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### Publication Date

1989-09-16

UC-406

LBL-27802

Preprint



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

Submitted to Journal of Applied Electrochemistry

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September 1989

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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# Software Control of Galvanostatic Battery Cycling and Cell Evaluation

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## Nomenclature

$\alpha_a$	anodic transfer coefficient ( $V^{-1}$ )	F	Faraday constant ( $96,487 \text{ C mol}^{-1}$ )
$\alpha_c$	cathodic transfer coefficient ( $V^{-1}$ )	$R_{\text{ohmic}}$	Ohmic resistance ( $\Omega$ )
$C_{dl}$	double layer capacitance (F)	$R_F$	Faradaic resistance ( $\Omega$ )
$i_g$	total current density ( $\text{A cm}^{-2}$ )	R	gas constant ( $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ )
$\eta_t$	electrode polarization at time t (V)	T	temperature (K)

## 1 Introduction

In the course of investigation of a series of alkali metal/organosulfur batteries<sup>[1][2][3]</sup> a software package was created to cycle and test these cells. Although the galvanostatic cycling of experimental batteries is conceptually one of the most elementary electrochemical techniques, it can often be quite tedious due to the paucity of hardware and/or software to accomplish this task. Accordingly a program was written, BATTERY.TST, which not only affords complete galvanostatic control of cell charge/discharge cycling, but also furnishes an array of single pulse and multi-pulse current transient routines which aid in the electrochemical characterization of cells under test. The program is completely menu-driven; all parameters for charge/discharge cycling and transient testing are interactively chosen by the user including upper and lower voltage cutoffs to prevent excessive polarization of cells and a coulomb cutoff to prevent overdischarge/overcharge. The program also allows continuous monitoring of cell pressure and temperature through the use of a pressure transducer; it was found to be useful to monitor pressure buildup in the positive electrode compartment of sodium/ $\beta''$ /organosulfur cells<sup>[4]</sup>. Upon program execution the software provides continuous real-time display of cell voltage, current, coulombs, temperature, and cell pressure (if desired), with high-resolution graphics display of cell potential as a function of time. Furthermore, current transient routines subject batteries to various pulse sequences in order to determine the internal cell resistance, power, and energy efficiency, as a function of current load; the option of calculating and plotting a gravimetric Ragone plot is also offered. Moreover, the acquired data can be automatically stored in a variety of ways, including transferral to a Lotus 123 spreadsheet file. Importantly, the software described is not specific to the hardware employed in this laboratory, and consequently can be used to control any commercial (or otherwise) galvanostat which allows remote control of current load by application of an external voltage (most galvanostats do).

## ABSTRACT

A software package was created which not only affords complete galvanostatic control of charge/discharge cycling, but also furnishes an array of single-pulse and multi-pulse transient routines which aid in the electrochemical characterization of batteries under test. The program, BATTERY.TST, is completely menu-driven and includes high-resolution, real-time display of cell voltage behavior as well as concurrent text display of cell voltage, coulombs, temperature, current, and % charge/discharge. All parameters for charge/discharge cycling and transient testing are interactively chosen by the user including upper and lower voltage cutoffs to prevent excessive polarization of cells under test and a coulomb cutoff to prevent overdischarge/overcharge if desired. Current transient routines subject test batteries to various pulse sequences in order to determine the internal cell resistance, power, and energy efficiency as a function of current load; the option of calculating and plotting a gravimetric Ragone plot is also offered. Further, a multi-pulse sequence allows estimation of the cell resistance, effective exchange current, and limiting current by non-linear curve-fitting of the overpotential/current data. Importantly, the software described is not specific to the hardware employed in this laboratory, and consequently can be used to control any commercial (or otherwise) galvanostat which allows remote control of current load by application of an external voltage.

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, United States Department of Energy, under Contract No. DE-AC03-76SF00098.

## 2 Experimental

### 2.1 Hardware

The workstation used for computer control was an IBM PC/AT, although any PC or compatible would suffice. Data acquisition and control was achieved with a Data Translation DT-2801A board, having a maximum throughput rate of 27.5 KHz ( $37\mu\text{sec}/\text{data point}$ ), and 12 bit resolution allowing maximum signal resolution of about 1 millivolt ( $5\text{ volts}/2^{12}$ ); the 2 D/A output channels were jumpered to yield the maximum voltage range, -10 to 10 volts. The galvanostat interfaced was a Princeton Applied Research model 371 (and a PAR 173/179), with a maximum current of  $\pm 7$  amps (140 watts) and a rise time of  $4\mu\text{secs}$ . Cell potential was monitored by non-current-carrying leads in parallel with the cell. Battery temperature was monitored with a Type K thermocouple with an Omega CJ-K Cold Junction Compensator. Cell pressure was monitored by an Omega PX 600-200G V pressure transducer mounted in the positive electrode compartment wall<sup>[4]</sup>. Cell current was monitored by the potential drop over the control resistor of the PAR 371 Galvanostat (or the voltage output of the current monitor of the PAR 173/176). The data acquisition card and the computer were protected from the analog input signals by means of low watt resistors in series with the voltage signals and transorbs in parallel with the signal.

Control of the PAR 371 galvanostat is accomplished by application of an external analogue input (computer generated) on the front panel. The current output of the galvanostat is proportional to the potential applied at the external input to the current control resistor mounted on the front panel ( $I = V/R$ ).

Thus for a control resistor of  $100\ \Omega$  and a D/A output range of -10 to 10 volts, the galvanostat can be driven to  $\pm 100\ \text{mA}$  with a current resolution of  $200\ \text{mA}/2^{12} = 0.05\ \text{mA}$ .

### 2.2 Organosulfur Batteries

Actual battery cycling was performed on various sodium/ $\beta''$ /organosulfur cells operating in the temperature range of 100 to  $150^\circ\text{C}$ <sup>[1]</sup>. Careful control of cycling of these cells was necessary since serious uncontrolled polarization and/or pressure buildup could lead to catastrophic cell failure.

