# Lawrence Berkeley National Laboratory
## LBL Publications

**Title**
Zinc-Air Design Concept for the DOE-EHP IDSEP Van

**Permalink**
https://escholarship.org/uc/item/3sp5n08q

**Author**
Ross, P N, Jr

**Publication Date**
1988

**Copyright Information**

# Lawrence Berkeley Laboratory
## UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

### Zinc-Air Design Concept for the DOE-EHP IDSEP Van

P.N. Ross, Jr.

January 1988

# DISCLAIMER

ZINC-AIR DESIGN CONCEPT FOR THE DOE-EHP

IDSEP VAN

Philip N. Ross, Jr.

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

## SUMMARY

The present Zn-air battery concept design exhibits some of the same characteristics as earlier versions of this battery, in particular, the energy densities of 100–110 Wh/kg and 50–60 Wh/L are typical of all the previous circulating electrolyte designs. These energy densities are much lower than the "golden rule" of 25% of the theoretical (894 Wh/kg), but this result is inherent in the fact that the electrolyte is really the active material rather than Zn metal (12 M KOH containing 260 g Zn/L has a theoretical energy density of 368 Wh/L or ca. 230 Wh/kg). The major departure of the present system from all other Zn-air versions is in the power density, electrical efficiency, cycle life, and cost. The new zinc electrode concept has eliminated the zinc electrode as a life limiting factor, and the improvements in power, efficiency, and cost have come from the improvements made in air electrode technology.

The advantages of the Zn-air battery, as realized in this design for the IDSEP van, over other battery systems are:

1)   energy capacity, exceeds the minimum by 50%;

2)   low weight, less than maximum allowed weight by 50%;

3)   minimal environmental impact and superior safety;

4)   constructed entirely of common materials;

5)   low materials cost, uncomplicated manufacture.

The anticipated difficulties in realizing these advantages will be in sustaining the power required for acceleration over the lifetime needed for economic life-cycle cost.
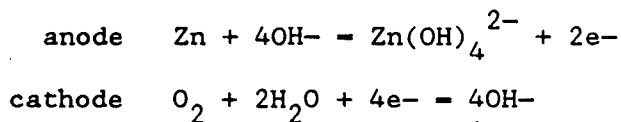
## Background

The basic concept behind the zinc-air battery design specified here is described in previous publications [1,2]. The air electrode performance has been substantially improved since these papers were written, and the new data will be presented here and used as a basis for design calculations. In all other respects the background information remains the same. A summary description of the system and its characteristics is given here in order to outline the anticipated advantages inherent in this concept relative to other battery systems.

The zinc-air system proposed here is a hybrid of many other zinc battery concepts, and was prompted by two significant developments in materials: new corrosion resistant carbon materials and new low-cost processes for making metal-foams out of a wide variety of metals. The former suggested that bifunctional air electrodes could be fabricated from carbon materials and achieve both low cost and low weight with adequate lifetime for electric vehicle applications. The metal foam development suggested a new zinc electrode concept that is a derivative of the CGE particulate zinc electrode: zincate stabilized to supersaturation in KOH by silicate (or other additives) is circulated through a stationary metal foam substrate onto which zinc is deposited (during charge) and subsequently stripped (during discharge). Substantial fundamental work on the zinc electrode in recent years has indicated that zinc electrodes of the flow type (with soluble zinc) should have excellent life-cycle properties, expectations which have been largely born out in recent engineering studies of zinc-halogen flow batteries. However, the deposition of zinc onto a substrate from alkaline zincate has
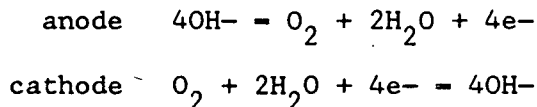
not been as well-studied and life-cycle characteristics of such an electrode were not known. Furthermore, the solubility of zincate in KOH is much lower than zinc ion in acids, even with additives like silicate. Thus, as is often the case in batteries, one is trading volume (and to a lesser extent weight) and systems complexity for cycle life. The objective of our recent engineering studies has been to examine this tradeoff in the zinc-air system that employs these new materials.

