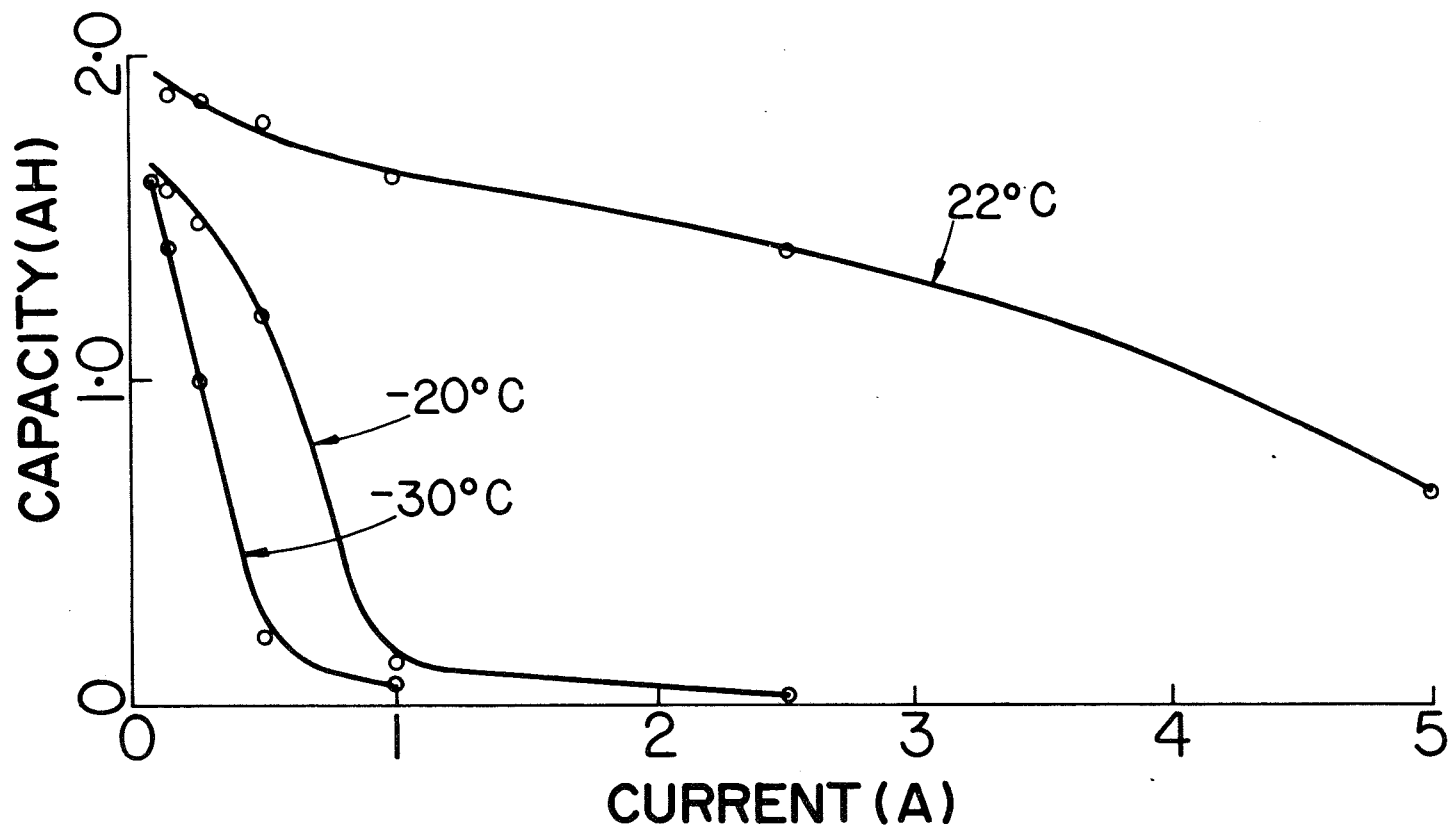


Figure 4 - Capacity vs. discharge current for three different temperatures. 'C' cell at cycle number 10.