Sodium/ $\beta''$ -alumina/organodisulfide (Na/RSSR) cells were assembled as described in a previous publication<sup>[4]</sup>. One of the Na/RSSR cells had a positive electrode consisting of 0.60 Ah of bis-(2-mercapto-1-methylimidazole) disulfide (MMIZ) with 50 wt% dimethylsulfoxide, and another cell had a positive electrode consisting of 0.64 Ah of ethoxyethyl disulfide (EEDS) with 50 wt% 1-methyl-2-pyrrolidinone. Also tested with the program were novel all-solid-state, alkali metal/polyethylene oxide/organosulfur cells<sup>[5][6][7]</sup>, as well as commercial nickel/cadmium and alkaline cells.

## 3 Control/Aquisition Program

### 3.1 Control Language

The control program presented in this manuscript was written in ASYST\* which is a high level language based on FOURTH, and geared towards laboratory control/data acquisition. Further, ASYST uses array-based mathematics which is well suited to D/A control; using this language allowed very rapid development of software to control a variety of electroanalytical techniques (chronoamperometry, chronocoulometry, cyclic chronopotentiometry, etc.)

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\* ASYST Software Technologies, Inc., 100 Corporate Woods, Rochester, New York 14623

### 3.2 Arrays for D/A Output to the Galvanostat: Charge/Discharge Cycling

The main program BATTERY.TST for battery testing is actually composed of 5 interrelated subprograms: CONTROL.DISCHARGE, CONTROL.CHARGE, and DISCHARGE.CYCLE, as well as the transient current pulse programs POLARIZE, POLAR2, and TRANSIENT.POL (fig. 1)



Figure 1. Main menu for BATT.TST

In order to output the appropriate control voltages to the galvanostat, the correct integer values have to be sent to the DT2801 board from the ASYST environment. This is accomplished by the use of control arrays which are filled with the appropriate values after completion of a series of prompts to the user.

The 100 element integer array CONTROL.OUT is generated interactively upon selection of either subprogram CONTROL.DISCHARGE or CONTROL.CHARGE, fig. 1. The D/A array CONTROL.OUT is output in a cyclic fashion, allowing periodic monitoring of the open circuit voltage. At the start of either subprogram the user is prompted for the charge or discharge rate desired. This real value is converted to the corresponding integer value for D/A output and all 100 elements of CONTROL.OUT are set equal to this integer. Next, the first four elements of the control array are set equal to 2048 (zero volts = zero current) if the user previously answered the prompt during loading of the main program, "MEASURE THE CELL OCV, Yes or No," with an affirmative. Since the control/acquisition routines in the CONTROL.DISCHARGE and CONTROL.CHARGE consist of a 1000 step synchronized loop, the 100 D/A values in the CONTROL.OUT array are output in a cyclic manner ten times, driving the galvanostat to the current output seen in fig 10a,c. In this way one has an indication of whether the voltage behavior of a cell under load is due to polarization or changes in the open circuit potential, however this OCV measurement is an estimate since the cell is only turned off for 4/1000 of the total test time. If one wants continuous charge or discharge without periodic cell shutoff, all elements of the control array are merely left equal to the entered charge/discharge rate. Further, if the battery under test polarizes beyond the user voltage cutoff (described below), the CONTROL.OUT array is automatically re-generated at 1/2 the previous current level, during one execution of a program loop fig. 2.

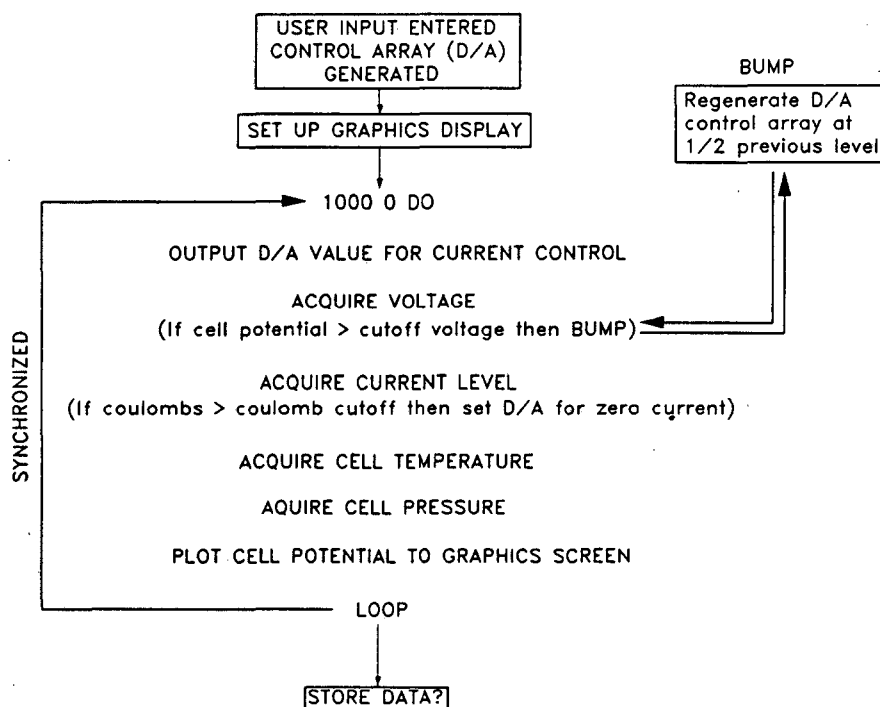


Fig. 2 Flow chart for control/acquisition in CONTROL.DISCHARGE, CONTROL.CHARGE, and BATTERY.CYCLE subprograms.

The D/A array for continuous cycling of cells is CONTROL.CYCLIC.OUT. This 1000 element integer is also generated interactively (fig. 1) upon selection of the BATTERY.CYCLE routine. The 1000 element array is handled as  $2n$  subarrays of  $n$  charge and  $n$  discharge arrays. The program assigns the number of elements per subarray based on the user chosen charge/discharge rates, cell capacity, and total number of cycles, and then builds the CONTROL.CYCLIC.OUT array by filling it with the appropriate integer values, furnishing control of the galvanostat as shown in fig. 11. If during control/acquisition, the cell polarizes beyond the user-selected upper and lower voltage limits, the control array is reset to correspond to zero current and the cell is effectively shut off.