The basic chemistry of the zinc-air system in alkaline electrolyte is as follows:

Discharge

$$\text{anode} \quad Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$$

$$\text{cathode} \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Overdischarge

$$\text{anode} \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

$$\text{cathode} \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Charge

$$\text{anode} \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

$$\text{cathode} \quad Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$$

Overcharge

$$\text{anode} \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

$$\text{cathode} \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
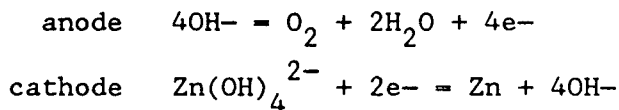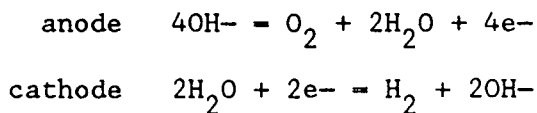
The chemistry of the system is inherently tolerant to both overdischarge and overcharge, in that the only other chemistry occurring is electrolysis of water (overcharge) or Ohmic heating (overdischarge). A "dead" cell driven to reversal during discharge by other cells will reduce the stack voltage (by about 2 V), but should not cause a

3

cascading failure of neighboring cells. Overcharge will evolve hydrogen in large quantities, and could present a safety hazard, but no more than for other aqueous battery systems, e.g. lead-acid, zinc-nickel oxide, or zinc-bromine, and significantly less of a hazard than for iron-nickel oxide or iron-air batteries.

In terms of performance characteristics such as power vs. depth of discharge, energy capacity vs. power, etc., a metal-air battery lies characteristically between a fuel cell and a conventional battery. In the case of the recirculating zinc-air electrode concept described here, the characteristics on discharge are very fuel cell-like, i.e. power is nearly invariant with depth of discharge, and energy capacity can be varied with only a modest effect on power density. The state of charge of the battery at any time is solely defined by the amount of zinc in the negative electrode (or in the electrolyte), so that the positives and negatives in individual cells can never be "out of balance." This turns out to be an enormous advantage in achieving long cycle life for the zinc electrode. In fact, it is our finding that cell lifetime is defined entirely by the air electrode in this system.

## Specifications of the system design

The engineering calculations based on the results of single-cell testing indicate that the system is volume and peak-power limited, due to the characteristics of the air electrode. Therefore, the design is based on meeting technical requirements for maximum volume (600 L), minimum power (55 kW), and minimum voltage (120), and exceeding (better-ing) the requirements for weight (300 kg vs. 700 kg) and energy capacity (32 kWh vs. 21 kWh).

4

The basic configuration of the individual cells follows the 1.5 Ah single cell described in [1,2]. The principal structural material in the battery casing and manifolding is polypropylene. The air-scrubbing components and the thermal management system were the same as that developed for the Al-air battery [3]. Multicell modules are formed from a series interconnection of 125 single cells with 50 Ah (32 cm $\times$ 32 cm $\times$ 0.8 cm) capacity. Four modules are connected (electrically) in parallel to form the total power source. The modules have independent electrolyte circulation systems each with a 1/20 hp dc electric pump. At the C/4 rate, the current density in each cell is 12.5 mA/cm$^2$, and for standard overnight (16 hr.) charging would be 3.125 mA/cm$^2$. The zinc loading at full charge is designed to be 50 mAh/cm$^2$. The design temperature for discharge is 50-55 C, thermostatically controlled via the circulating electrolyte; for charging the design temperature is 40-45C. The electrolyte is 12 M KOH containing 260 g Zn/L at complete discharge, and for a capacity of 32 kWh, an electrolyte volume of 116 L is required (about 40 L in the stacks and 80 L in external components (reservoir, pumps, manifold)).

The resulting power source characteristics are:

Volume:   600 L

Weight:   300 kg

Capacity:   32 kWh

Average power:   7.8 kW

Peak power (20 sec.):   65 kW (BOL), 55 kW (EOL)

Current-voltage:

              (BOL)     162 V/50 A at C/4

5

| Discharge | | 143 V/460 A at peak |
| | (EOL) | 156 V/50 A at C/4 |
| | | 125 V/460 A at peak |
| Charge | (BOL) | 230 V at C/8 |
| | | 227 V at C/16 |
| | (EOL) | 235 V at C/8 |
| | | 232 V at C/16 |

## Analysis

Performance

The anticipated performance of the total battery system was derived from 1.5 Ah single cell testing by linear scaling of the current-voltage curve to the cell area and the number of cells in series/parallel connection to produce a power source that would fit in the 600 L space. The resulting beginning-of-life (BOL) and end-of-life (EOL) curves for current-voltage and voltage-time are shown in Figs. 1 and 2. Note the fuel cell-like character of the voltage-time curve that is characteristic of this battery as well. There is only a transient "delay" in the voltage at the start of either the charge or discharge cycle due to the movement of electrolyte within the air electrode structure on the change-over from oxygen (gas) evolution to oxygen reduction (or vice-versa). As in a fuel cell, the battery power and the energy capacity are essentially independent (±5%) of the depth of discharge, i.e. 65 kW (BOL) throughout the discharge. The fact that the cell voltage cannot be used as a state-of-charge monitor to tell the operator how much capacity remains presents a practical problem which needs to be addressed. A sensor for the zinc content in the electrolyte needs to be developed

6

to serve as a state of charge monitor.