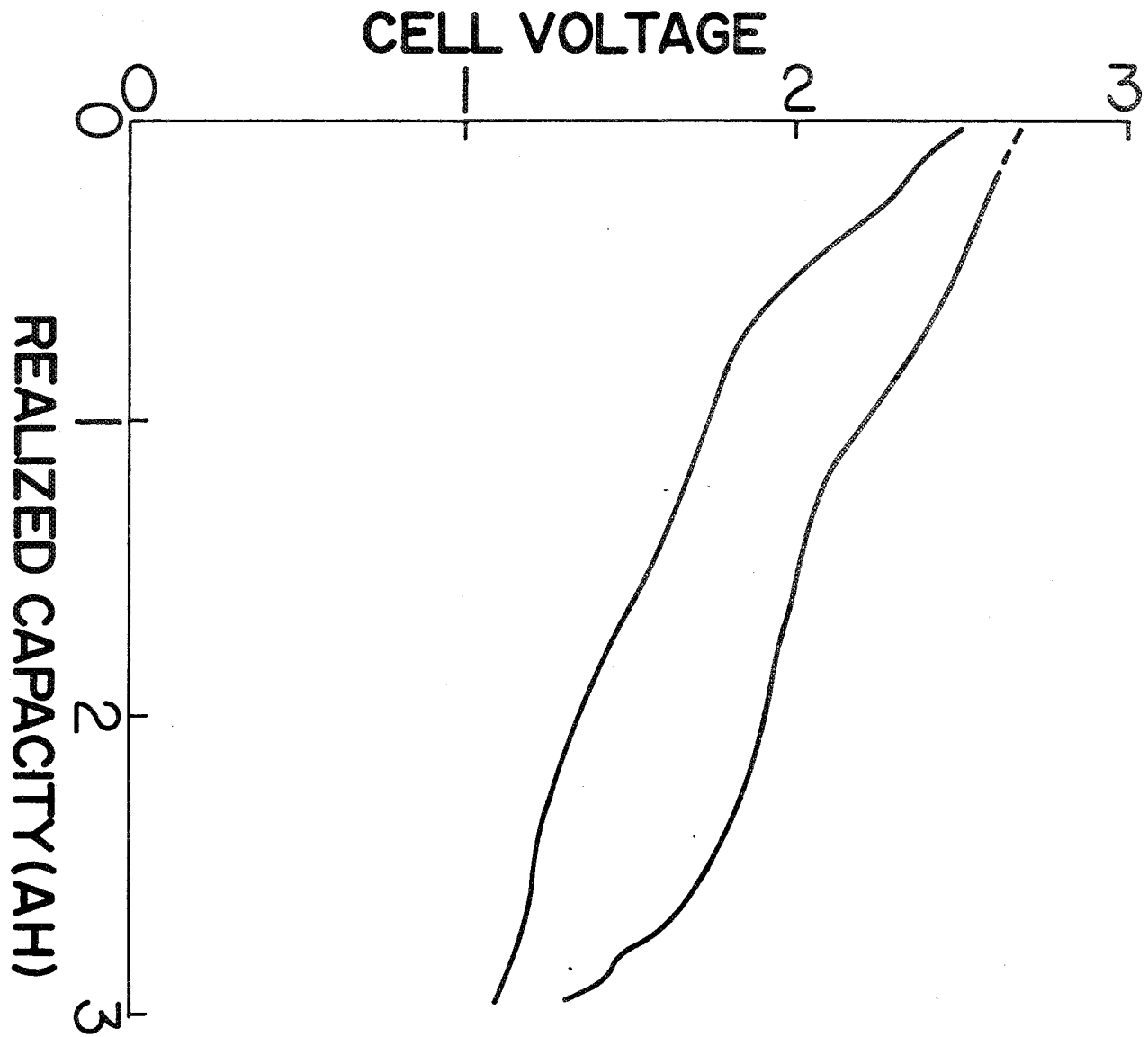


Figure 5 - Charge/discharge profile for a 'C' cell cycled over the extended voltage range. Charge current 280 mA, discharge current 840 mA. Cell at cycle number 1.