### 3.3 Arrays for D/A Output to the Galvanostat: Current Transients

#### A. Theory

Since batteries under load rarely follow Ohms law ( $V=iR$ ), it is often desirable to determine the voltage response of a cell as a function of current drain. If the current load is applied for a sufficiently short duration (dependent on current load), the voltage response should not include mass transport effects. Further, for batteries in which the polarization behavior is dominated by one electrode (metallic negative electrodes are frequently non-polarizable) the cell overpotential can be approximated by the response of a single polarizable electrode. The response of an electrode to a current step can be viewed in terms of a simplified equivalent circuit,



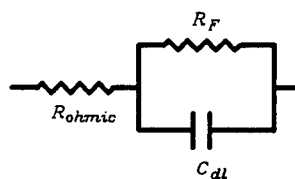


Fig. 3 Simplified equivalent circuit for an electrode.

where  $R_{ohmic}$  is the sum of all the ohmic terms such as electrolyte resistance, lead resistance, etc.,  $R_F$  is the faradaic impedance due to charge-transfer, and  $C_{DL}$  is the double-layer capacitance. The total current then flowing through the parallel circuit is  $i_g = i_{DL} + i_F$  which can be expanded to give

$$i_g = C_{DL} \frac{d\eta_t}{dt} + i_o \left[ e^{\frac{\alpha_a F \eta_t}{RT}} - e^{-\frac{\alpha_c \eta_t}{RT}} \right] \quad \text{Eq. 1.}$$

where  $\eta_t$  is the electrode polarization at time  $t$ , and  $\alpha_a$  and  $\alpha_c$  are the anodic and cathodic transfer coefficients, respectively. The current flowing in the circuit can be represented as in figs. 4a,b,c. As can be seen in fig. 4, after a current step, current initially flows into the capacitor since  $d\eta_t/dt$  is greatest initially, then current flows due to charge transfer as  $\eta_t$  increases in magnitude, with current flow eventually being supported almost completely by charge transfer.

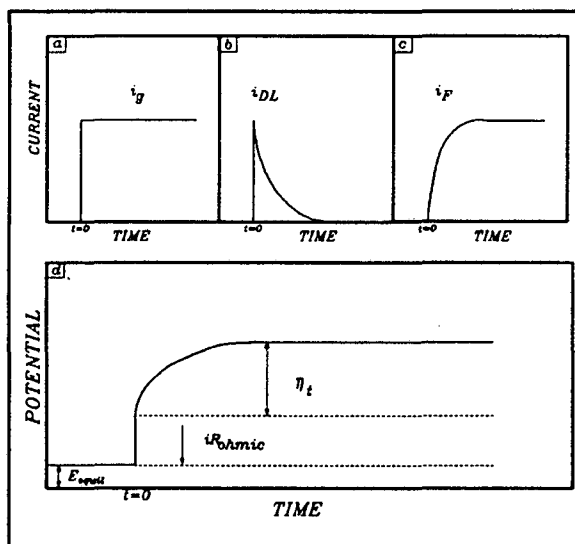


Figure 4. Current and potential profiles for equivalent circuit subjected to a current step.

From basic circuit theory the voltage response of a parallel RC circuit to a current step is given by,

$$V_t = V_\infty \left( 1 - e^{-\frac{t}{\tau}} \right), \quad \text{where } \tau = RC \quad \text{Eq. 2.}$$

When  $t = \tau$ ,  $V_t = V^\infty(1 - e^{-1})$ , or  $V_t/V^\infty = 0.63$ , in other words the voltage has reached 63% of the value at infinity at one time constant. When  $t = 5\tau$ , the voltage is 99.3% of the value at infinity. A similar approach can be used for the electrochemical circuit if the charge transfer resistance<sup>[8]</sup> is used for  $R_F$ ,

$$R_{ct} = \frac{RT}{nFi_o} \quad \text{Eq. 3.}$$

The analogous equation is then,

$$\eta_t = \eta_\infty \left( 1 - e^{-\frac{t}{\tau}} \right), \quad \text{where } \tau = \frac{RTC_{dl}}{nFi_o} \quad \text{Eq. 4.}$$

If one uses reasonable values of  $i_o = 10^{-4}$  A/cm<sup>2</sup> and  $C_{dl} = 20$   $\mu$ F/cm<sup>2</sup>, then  $\tau = 0.005$  seconds. Therefore in 5 ms the voltage would be at 63% of the final value and at 25 ms would be at 99.3% of the final value. In fact, for all the batteries we tested the time constant was much smaller since the exponential decay was not seen even on a 50  $\mu$ sec timescale. In any case, for most systems 100 ms current pulses should be more than sufficient to measure the impedance due to charge transfer and ohmic losses. Further, unless the magnitude of the current pulse is fairly close to the limiting current  $i_L$  (or at much longer pulse widths), the mass transfer overpotential ( $\eta_{mt} = \frac{RT}{nF} \ln[1 - i/i_L]$ ) will be negligible. Therefore, the total voltage drop in the cell is represented by,  $V = i_g (R_{ohmic} + R_F)$ , as shown in Fig. 4d. For batteries in which both electrodes contribute significantly to the cell overpotential under load, the potential response of both electrodes (and the electrolyte) to a current transient can be isolated and characterized by the use of reference electrodes (4-probe technique) precisely positioned between the anode and cathode<sup>[9]</sup>.

The shape of the overpotential vs. current plot can furnish information on the types of processes controlling the performance of the cell (fig. 10). If overvoltage is plotted as a function of current, under charge-transfer polarization (Butler-Volmer equation) the slope decreases as a function of current. In the case of mass transfer polarization, the slope increases with current as diffusion cannot keep up with the current demand (ultimately tending towards infinity). Further, the voltage response of a cell to a current load allows the determination of power output and voltage efficiency as a function of current.

### B. Transient Control Arrays

The control array for the POLARIZE subprogram is DATA.OUT. This array is generated on loading of the main program when the user is prompted with "ENTER MAX DISCHARGE RATE (AMPS) FOR PULSE TEST." The control array is then configured as 7 square waves (2 elements each) followed by 4 elements of zero current between each pulse, monotonically increasing to the maximum discharge rate, followed by a large rest period (50 elements), and then 7 symmetric pulses of opposite polarity (fig. 9). The POLARIZE program (described below) outputs this control array with a synchronization of 50 msec per element, in other words each current pulse is held for 100 msec before the cell is returned to zero current, and the total time for the test is 5 seconds (fig. 9). The

first four elements of this array are set to zero current in order to determine the open circuit voltage prior to application of the transient. If a different pulse height maximum is desired, this can be altered at any time by entering SET.PULSE at the keyboard.

