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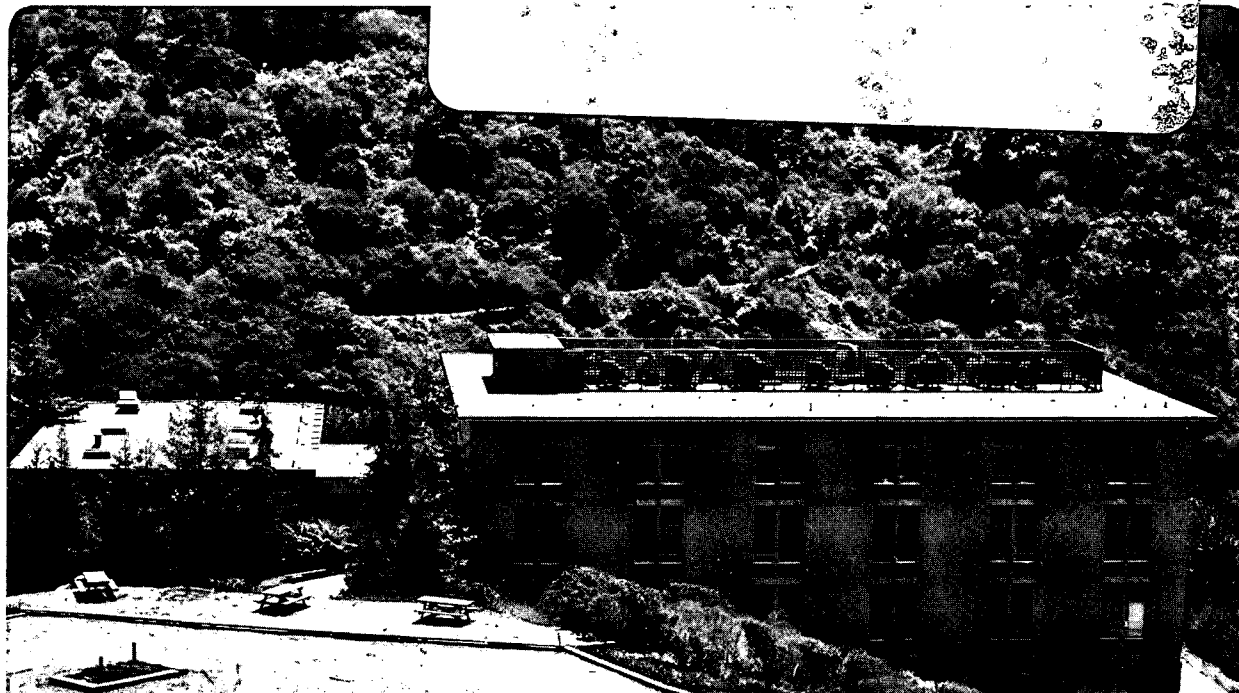**A NOVEL CLASS OF ORGANOSULFUR ELECTRODES
FOR ENERGY STORAGE**

S.J. Visco, C.C. Mailhe, L.C. De Jonghe,
and M.B. Armand

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## DISCLAIMER

# A Novel Class of Organosulfur Electrodes

# for Energy Storage

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# ABSTRACT

A broad class of organosulfur compounds is introduced which may offer unique advantages as positive electrodes in advanced secondary batteries operating at intermediate or ambient temperatures.  These novel electrode materials have physicochemical and electrochemical properties which make them particularly suitable for energy storage applications including low melting points, ease of synthesis and handling, low cost, favorable electrode kinetics, and non-corrosive behavior towards many metals.  Theoretical energy densities range from 350 to 600 Whrs/Kg for intermediate temperature (110 to $150^{\circ}$C ) sodium/organosulfur cells, and from 700 to 1000 Whrs/Kg for ambient temperature lithium/organosulfur cells.

# A Novel Class of Organosulfur Electrodes
## for Energy Storage

Impressive advances have been made in the past decade towards the efficient storage of energy with high energy density batteries. With rare exception advanced secondary cells have been based on inorganic electrochemical couples operating at high temperatures; 300 to 400°C. These temperatures necessitate the use of solid state or molten salt electrolytes while permitting the use of low equivalent weight/high voltage electrochemical couples such as $Li/FeS_2$, $Li/Cl_2$, $Na/Na_2S_x$, etc. Among the advantages of the relatively high cell operating temperatures is that the rates of electrode processes are increased to such an extent that high current/power levels are possible. However, the disadvantage of high operating temperatures is that corrosion rates are also greatly enhanced thereby requiring the use of complex seals, anti-corrosion coatings, and an expensive cell technology.

One of the most promising advanced battery systems is the sodium/sulfur cell, consisting of a molten sodium metal negative electrode and molten sodium polysulfide electrode separated by a beta"-alumina solid electrolyte barrier. This cell is capable of high specific power and energy as well as long cycle life. To date, the limiting factor to cell reliability is corrosion of the positive electrode container by molten polysulfide at the temperature of operation; 320 to 350°C. The lower temperature limit ( 300°C ) for the Na/S cell is determined by the melting point of the sodium polysulfide electrode. The development of advanced secondary batteries operating at intermediate temperatures presents a compromise between lower power density systems and greatly reduced problems of corrosion, thereby minimizing the complexity and expense of cell technology while increasing reliability and safety factors. The organosulfur storage electrodes have physiochemical and electrochemical properties that differ significantly from the inorganic salt electrodes, encouraging the pursuit of high energy density batteries operating at moderate

temperatures, and offer an area of extensive fundamental investigation as well as of technical application.