## Cost

The materials cost is estimated to be $500–$1000 for the total power source. If the production cost is estimated to be 2 to 3 times the materials cost, the power source production cost is estimated to be $2500 ± 500.

## Life

We have cycled 1.5 Ah cells with constant current charge-discharge cycles and achieved 600 C/4 cycles, with end of life defined as loss of capacity at the C/4 rate. However, it is a fundamental characteristic of bifunctional air electrodes that they will cause loss of peak power much faster than the loss of capacity. Hence, the electrodes we have developed to date would not meet the life requirements as defined here. Our research studies of the corrosion processes in the air electrode do indicate that there are no fundamental limitations to developing elec- trodes that would meet the life requirement.

## Efficiency

The BOL 1.5 Ah single cell voltages were 1.29 V out–1.85 V in, and EOL 1.25 V out–1.90 V in. Assuring no loss in efficiency in multicell modules due to shunt currents or zinc corrosion (self-discharge), the round-trip efficiency would be 70% BOL, 66% EOL. In practice, self discharge should not be a problem, but shunt currents are potentially a significant source of difficulty and require study in multicell proto- types.

## Abuse Resistance

The chemistry of overcharge and overdischarge reactions was identified in the Background material. The cell chemistry is inherently tolerant to either, in the sense that an overcharged or overdischarged zinc electrode suffers no loss in capacity as a result of these excursions. Overcharge results in the electrolysis of water in the electrolyte, with accumulation of a potentially hazardous amount of hydrogen in the battery environment. Overdischarge produces only cell heating, which can be handled with a standard air-cooled thermal management subsystem [3]. A failed air electrode will evolve hydrogen on discharge, and reduce the module voltage by about 0.9 V, but will still evolve oxygen on charge at a slightly (0.1 to 0.2 V) increased voltage. A failed zinc electrode is more costly on discharge, as the cell will be driven to reversal, with oxygen evolving at the failed zinc electrode and a loss in cell voltage of 2 to 2.5 V. On charge, a failed zinc electrode will evolve hydrogen at a slightly increased (0.1 to 0.2 V) voltage per cell. However, there is no obvious reason for a cascading failure mode.

## Safety

Hydrogen build-up is the only significant safety issue for this power source. In a vehicle crash, hot caustic electrolyte would present a hazard to the occupants. The safety would be comparable to lead-acid or zinc-nickel oxide.

## Environmental Impact

For the most part, this battery contains the same materials as are found in a common alkaline battery, e.g. zinc, carbon and KOH. The

environmental impact should be nil.

Critical Materials

The power source uses a modest amount of cobalt and nickel, about 10 kg of Ni and 5 kg of Co.

User Issues

The cell power is very temperature sensitive, and instant drive-away capability after standing in a low temperature (well below 25 C) ambient would not be possible. An accurate and rugged state-of-charge sensor needs to be developed, as the cell voltage cannot be used to determine the capacity remaining in the battery. Once this is developed, the user interface is especially simple. There is no need for concern about cell balancing. Periodic maintenance items are: water make-up, and replacement of the air scrubbing canisters (throw away and replace) and the caustic electrolyte (throw away after a complete recharge and replace). The maintenance interval for both these items would be the same, after approximately 500 operating hours (discharge time).

Technology Status

The supersaturated alkaline zincate electrolyte used here is similar to that used previously by CGE [4] and Foller [5] in their particulate zinc electrode studies. The structure of zincate in the supersaturated state, and the role of additives in stabilizing the super-saturation, is not understood. LBL currently has a DOE subcontract with Pinnacle Research Institute to study the influence of additives on zincate ion stability. In our own work, we studied the characteristics of