A more powerful version of the POLARIZE subprogram is the POLAR2 program; more overpotential/current information is extracted, and the synchronization speed is user selectable. The D/A array for this program is CONTROL.CYCLIC.OUT. In this case the array is filled during execution of the program (fig. 1) to consist of a waveform of 180 monotonically increasing bipolar current square waves (+90/-90) as shown in figure 5. The magnitude of the waveform envelope is determined by the user-entered value for the maximum discharge rate. The CONTROL.CYCLIC.OUT array is constructed by two routines which fill the 90 discharge and then 90 charge subarrays, to give a final array consisting of bipolar square waves having a 2-time-increment pulse (100 ms) followed by a 3 increment rest (150 ms), followed by a reverse polarity pulse of the same shape and magnitude; the first 50 (and last 50) elements of this array are set to zero to determine the open circuit voltage (OCV) prior to the pulse sequence (fig. 5). The shape of the output as shown in fig. 5 was chosen to allow a lot of polarization data to be collected on a test cell without causing a net change in the capacity of either electrode during the test. Still, the user should be aware that depending on the magnitude of the pulse sequence chosen, and the internal resistance of the cell, IR heating of the battery under test could lead to enhanced kinetics (particularly toward the end of the pulse sequence), effecting interpretation of the data.

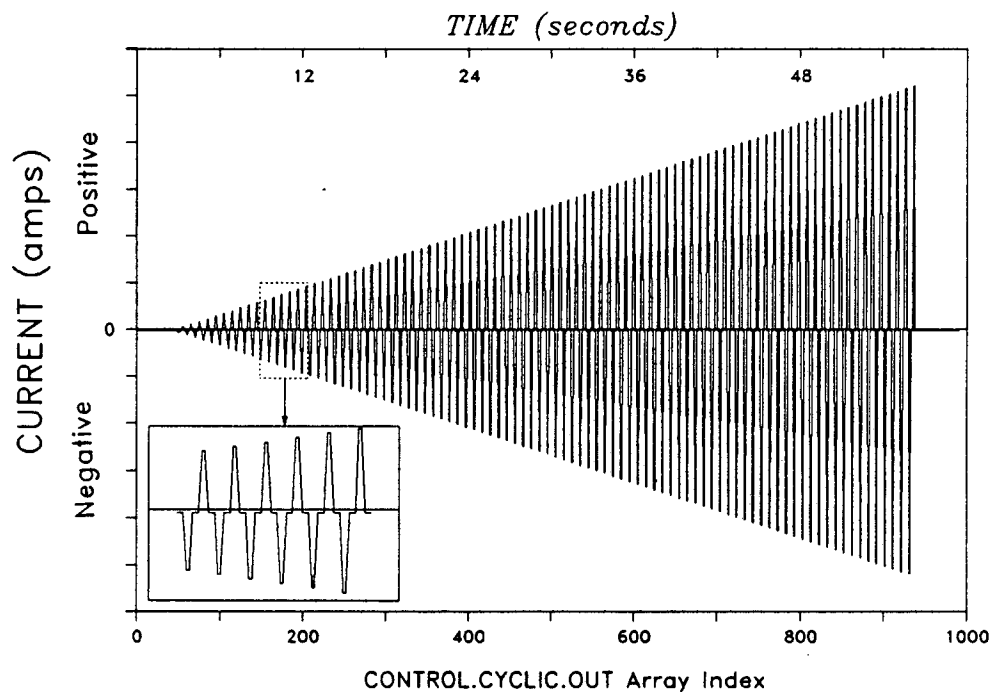


Figure 5. D/A Array for POLAR2 Program

### **3.4 Arrays for A/D Data Acquisition and Storage**

In the CONTROL.DISCHARGE, CONTROL.CHARGE, and DISCHARGE.CYCLE, programs all A/D input is stored in arrays except for the temperature data since it is generally invariant over the test. The input data is stored in 1000 element integer arrays VST.DATA, IST.DATA, and PST.DATA, for the cell voltage, current, and pressure, respectively. The voltage and current waveforms acquired in the POLARIZE program is stored in the 100 element integer arrays FOR.DATA and FOR.CUR.DATA, respectively, and the overpotential and current data acquired in the POLAR2 program is stored in the 90 element integer arrays CUR.PULSE.3, OVER.VOLT.3, CUR.PULSE.4, and OVER.VOLT.4. Upon completion of all of the cell testing programs the user is prompted with "Store the data, Yes or No? ". If affirmative, the integer data is converted to real voltages, and stored along with appropriate text comments describing the conditions of the experiment in ASYST file format. If desired, the user is also allowed to automatically transfer the acquired data along with comments to a Lotus Spreadsheet file.

### **3.5 Graphics Display**

The current program is written to take advantage of the IBM enhanced color graphics card and corresponding monitor, but also works with a high resolution monochrome setup. The color display was divided into two major windows with top and bottom windows being further divided in two, furnishing six graphics windows, and allowing simultaneous graphic display in four windows. Further, 17 multi-colored text windows were defined, allowing text display concurrent with graphics. Text windows are used to display A/D values as they are measured, such as cell voltage, pressure, temperature, coulombs, etc. In this way, all values being processed from the A/D channels are simultaneously displayed, in addition to real-time graphics display of cell potential behavior.

### **3.6 Loading the Main Program**

Prior to running the BATT.TST program one must configure ASYST for the type of data acquisition board in use, memory requirements, and ASYST overlays needed. Once ASYST has been configured properly, it is given a filename and saved, in this case the executable configuration file is BATTERY (the configuration procedure need not be repeated unless a different data acquisition card is used, etc.). The ASYST environment is therefore invoked by issuing the command BATTERY, and the program is brought up by the command LOAD BATT.TST. While in the process of loading the program, the user receives several prompts: (1) " ENTER VALUE IN OHMS FOR CONTROL RESISTOR ", this supplies the program with proportionality constant needed for accurately controlling the PAR current levels ( $I = V/R$ ), whereupon the program displays the maximum current attainable with this resistor; (2) " DO YOU WANT PRESSURE MEASUREMENT? ", this toggles the acquisition of pressure data; (3) " DO YOU WANT THE CELL OCV MONITORED? ", determines whether or not the first 4 elements of CONTROL.OUT are set to zero volts; (4) " DO YOU WANT THE CURRENT DISPLAY IN AMPS OR mA? ", which scales the ammeter for the screen display. The rest of the BATT.TST program is then loaded, and the program banner and menu are displayed.