The novel organosulfur electrodes are based on the reversible electrochemical oxidation of alkali metal thio salts to the corresponding disulfides,

$$2 \ RS^- \quad \rightarrow \quad RSSR + 2 \ e^-$$

where R is an organic moiety. The oxidation of thiols to disulfides has been long established ( 1-6 ) but has not been previously considered in the context of energy conversion. The attraction of such a generic organic redox couple for battery research is the ability to tailor the physical, chemical, and to a lesser extent electrochemical properties of the molecule through choice of an organic moiety. Very little thermodynamic or electrochemical data are available for the alkali metal thio salts. The few reported redox potentials ( 2,5 ) for the thio/disulfide couples indicate a range of -0.1 to -0.4 volts vs. the normal hydrogen electrode. A slight dependence of the redox potential on R groups was observed. This corresponds to open circuit voltages of 2.3 to 2.6 volts for Na/organosulfur electrochemical couples, which is consistent with observations in this study.

Of the many thio/disulfide couples to choose from (Table 1), the present investigation has centered on the dithiocarbamate/thiuram disulfide system. The overall reaction for a cell based on this couple is,
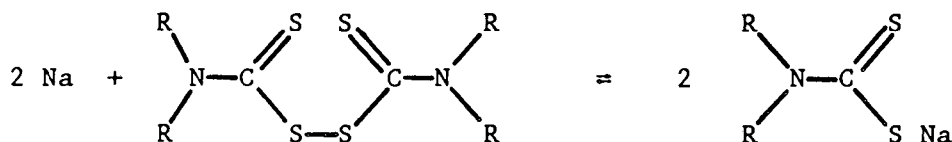


where R = an organic functional group ( $C_2H_5$, $CH_3$, $C_6H_5$, etc. ). The sodium dithiocarbamates are characterized by their low melting points due to strong resonance stabilization of the thio anion, and reversible oxidation to the

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thiuram disulfide ( 1-6 ). The electrosynthesis of the disulfide is reported to be of industrial interest ( 7 ). Depending on the electronic and/or steric influence of the R groups on the nitrogen atom, the sodium salts can melt at surprisingly low temperatures: 50 to 150$^{o}$C. The oxidized species, the thiuram disulfides $(R_2NCSS)_2$, melt at even lower temperatures, ambient to 100$^{o}$C, and are easily recrystallized to high purity. Fortunately, the dithiocarbamate salts are also very soluble in the corresponding liquid disulfides, allowing electrodes to be operating at temperatures somewhat below the melting point of the salt.

The theoretical energy density of a Na/TETD cell is 360 Whrs/Kg. The basic components of a practical cell of this type include ( figure 1 ) a molten sodium electrode chemically isolated from a molten TETD electrode by a sodium ion conductive ceramic, such as beta"-alumina. The sodium electrode was purified as previously described ( 8 ), and the TETD compound was recrystallized from butanol prior to use in the cell. Pure TETD melts at approximately 74$^{o}$C, while its corresponding anhydrous salt, sodium diethyldithiocarbamate ( NaDEDC ) has a melting point of about 145$^{o}$C. The sodium salt has an appreciable solubility in the disulfide at 130$^{o}$C; about 60 wt% which can be increased to close to 90% upon addition of 10% of a high dielectric constant solvent such as DMSO, sulfolane, etc., thus allowing low cell operating temperatures. Ionic conductivity studies of NaDEDC dissolved in molten TETD have been performed as a function of both temperature and salt concentration ( figures 2,3 ). The results indicate reasonable conductivity in the melt which can be further increased by a small addition of a high dielectric constant solvent. The increase in equivalent conductivity with concentration, seen in figure 3, indicates the formation of triplet ions, in agreement with similar investigations on concentrated non-aqueous electrolyte systems ( 9,10 ). The viscosity of pure TETD was determined at 130$^{o}$C with an Ostwald viscometer to be 10 centipoise. Potentiostatic corrosion measurements in 50-50 wt% TETD/NaDEDC melts at 130$^{o}$C indicated that while copper electrodes were attacked, platinum and carbon were inert and aluminum was passivated by an electronically conductive film; static chemical corrosion

tests led to the same conclusions.  The passive behavior of aluminum towards the positive electrode melt offers a large technical advantage for cell design.

More than thirty Na/TETD batteries of varying design and positive electrode composition have been tested ( figure 1 ).  The sodium electrode was chemically isolated from the positive electrode by a beta"-alumina electrolyte tube sealed to an aluminum cap with a high temperature epoxy.  All batteries were assembled in the 100 % charged state.  High surface area graphite felt in contact with an aluminum container was used as the current collector matrix for the molten positive electrode. The electrolyte surface area in contact with the felt was 20 to 25 $cm^2$.  The available capacities of these cells was typically between 2.0 and 2.5 Ah.  The respective total mass of these cells ranged from 50 to 53 g, resulting in energy densities of 90 to 110 Whrs/Kg at zero current drain ( OCV - 2.3 volts ).  The internal resistance of the laboratory cells ranged from 0.5 to 2.0 ohms, 0.025 to 0.10 ohms/$cm^2$, which varied somewhat with art of assembly, state of charge, and current load.  The transient current/power capabilities of laboratory cells were relatively insensitive to the presence of added solvents in the positive electrode.  A number of batteries were capable of delivering current densities of over 100 mA/$cm^2$ ( 2 amps ) at 1 volt for a period of a minute or more (figure 4,5 ), or 25 mA/$cm^2$ at 1.5 V nominal for 8 % of available capacity.  For discharge depths of greater than 60 % of capacity, the presence 10 to 20 % solvent in the positive electrode reduced polarization losses ( figure 6 ), presumably by preventing precipitation of NaDEDC and increasing diffusion rates by lowering the melt viscosity.  Cells were cycled between 10 and 90 % of available capacity at current densities of 5 mA/$cm^2$, achieving power densities of up to 6 W/Kg at an average closed circuit voltage of 2.0 volts, overall energy efficiencies of charge/discharge cycling of 75 %, and actual energy densities of 80 Whr/Kg.  Although these cells were far from being optimized, the preliminary results were quite encouraging.