9

our zinc electrode concept using nickel positives in place of air electrodes, but otherwise kept the same cell geometry as in our zinc-air design. We achieved immediate success with very uniform zinc deposition and stripping over a wide variety of conditions of current density, flow rate and zinc concentration. Even early in the program, we started cycle life testing with 12 M KOH containing 200 g Zn per liter in 1.5 Ah zinc-nickel oxide cells and achieved over 600 cycles at the C/4 rate to a 80 mAh/cm$^2$ capacity, with failure due to loss of capacity in the Ni electrodes. Encouraged by these early results, we obtained higher capacity Ni electrodes and built a much larger (X10) cell with the same geometry. The 15 Ah size (10 cm × 20 cm) was 1/5 of full scale, and permitted circulation of a realistic volume of electrolyte (100 mL) and realistic swings in the zinc concentration (from 200 g/L down to 20 g/L). Cycling at the C/4 rate (12.5 mA/cm$^2$ at constant current) continued for 300 cycles, and was stopped due to failure (capacity loss) of the Ni electrodes. The Ni electrodes were replaced with new ones, and cycling was continued. At the end of the 370th charge cycle, fresh 12 M KOH was added to simulate the electrolyte maintenance needed for controlling the carbonate content in the real cell, and an additional 300 cycles were achieved without difficulty. Thus, the zinc electrode concept has proven cycle life as required for the IDSEP van application.

The air electrodes are in a lower state of development. We have conducted extensive studies on catalysts for the air electrode, and on the corrosion behavior of various types of carbon materials [6-8]. LBL has also supported a very substantial program at Case Western Reserve University on oxygen electrocatalysis, including bifunctional catalysis.

10

The catalyst studies have been disappointing, in that they have not identified any really new materials that are effective _in the bifunctional mode_. We have achieved our best results with familiar catalysts, cobalt oxide as the reduction catalyst, and nickel oxide as the evolution catalyst. On the other hand, the carbon corrosion studies have greatly enhanced our understanding of the relation of carbon chemistry to corrosion resistance, and has led to the development of new carbon materials with "tailor-made" properties, e.g. corrosion resistant high area graphitized carbon black with a functionalized surface for controlled wettability. However, in terms of using the new carbon materials together with the cobalt/nickel oxide catalysts, our work is still in the formative stage. We have succeeded in producing one set of electrodes (in 1.5 Ah size) which produced the performance curves used in this design analysis, but we do not consider these to be optimized. There are fundamental technical reasons to be confident that the performance characteristics of the air electrode used in the analysis can be met and even exceeded in a full-scale mass-produced component, and that the lifetime requirements for the IDSEP van can be met.

The major technical issues are:

1) Shunt currents in the common electrolyte manifold in the multicell modules, and their effect on zinc rechargeability, cell voltage and capacity. Manifold designs that minimize shunt current without increasing pumping requirements.

2) Air electrode optimization. New catalysts to improve cell voltage and/or power density.

3) Sensor development for on-stream determination of zinc concentration in the electrolyte (state-of-charge indicator).

4) Stabilization of supersaturated zincate at concentrations exceeding 200 Ah/L.

5) Unanticipated problems from scale-up of single cells to 100 Ah, in the engineering of multicell modules, and in thermal management.

## Program Plan and Costs

LBL, through its Technology Base Research Project conducted for the DOE Conservation and Renewable Energy Program plans to continue research, both in-house and subcontracted, on those areas of the Zn-air battery technology where research, as opposed to engineering, is required. However, the level of funding provided to LBL to pursue this research is well below that needed to move the technology forward in the time frame suggested, e.g. a full scale prototype battery meeting the van mission requirements by 1992. Further, LBL has neither the mission assignment nor the expertise in multicell battery engineering to pursue the engineering development that the concept needs to proceed to the prototype stage. This Zn-air battery concept is at a critical stage of development where the participation of a battery engineering/manufacturing organization is required for significant further progress. Regardless of how successful we are in air electrode development in the laboratory, the progress will be meaningless without an engineering organization to make the laboratory advances a reality.

The current research being conducted by LBL in support of this technology is indicated below, with the organization and approximate

funding level.

| Research | Organization | FY'87 Funding |
|---|---|---|
| 1) electrocatalysis | CWRU | $300 K |
| 2) surface chemistry of carbon materials, the control if air electrode structures via carbon chemistry and the testing of new air electrode concepts. | LBL | $150 K |
| 3) behavior of particulate zinc electrodes in zincate electrolyte | LBL, Pinnacle | $200 K |
| 4) stability of supersaturated zincate solutions, and role additives | Pinnacle | $100 K |
| 5) multicell engineering and subscale testing | TBD | FY'88 $ |

## References

1.   P.N. Ross, "Feasibility Study of a New Zinc-Air Battery Concept Using Flowing Alkaline Electrolyte," Proc. 21st Int. Energy Conver. Eng. Conf., The American Chemical Society, Washington DC, 1986.