All test programs can be called from the function keys as shown in figure 1. The main menu is displayed in the normal display mode. Since all programs are run in the graphics display mode, one must switch to the graphics screen ( F3 ) before running routines F4 through F9, unless F2 is executed from the main menu which automatically switches to graphics.

## 4 Results and Discussion: Running the Programs

### 4.1 POLARIZE (F5)

The POLARIZE program applies a series of 14 preset current pulses through the cell while monitoring the voltage response to this stimulus. This is an extremely convenient means of quickly determining (5 secs) the cell internal resistance on charge and discharge, allowable current levels, and the polarity of all connections to the cell. The program is initiated by pressing F5, after which the monitor displays the output waveform as shown in fig. 6.

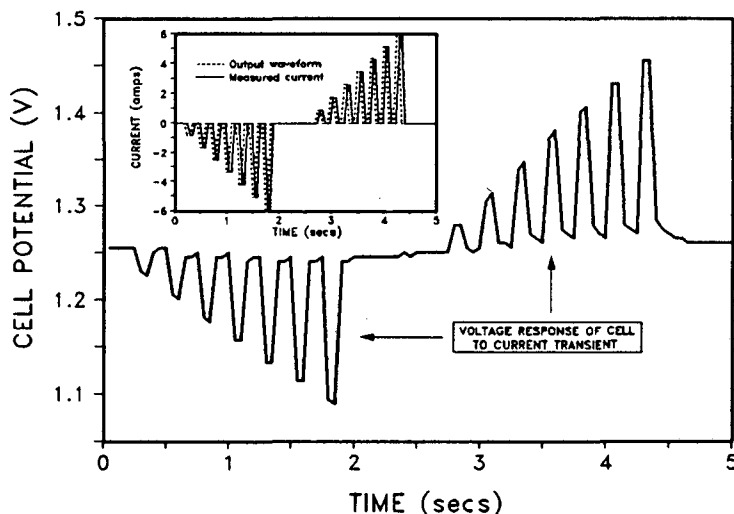


Figure 6. Voltage response of commercial Nicad (D) battery to transient pulse sequence in POLARIZE program.

The D/A and A/D operations are completed in a total of 5 secs, after which the measured current and voltage response are plotted to the monitor (fig. 6). The current and voltage maximum and minimum values are selected from the data acquisition arrays and the corresponding internal cell resistance is calculated and displayed. The user is then prompted for data file storage, and finally the overpotential ( $V - V_{OCV}$ ) vs. cell current for charge and discharge, as well as the power output and energy efficiency vs. current load are plotted to the monitor.

The internal resistance values and shape of the ( $V - V_{OCV}$ ) vs.  $I$  curve is a quick way to evaluate transient cell performance and qualitatively identify limiting processes in cell performance, i.e. charge transfer, ohmic drop ( ionic conductivity, etc. ), or mass transfer. The only drawback to the POLARIZE program is that the amount of polarization data collected is insufficient for effective curve fitting routines to estimate the polarization parameters. For this purpose the POLAR2 program was written.

### 4.2 POLAR2 (F1)

The POLAR2 program is a more powerful version of the POLARIZE program for accurate determination of cell polarization. In this routine, a symmetric bipolar array of 180 linearly increasing current pulses are applied to the cell ( fig. 5). The user-entered current maximum is limited only by the maximum current obtainable by the galvanostat. In this way, the cell can be polarized to whatever extent desired, within the allowable current range of the galvanostat. If desired, the user can first run the TRANSIENT program in order to determine an appropriate current maximum for the POLAR2 routine. The POLAR2

program is started by hitting F1 while in graphics mode. The user is prompted with " ENTER MAX DISCHARGE RATE IN AMPS ", after which the program constructs the D/A array and applies the output waveform to the test cell with simultaneous monitoring of the actual cell current (current monitor voltage) and cell voltage. The program then extracts 4 x 90 data points corresponding to the cell current and potential response for each of the current spikes in the output waveform. The program then calculates and sequentially displays the cell polarization, power output/input, and voltage efficiency, as a function of cell current for charge and discharge. Further, the user is allowed the option to fit the experimental polarization data to the following non-linear equation which describes the relation between overpotential and current for a single electrode,

$$\eta = -\frac{RT}{\alpha nF} \left[ \ln\left(\frac{i}{i_0}\right) + \ln\left(1 - \frac{i}{i_L}\right) \right] - iR_{int} \quad \text{Eq. 5.}$$

This is done by using a non-linear least squares fit with three adjustable parameters, R,  $i_0$ , and  $i_L$ . The user has the option of a one parameter fit which neglects the exponential terms and fits the data to ohms law ( $V=iR$ ), or a two parameter fit which neglects the mass transfer term and solves simultaneously for R and  $i_0$ , or a three parameter fit which finds the best fit to equation 5.

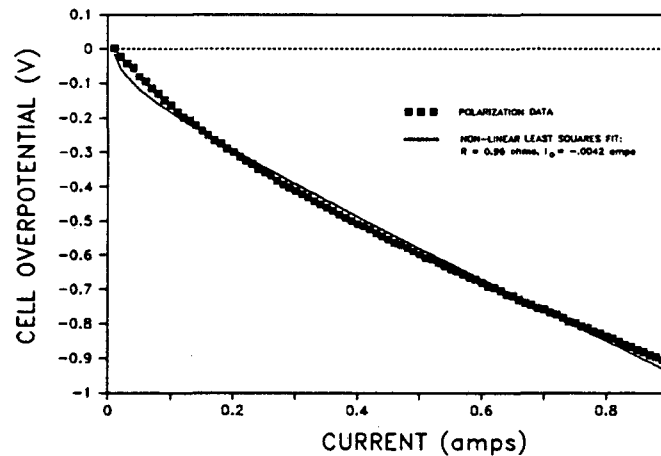


Fig. 7. Overpotential behavior of Na/ $\beta''$ -alumina/EEDS cell during POLAR2 transient; maximum current was 1 amp.