The dithiocarbamate/thiuram disulfides represent but one type of a series of

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resonance stabilized thio anions; other systems include the dithiocarboxylates, xanthates, and dithiophosphinates, etc. There are also a large number of simple aliphatic thio salts which, although lacking the low melting points of the above species, might function well as positive electrodes due to high solubility of the salt in the corresponding disulfide. The simple disulfides offer additional advantages of being liquid at room temperature, having higher theoretical energy densities, 500 - 800 Whrs/Kg ( Table 2 ), and possibly greater chemical and thermal stabilities. Although the simple alkyl disulfides have very low equivalent weights, a $Na/CH_3SSCH_3$ cell has a theoretical energy density of 780 Whrs/Kg, they are too non-polar to dissolve the thioalkyl salts generated on discharge. In fact, a $Na/C_3H_7SSC_3H_7$ laboratory battery demonstrated a discharge rate of merely a few $uA/cm^2$ at $120^oC$. However, the dielectric constant of these materials can be increased in various ways such as the incorporation of ether linkages in the disulfide ( Table 2 ). Although the alkoxyalkyl disulfides are not commercially available, a suitable isomer, hyroxyethyl disulfide ( $HOCH_2CH_2SSCH_2CH_2OH$ ), was evaluated as a positive electrode. Hydroxyethyl disulfide, HEDS, is liquid at room temperature and has strong solvating ability for many sodium salts, resulting in high measured ionic conductivities. A series of Na/HEDS cells were designed and tested. Preliminary results implied negligible reduction of the HEDS terminal hydrogens on the graphite felt matrix at the discharge potentials of the cells. The theoretical energy density for a Na/HEDS battery is 590 Whrs/Kg. The laboratory batteries had capacities of 4.5 Ah and maximum practical energy densities of 200 Whrs/Kg at zero current drain . At $120^oC$ the Na/HEDS cells were discharged to over half of the available capacities at current densities of 10 to 15 $mA/cm^2$ with remarkably little evidence of time dependant polarization, and one laboratory cell was recharged to 90 % of capacity. Although the internal cell resistances were higher than for the Na/TETD batteries ( figure 7 ), the HEDS electrodes were discharged without the use of solvents and showed no evidence of salt precipatation. Unfortunately the HEDS positive electrode suffers from its tendency towards polymerization due to auto-condensation at elevated temperatures ( 3 ) to yield viscous

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polysulfide polymers. However, the results from the Na/HEDS cells suggest that the use of low equivalent weight aliphatic disulfides as positive electrodes is both feasible and promising. Further, preliminary tests on room temperature analogs of the above described batteries using protected solid alkali metal electrodes suggest that organosulfur electrodes can in addition be exploited in ambient temperature high energy density batteries. In fact, room temperature organosulfur cells using lithium negative electrodes have theoretical energy densities approaching 1000 Whrs/Kg at open circuit voltages of 3.5 volts.

In summary, the discovery of a novel class of organosulfur electrodes provides new avenues for research in advanced battery systems. The generic nature of the organosulfur electrodes coupled with factors of low cost, low toxicity, low corrosivity, and low operating temperature, make these materials particulary promising for energy storage applications.

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Figure Captions


Figure 1.   Schematic diagram of experimental sodium/organosulfur battery.
Graphite felt matrix is impregnated with organosulfur compound to form
the positive electrode.   Typical cell weight is 50 grams.


Figure 2.   Ionic conductivity of 8 wt% NaDEDC dissolved in pure TETD as a
function of temperature.   The apparent activation energy for conduction
derived from the solid line fit of the data is 6.4 kcal/mole.


Figure 3.   The equivalent conductance of NaDEDC in TETD as a function of
concentration at 130°C.   The expected behavior at dilute concentrations
is indicated by the dotted line at the far left of the figure.   The effect on
the equivalent conductance by the addition of a solvent to the system,
tetramethylurea, is shown by the dotted line at the right of the figure.


Figure 4.   Transient power capabilities of the Na/TETD battery.


Figure 5.   Polarization behavior of the Na/TETD battery as a function of
current density ( 5 second current pulses ) at 130°C.


Figure 6.   Discharge curve for a Na/TETD cell with 20 wt% DMSO included in the
positive electrode matrix.


Figure 7.   Charge/discharge behavior of a Na/HEDS battery operating at 125°C.