2.   P.N. Ross, "New Carbon Materials for Metal Air Batteries," Ext. Abs. of 7th Battery and Electrochemical Contractor's Meeting, DOE Report CONF-8511460-Abs., 1985, pg. 323.

3.   J.L. Cooper, "Weight and Volume Estimates for Al/air Batteries Designed for EV Applications," Proc. 1st Internat. Workshop on Metal/Air Batteries," Bonn (1979).

4.   A.J. Appleby and J. Jacquier, J. Power Sources, 1(1976/77) 17.

5.   P. Foller, J. Appl. Electrochem. in press.

6.   P.N. Ross and H. Sokol, J. Electrochem. Soc. 131(1984)1742.

7.   N. Staud and P.N. Ross, J. Electrochem. Soc. 133(1986)1079.

8.   P.N. Ross and M. Sattler, J. Electrochem. Soc. in press.

Figure Captions

Figure 1.    Voltage-time curves for a 1.5 Ah Zn-air cell at the 25th
             cycle. Discharge was at the C/4 rate of 15 mA/cm$^2$, charg-
             ing at the C/8 rate. Electrolyte was 12 M KOH with 200 g
             Zn/L at 45 C. The electrolyte volume of 100 mL constituted
             a large excess of Zn relative to the amount deposited.

Figure 2.    Current-voltage curves for the full scale module in the
             IDSEP van.  a) Discharge.  The EOL solid curve shown is
             that obtained by scale-up of the curve for the 1.5 Ah cell
             at the 500 th cycle.  The dotted curve is that projected
             for EOL based on extension of life of the current electrode
             technology.  b) Charge.