Since the polarization behavior of a galvanic cell includes contributions from both the anode and cathode, equation 5 is a very rough approximation of the limiting parameters to cell performance. However, in many batteries, it is often the case that one electrode controls the polarization behavior of the cell. This is certainly the case for sodium/organosulfur cells, where the sodium electrode is essentially non-polarizable. Furthermore, the polarization behavior of both electrodes can easily be separated by the use of a reference electrode, and the response of each electrode can then individually be fit to equation 5. Since the real area of each electrode is rarely known, the fitted parameters can be termed the effective exchange current and limiting current. A two parameter fit ( $R, i_0$ ) to equation 5 is shown in figure 7.

Finally, the program prompts the user with " Calculate the Ragone plot? " which will calculate and plot the gravimetric power density vs. energy density of the cell as displayed in figure 8, given the user entered values of cell weight and capacity.

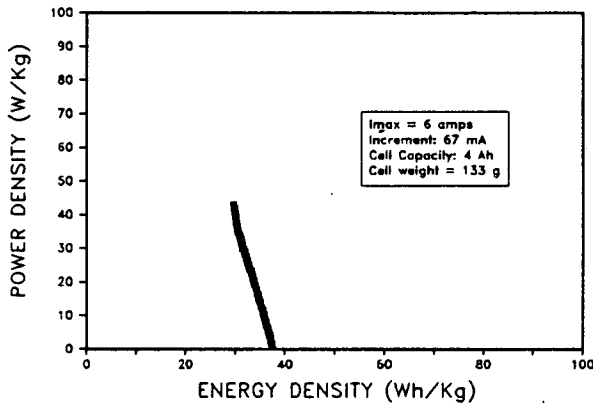


Fig. 8a Gravimetric Ragone plot for commercial nicad "D" cell; automatically plotted to screen display by POLAR2 subprogram.

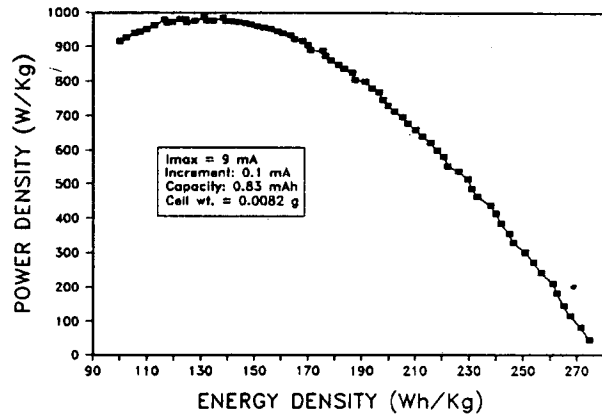


Fig. 8b Gravimetric Ragone plot for thin film, all-solid-state, lithium/polyethylene oxide/organosulfur cell.

#### 4.3 TRANSIENT (F4)

The transient program directs the galvanostat to output a square wave current pulse through the test cell as shown in fig. 9. This allows a quick determination of peak current and/or peak power for a single current pulse. The magnitude and sign of the current pulse is user-selected as is the time period for the test. The program is initiated by pressing the F4 key in the graphics mode, and prompts the user as shown in fig. 1. Since the output and acquisition arrays consist of 100 elements each, a choice of synchronization period of 5 ms would give a total test time of 0.5 seconds. If the choice of synchronization period is too small, the graphics display will flash "SYNC ERROR!", at which time the user should stop the program with CTRL BREAK. Upon entering values at the prompts, the graphics screen draws the expected current waveform and calculates the time axis. Upon completion of data acquisition the graphics display shows the measured current waveform, and the voltage response to the transient (fig. 9). Further, the cell resistance is calculated from the observed current and voltage values at the center of the waveforms. Finally, the user is prompted for data storage.

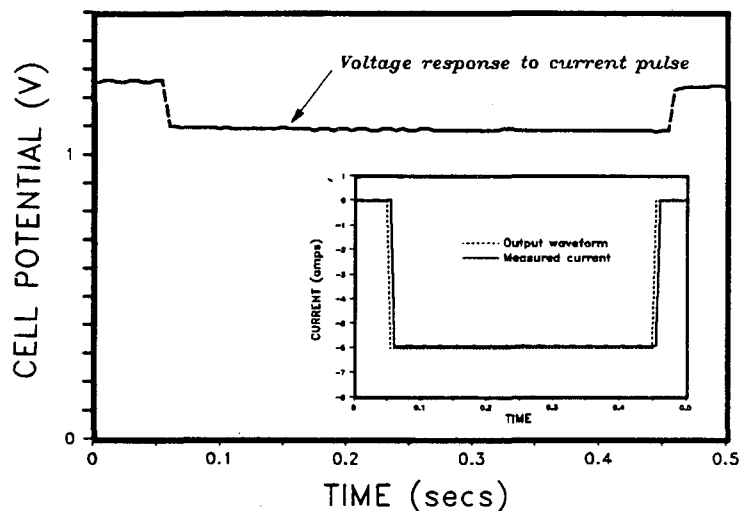


Figure 9. Voltage response of commercial Nicad (D) battery to square wave current output of TRANSIENT program.

#### 4.4 CONTROL.DISCHARGE (F6) and CONTROL.CHARGE (F7)

The CONTROLDISCHARGE and CONTROLCHARGE subprograms are virtually identical in their execution. These routines are very useful for characterization of experimental cells where the time-dependant polarization behavior is yet unknown. The CONTROLDISCHARGE/CHARGE subprograms allow full discharge or charge of test batteries by reducing the current level by a factor of 1/2 (or other factor) each time a upper or lower voltage cutoff is exceeded; one only needs to enter an initial current magnitude, voltage cutoff, coulomb cutoff, and sufficient time for the test and the cell is protected against excessive polarization and over-discharge/charge. The routines are initiated by entering F6 or F7, upon which the user is prompted for input, as shown in the flowchart in fig. 1.