## Dithiocarbamates/Thiuram Disulfides and Related Compounds
### ( Theoretical energy densities based on sodium/organosulfur cells   OCV = 2.3 volts )

| Organosulfur Compounds | M.P. Sodium Salt ($^{\circ}$C ) | M.P. Disulfide ($^{\circ}$C ) | Energy Density Whrs/Kg |
|---|---|---|---|
| $(CH_3)_2NCS_2Na$ | decomp | 156 | 431 |
| $(C_2H_5)_2NCS_2Na$ | 145 | 74 | 361 |
| $(CH_3OC_2H_5)_2NCS_2Na$ | 50 | < 25 | 276 |
| $C_2H_5OCS_2Na$ | 220 | 40 | 425 |
| $(NaS_2CNHCH_2-)_2$ | 80 | ? | 481 |

Table 2


# Alkoxyalkyl Disulfides and Related Compounds
( Energy densities based on sodium/organosulfur cells )

| Disulfides <br> (Liquid at RT) | Theoretical Energy Density <br> Whrs/Kg <br> ( OCV = 2.2 volts ) |
|---|---|
| $(CH_3 OCH_2 S)_2$ | 590 |
| $(CH_3 OCH_2 CH_2 S)_2$ | 517 |
| $(CH_3 OCH_2 CH_2 OCH_2 CH_2 S)_2$ | 373 |
| $(HOCH_2 CH_2 S)_2$  (HEDS) | 590 |

XBL 876-2504

# SODIUM/ORGANOSULFUR CELL

$T = 130^{\circ}C$

negative pole

epoxy–seals

epoxied stainless
steel cap

Beta°Alumina tube

sodium

graphite felt
+positive electrode material

cell casing
current collector
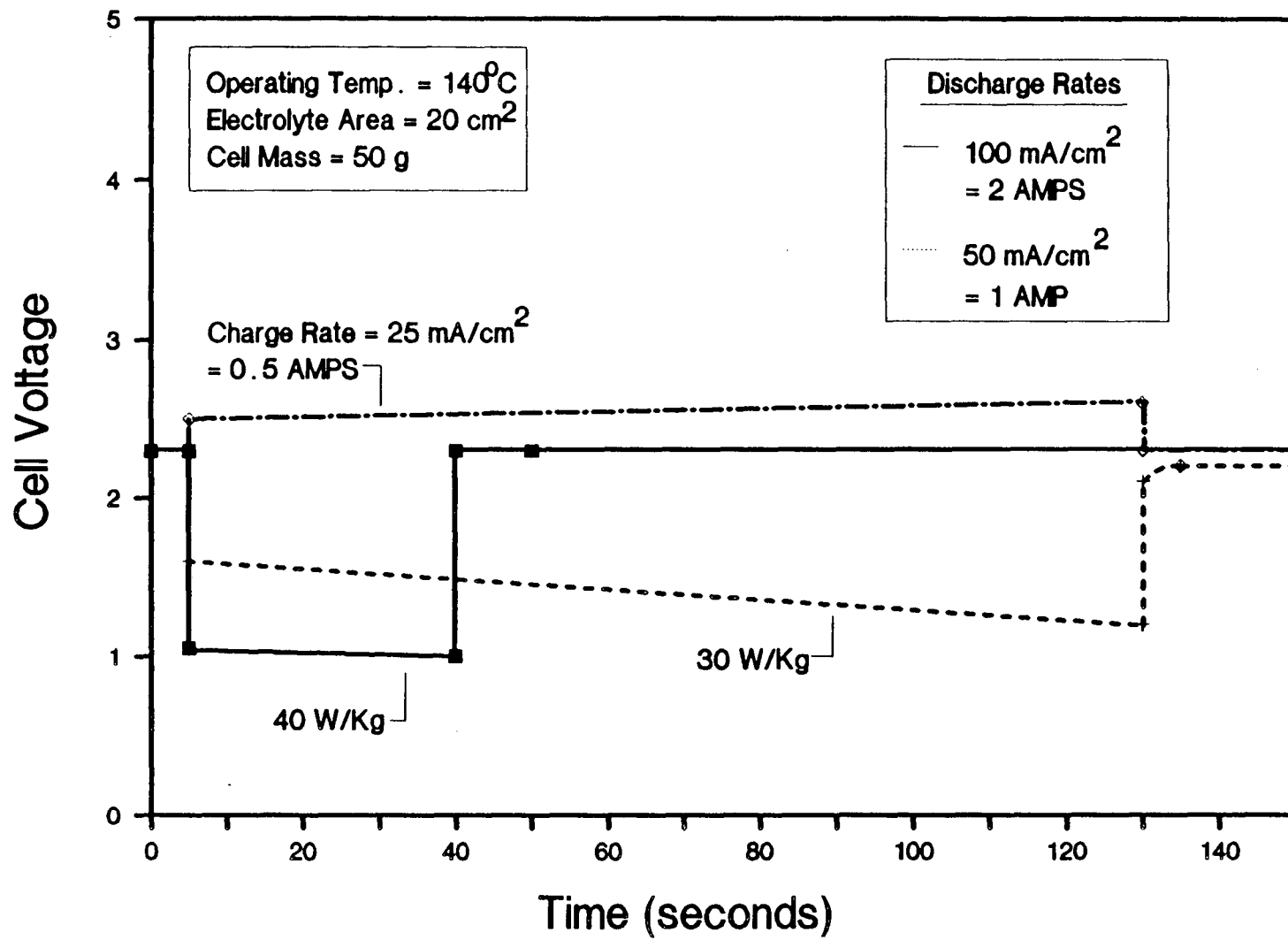positive pole
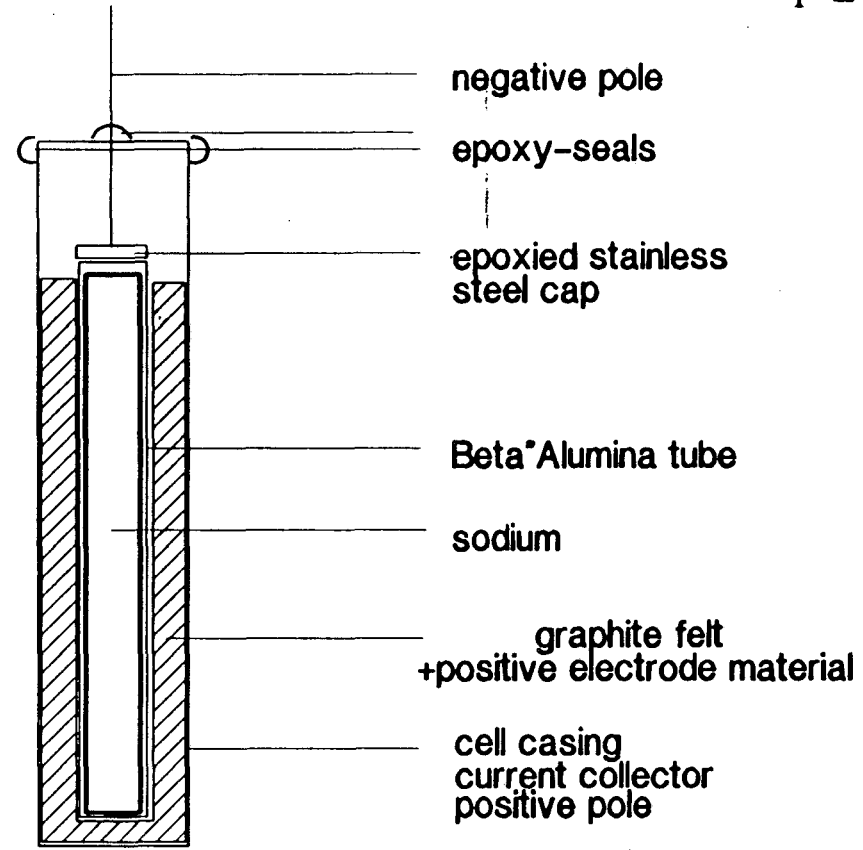
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Figure 1