Figure 3.    Current-voltage curves from th 1.5 Ah size Zn-air labora-
             tory cell on which the scale-up van battery module curves
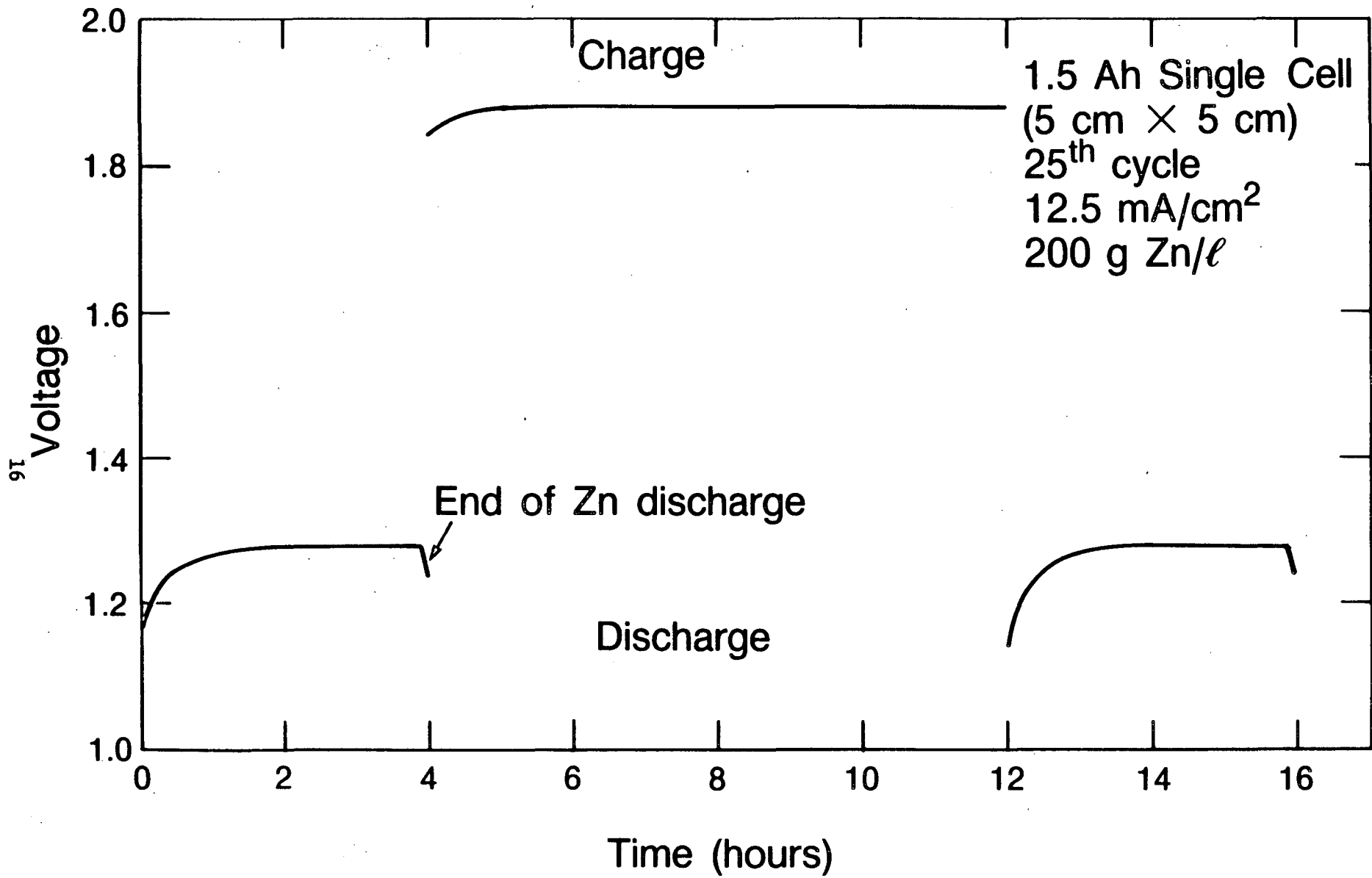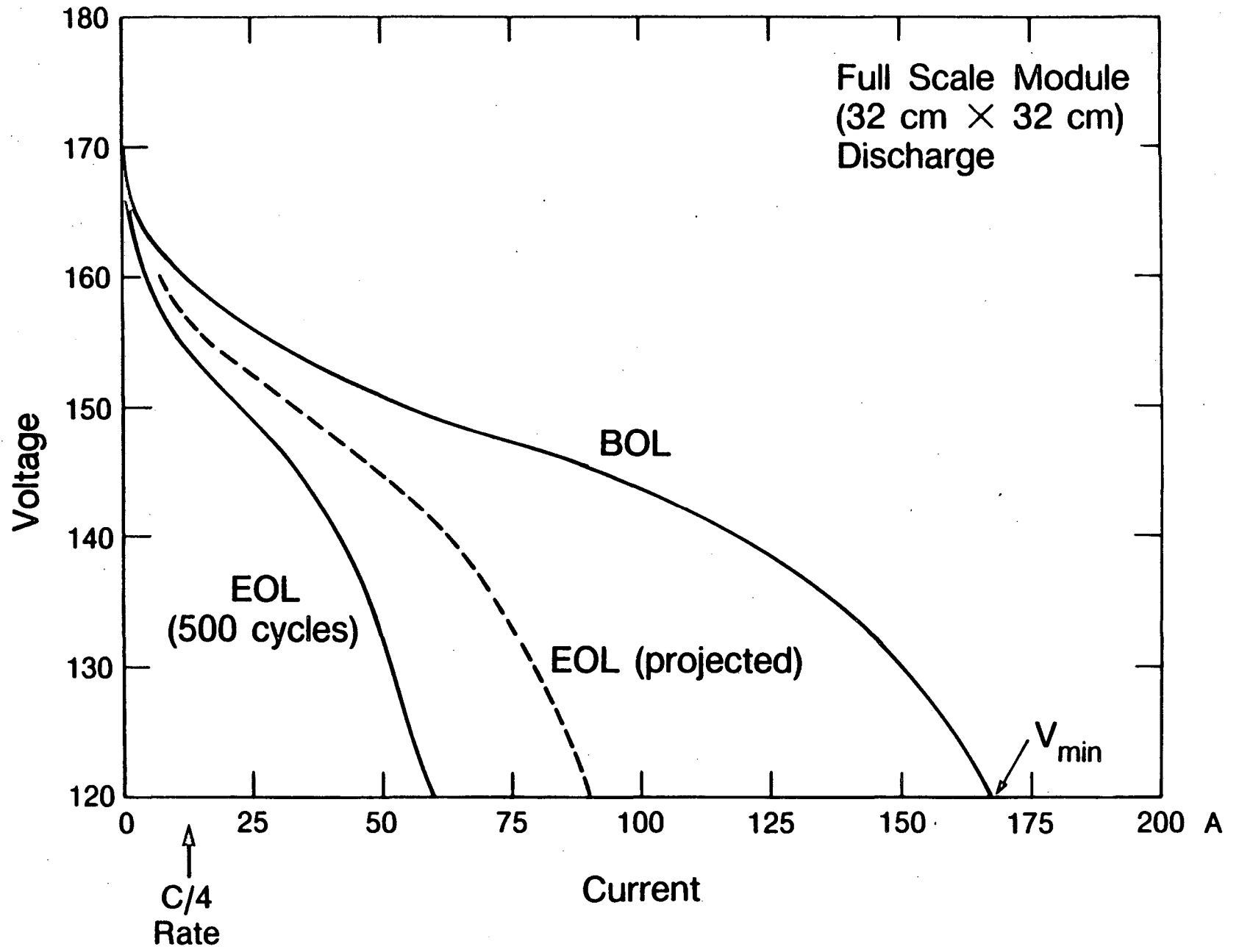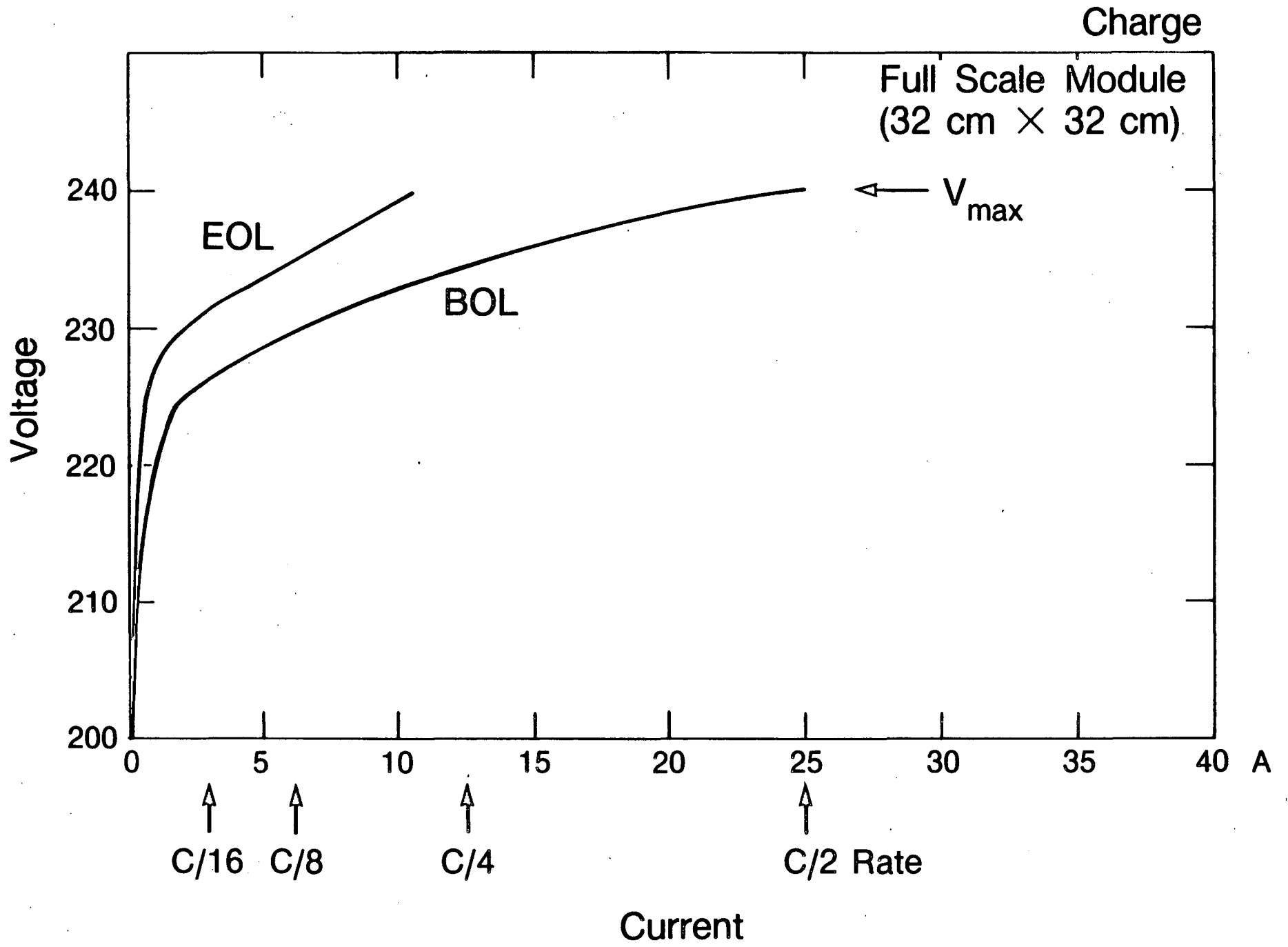             in Figure 2 are based.