After receiving the appropriate input, the CONTROLDISCHARGE and CONTROLCHARGE programs set up the graphics axes and start a 1000 step synchronized loop in which control of the electrochemical cell and data acquisition occur (figs. 1 & 2). The synchronization time entered is the exact time allowed for execution of one program loop; if the time entered is insufficient for the tasks in the loop, an error is generated and displayed. Since real-time graphics is a time consuming software task, the lower time limit with these programs is about 400 milliseconds/loop, which is more than adequate for battery testing. The synchronization time entered in milliseconds is also equal to the duration of the battery test in seconds, i.e. a synchronization time entry of 3600 milliseconds will discharge a battery for one hour at the chosen rate. The third and fourth user entries constitute conditional values ( if/then ) in the execution of the program loop. If the cell voltage drops below the entered alarm value on discharge, then program will reset the current level to one half of the present value. This is accomplished by reconstructing the CONTROLDISCHARGE ( or CONTROLCHARGE ) array within the execution of one program loop (figs. 2, 10a, 10c). Each time the cell voltage exceeds the alarm trigger the current is halved until the cell is ultimately turned off. Within both these programs is a software coulometer which converts the cell current and synchronization time into coulombs passed through the cell ( negative coulombs on discharge ). Consequently, the third user entry protects the cell from



overdischarge. Once the software coulometer exceeds the user entered value for maximum discharge, the cell is turned off. In the CONTROLCHARGE mode there is no user entered trigger, rather the cell is turned off at 0 coulombs ( zero capacity ). However, when the main program BATT.TST is started the coulometer is set to zero. Therefore, to charge a cell without first discharging it, one must enter the available capacity ( or other suitable value ) in negative coulombs into the coulometer. This is done by entering F8, the RESET program, which turns off the cell current, re-initializes the arrays for graphics, and allows user setting of the coulometer.

Once the user entered values are accepted, the bottom graphics viewport is drawn with the appropriate labels, as are all text windows. As the control/data acquisition program runs all converted A/D values are displayed in each execution of the program loop, and the cell voltage is plotted in real time on the lower graphics screen (fig. 10a).

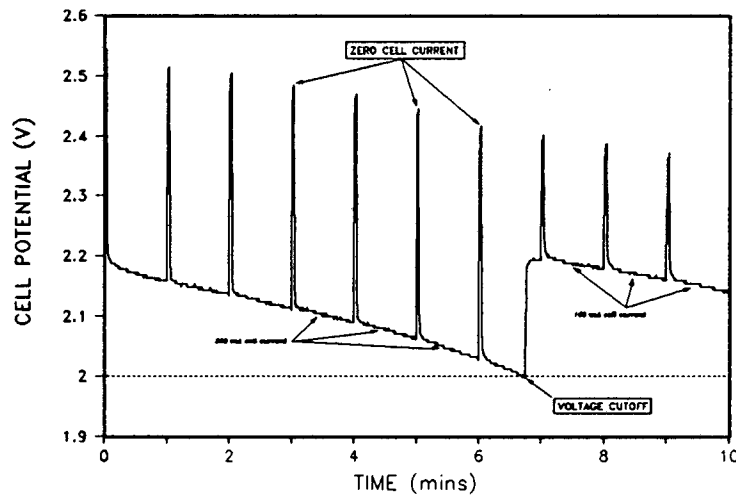


Figure 10a.

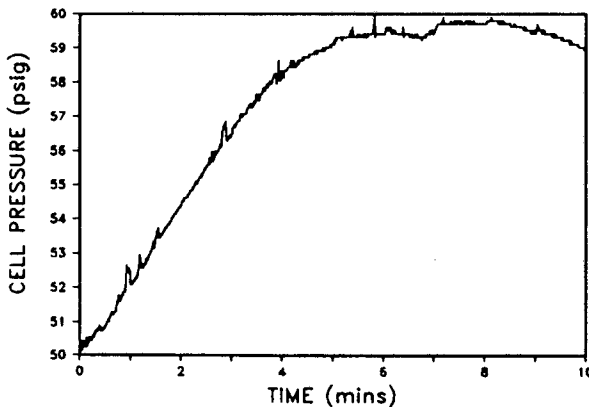


Figure 10b.

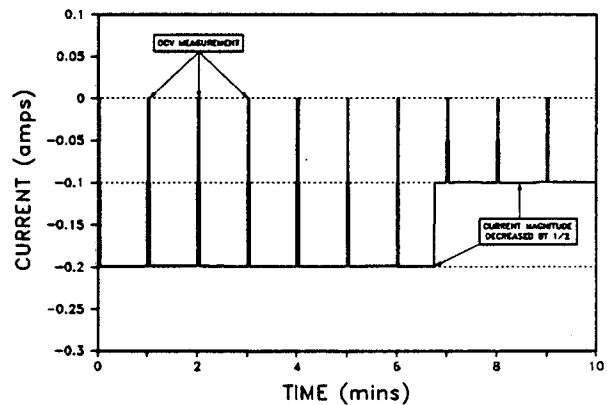


Figure 10c.

Figure 10. Na/ $\beta''$ -alumina/MMIZ cell operating at 120°C: (a) measured cell potential response to galvanostatic control as shown in 6c; (b) measured pressure in positive electrode; (c) actual current control of galvanostat by software generated signal.

After completion of the last control/data acquisition program loop, the user is prompted,

"STORE THIS DATA? YES(1) OR NO(0) "

which provides for storage of all acquired data arrays and associated control and acquisition parameters. Finally, the pressure data is plotted in the upper graphics screen (fig. 10b).

If desired, one can enter the command "P" which smooths the pressure data and calculates the pressure derivative.

#### 4.5 DISCHARGE.CYCLE (F9)

The DISCHARGE.CYCLE program allows the user to cycle a test cell at non-symmetric charge/discharge rates and capacities. The user does not enter a synchronization time, rather this is determined by the user-entered values for capacity, number of charge/discharge cycles, and corresponding current rates. Upon entering F9, the user is prompted as shown in fig. 1. The number of cycles achievable is technically limited only by the number of elements in the array CONTROL.CYCLIC.OUT (1000), which presently allows 500 cycles (1 data pt./charge or discharge). However, if more cycles are desired (or more data points/cycle), the dimensions of the D/A and A/D arrays can easily be increased. Once the user input is entered, the battery cycling program executes exactly as the above programs do, except that the cell is cycled at the designated charge and discharge rates between the entered upper and lower voltage limits, as indicated in figure 11. If the cell voltage exceeds either limit, the cell current is shut off. After the cell is cycled over the time allotted, the user is prompted for data storage as described above.