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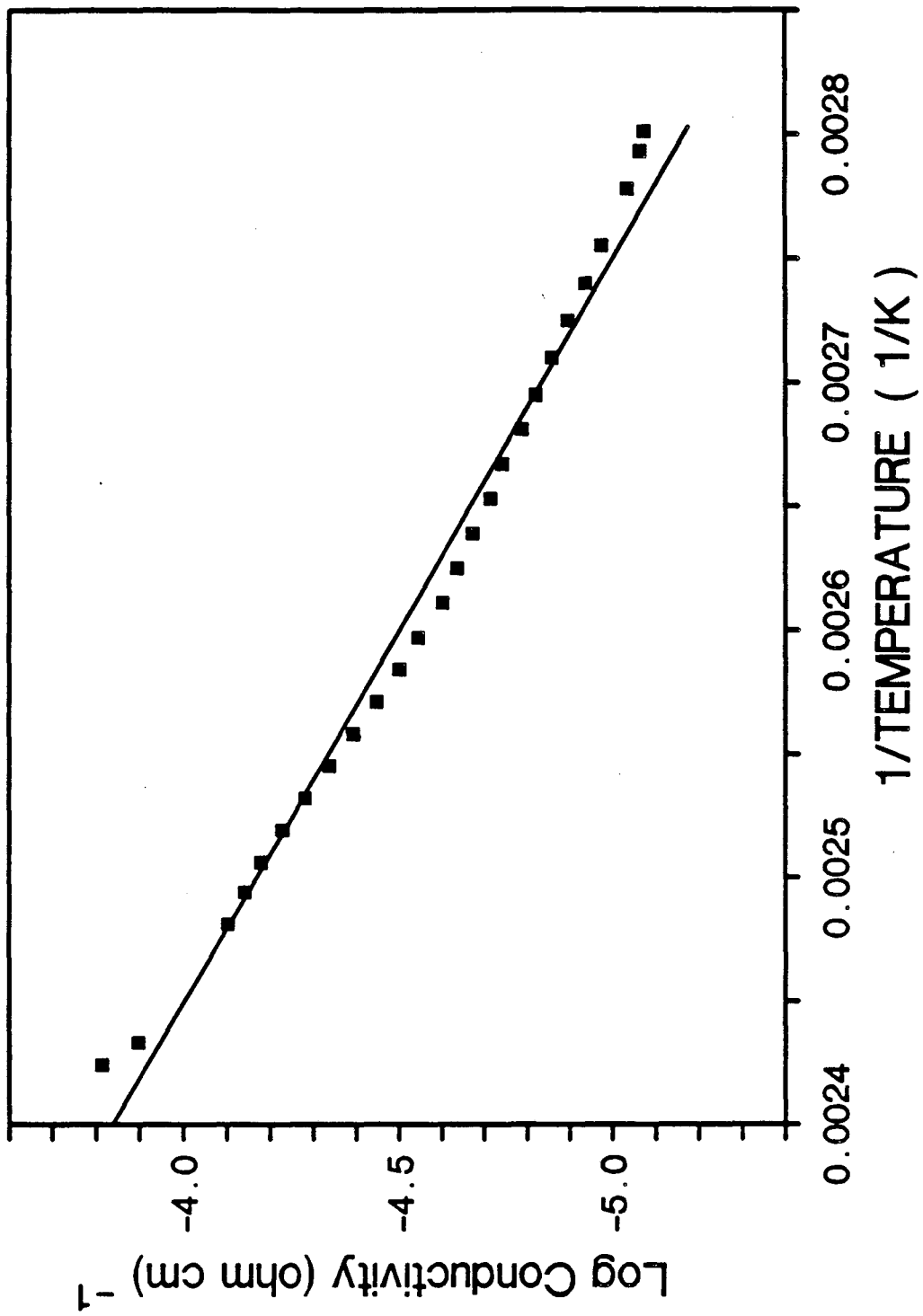
Figure 2