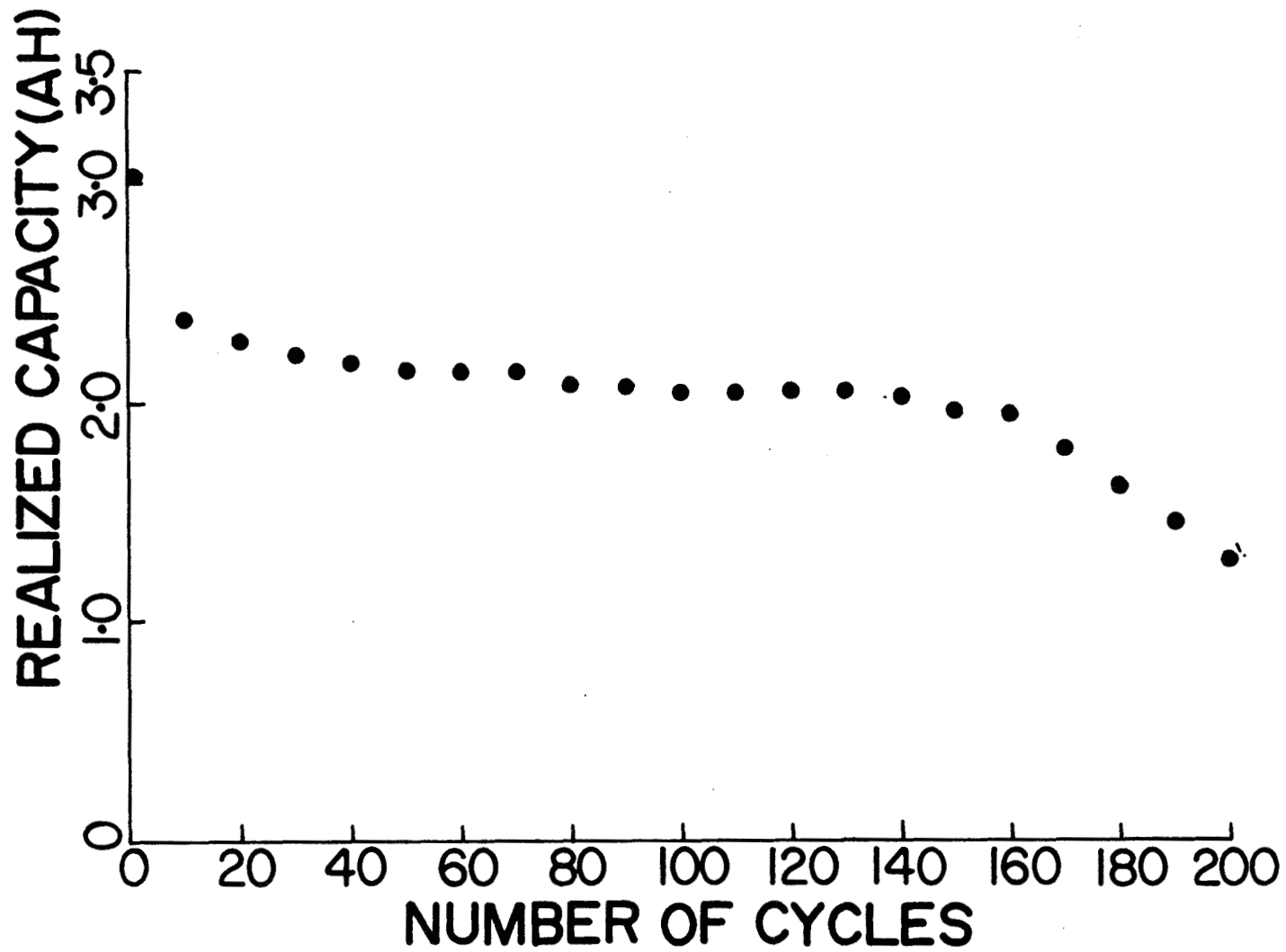


Figure 6 - Capacity vs. cycle number for a 'C' cell cycled in the extended voltage range. Charge current 280 mA, discharge current 840 mA.