Figure 1

XBL 881-9504

Figure 2a

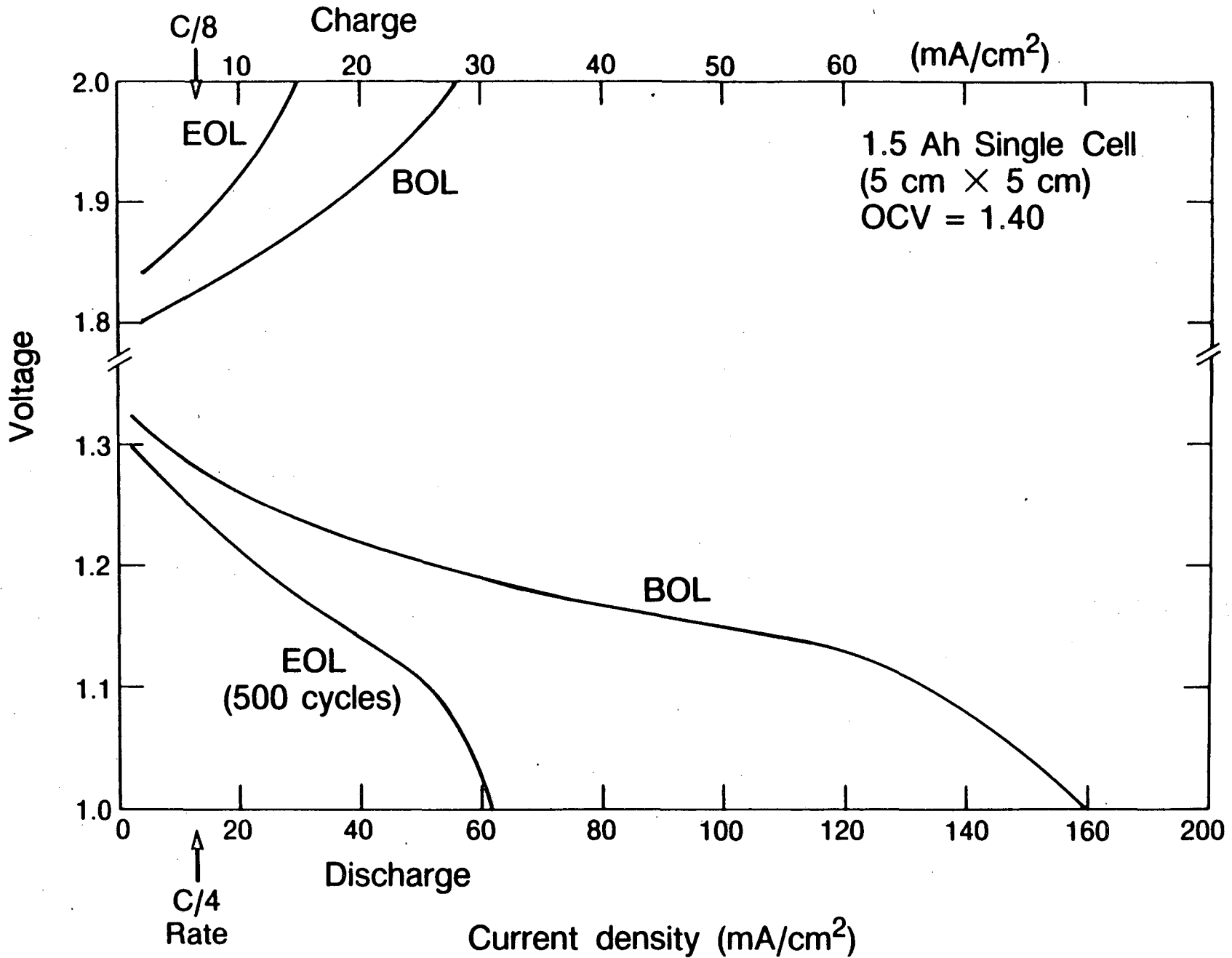XBL 881-9503

Figure 2b

XBL 881-9502

Figure 3

XBL 881-9501

*LAWRENCE BERKELEY LABORATORY*
*TECHNICAL INFORMATION DEPARTMENT*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*