XBL 876-2507

Figure 3

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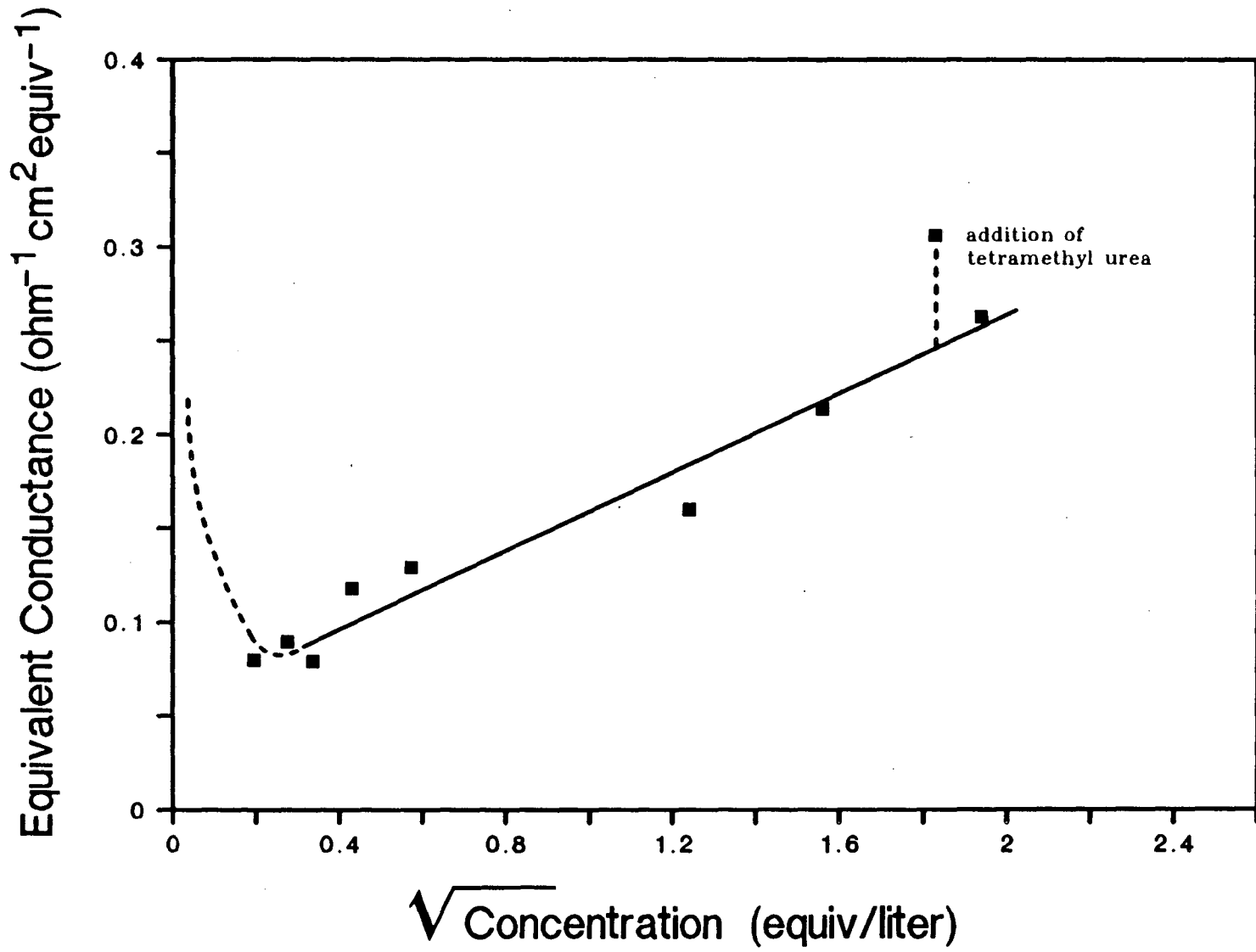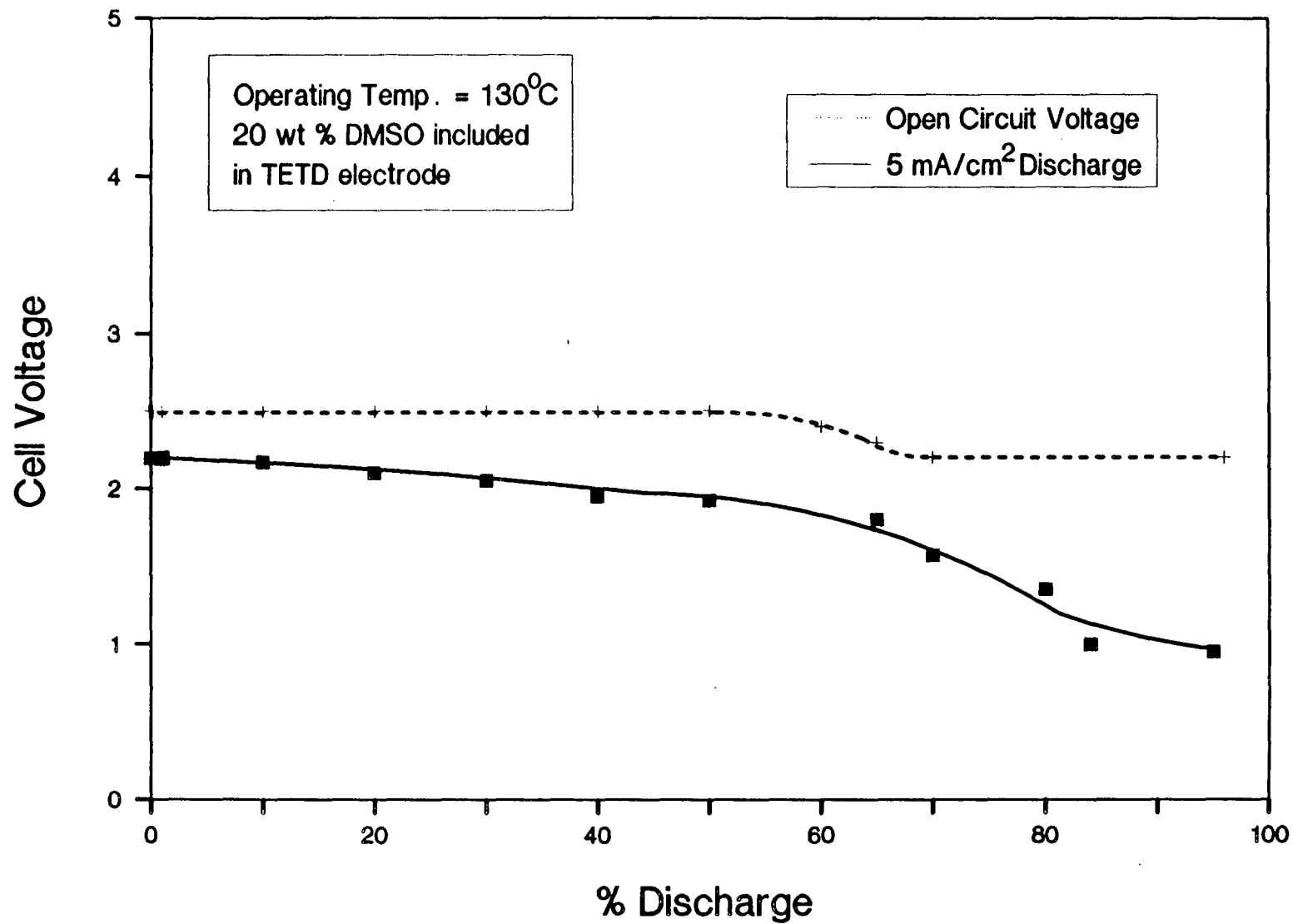
Figure 4