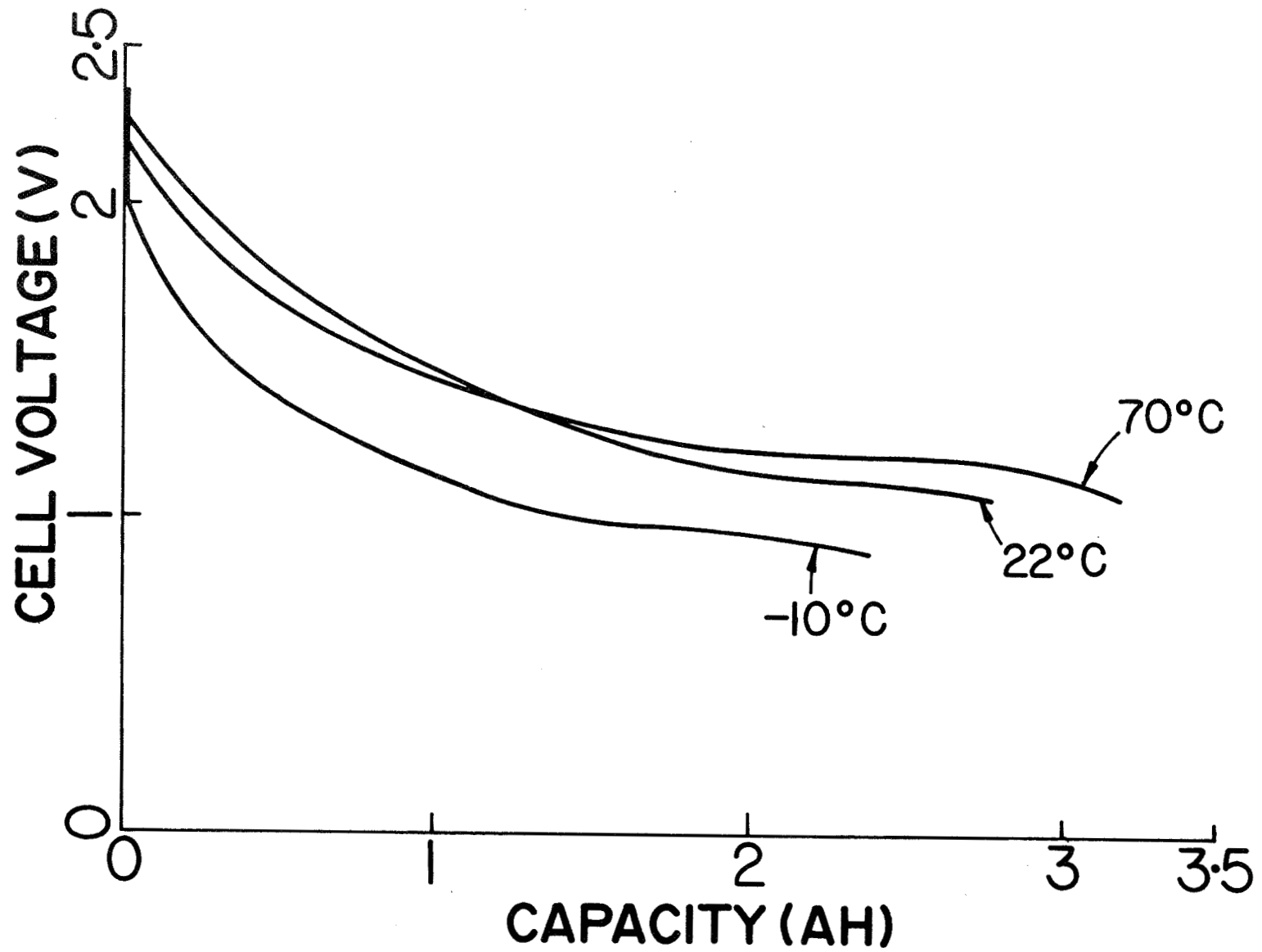


Figure 7 - Discharge profiles for 'C' cells at three different temperatures at a current of 840 mA. Charged at 280 mA to 2.6V. Cell at cycle number 1.