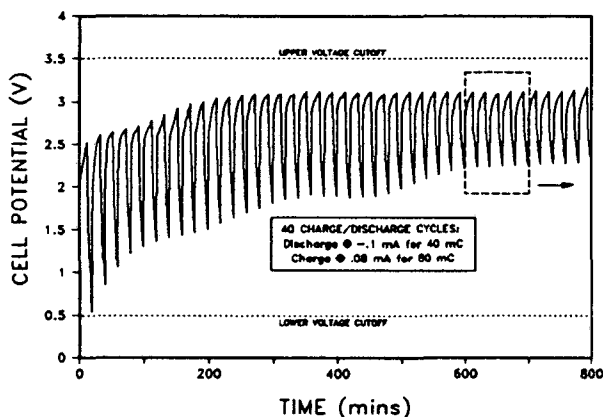


Figure 11a. Cell potential behavior of all-solid-state sodium/organosulfur battery under cyclic control.

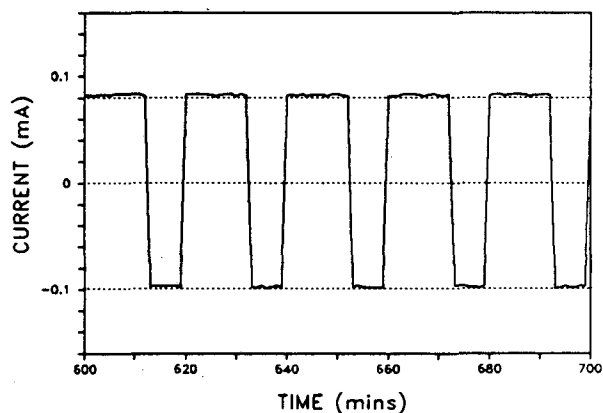


Figure 11b. Exploded view (box in 7a) of current control for cycling program.

#### 5 Conclusions

The BATTERY.TST program is an extremely useful electroanalytical tool for battery testing, both in the control of galvanostatic charge/discharge cycling, and in the determination of transient and continuous polarization behavior. The BATTERY.TST software is not hardware-specific and can be used with any galvanostat which allows remote operation of the current level by application of an external voltage. The BATTERY.TST program is entirely menu-driven, allowing many options in the evaluation of battery performance through the application of user-entered parameters for program execution. This program should find

particular utility in the exploration of new battery systems where there is little *a priori* knowledge of the polarization characteristics of the system, as well as in the testing and evaluation of commercial battery systems.

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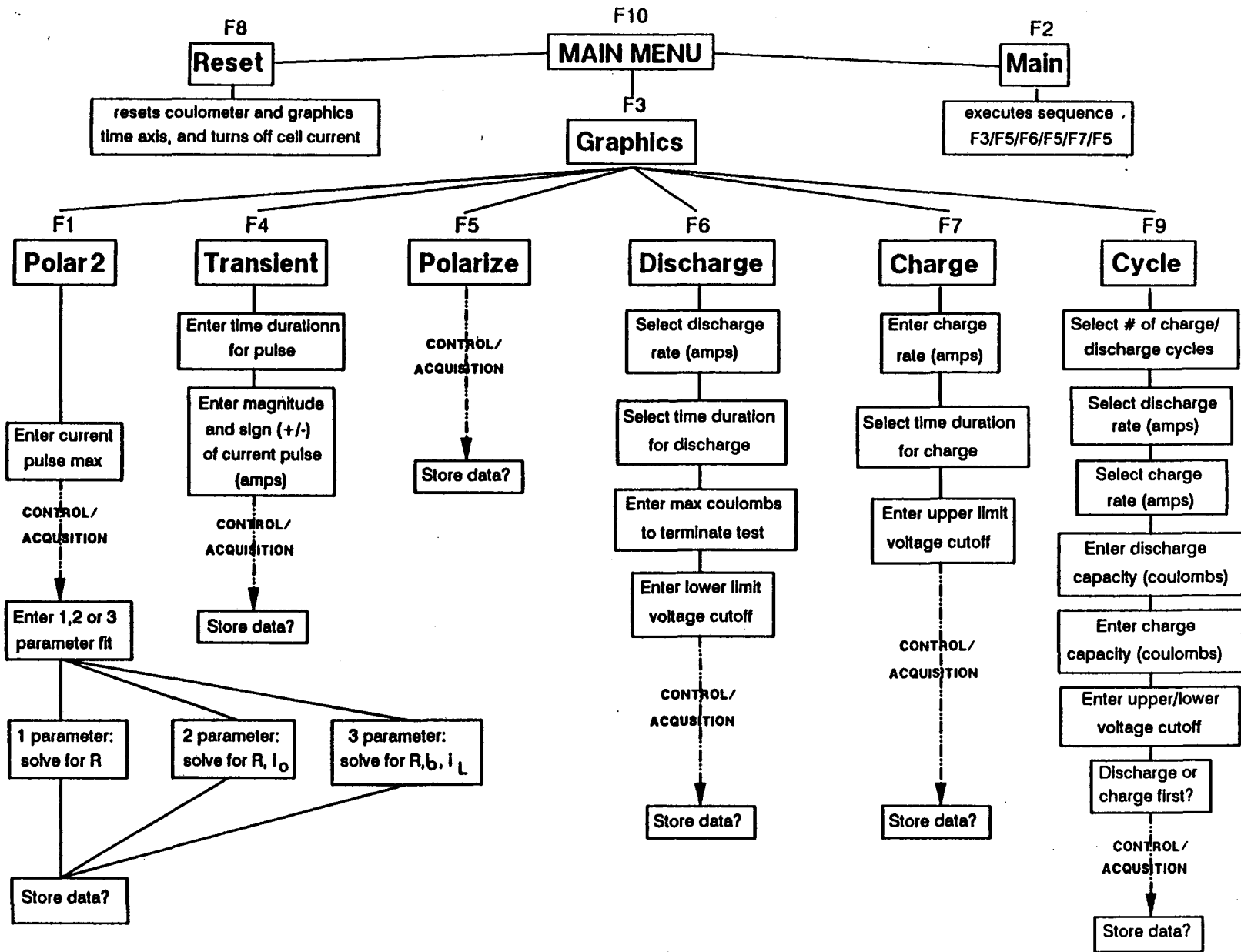


Figure 1.

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