Figure 5

Figure 6

XBL 876-2509

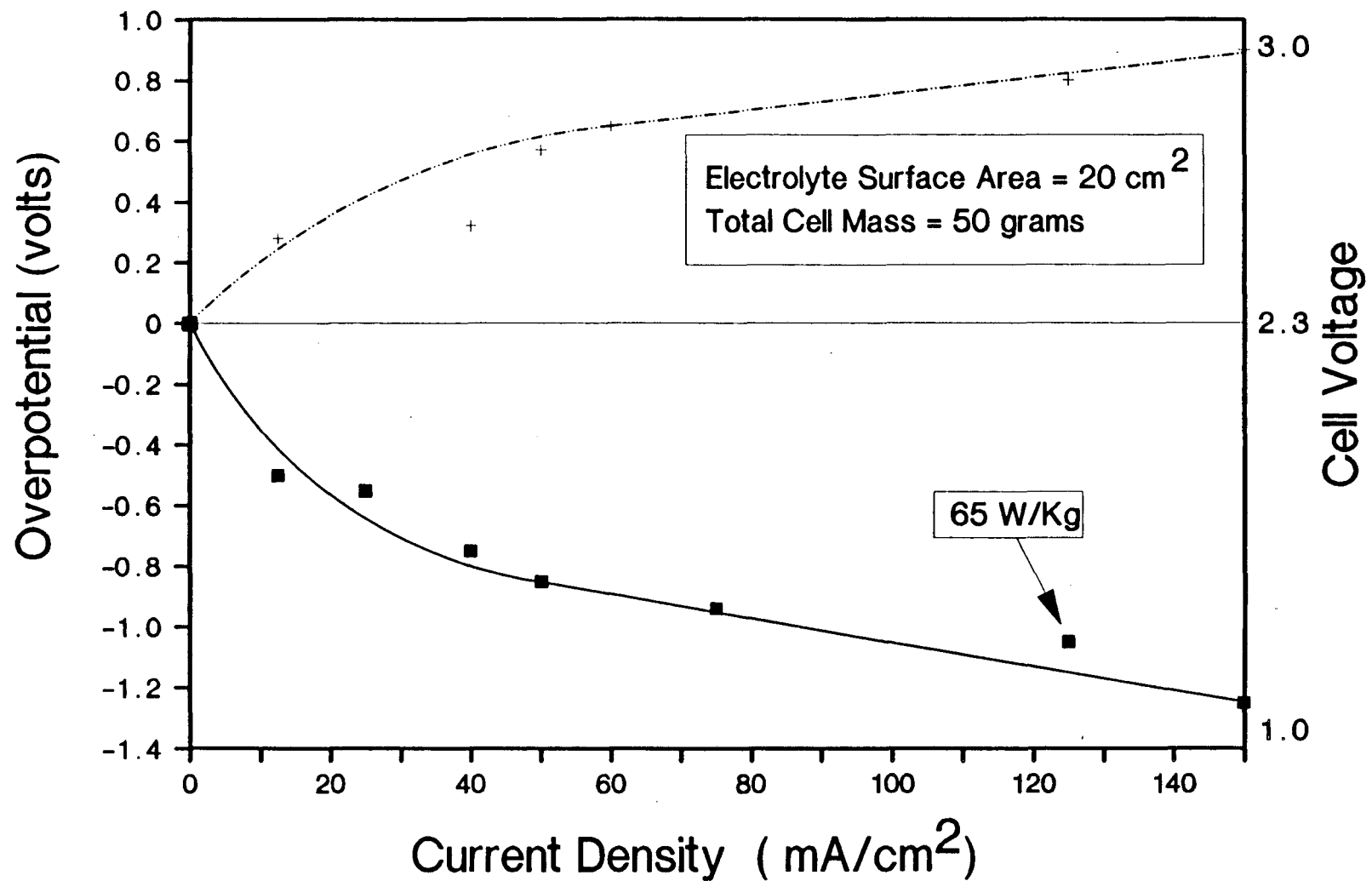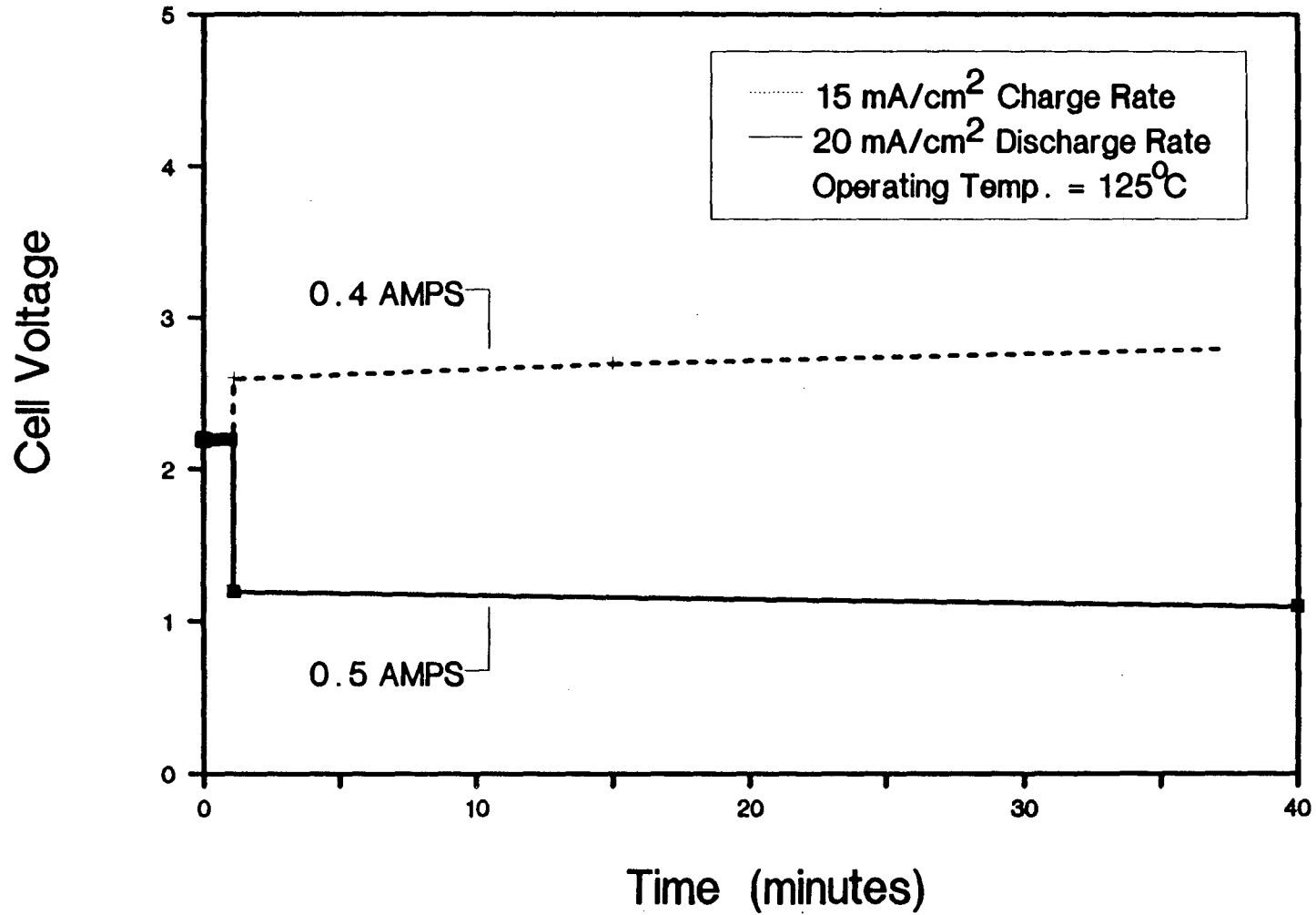Figure 7                                                          XBL 876-2517