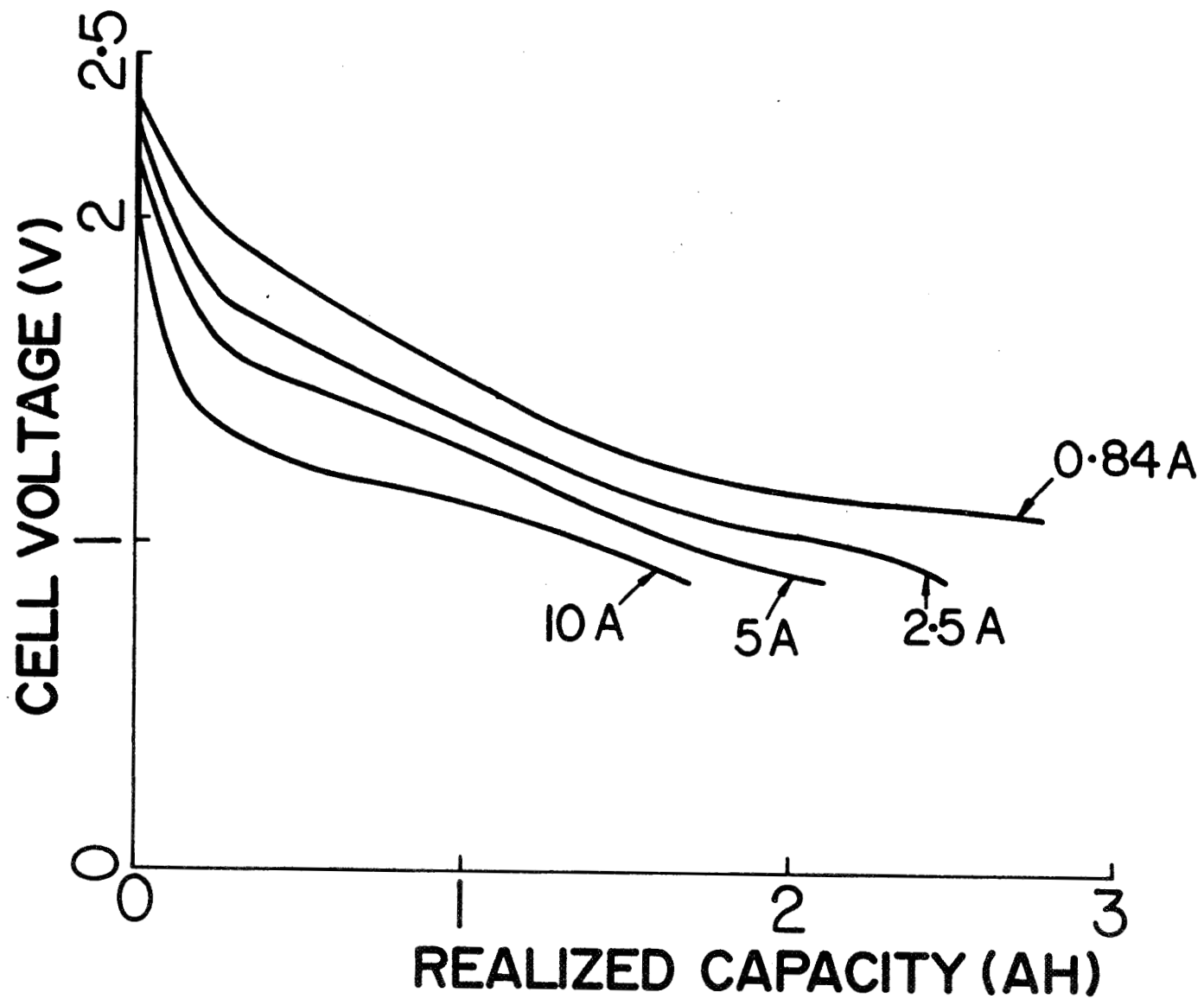


Figure 8 - Discharge profiles for 'C' cells for various discharge currents. Charged at 280 mA to 2.6V. Cell at cycle number 1.