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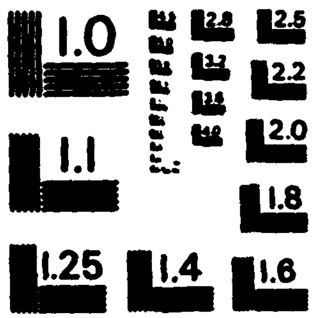

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Automatic Digital Battery Cell Capacitance Measurements

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15 June 1984

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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An instrument of general applicability constructed to automatically measure the capacitance (or impedance) of battery cells is described. Full, automatic, electrical characterization of a battery cell by a single device is made possible with the instrument's added ability to be programmed to charge and discharge the cells. The capacitance can be monitored with a precision of 0.05% and an accuracy of 1%. Data are presented for the capacitance of the nickel electrode at low states of charge as an example of application of the instrument.

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A1

FIGURES

I. INTRODUCTION

Capacitance of battery cells has been one of the most commonly measured battery electrode properties. Capacitance measurements have been correlated with electrode state of charge,[1,2] active surface areas,[3,4] and electrode composition and uniformity,[5] and have been used for performance monitoring and electrode characterization.[6,7] Numerous techniques have been used for such measurements, all of them involving application of either a controlled voltage or a controlled current to the battery cell in such a way that the cell current or voltage response permits capacitance to be determined. Battery cells typically have extremely large capacitance, so applying controlled currents is generally more convenient and accurate than applying controlled voltage.

The application techniques most commonly used are (1) sinusoidally varying currents and (2) step changes in the current. The first gives a sinusoidal voltage response that lags the current by a phase shift; the phase shift and amplitude of the voltage response yield the capacitance. The latter technique induces an exponential voltage change; capacitance is calculated from the initial slope of the change.

This report describes a microprocessor-based instrument that allows the capacitance to be continuously monitored with a high degree of accuracy. The instrument is particularly versatile because it can cycle the battery; measure its impedance; and monitor or plot voltage, current, or capacitance during battery operation. The microprocessor's flexibility makes it possible to assemble the instrument from only the microprocessor and a programmable power supply.

II. PRINCIPLES OF OPERATION

Battery cells are normally charged and discharged at a constant current. Considering that the current is to be controlled by the microprocessor program, we selected a capacitance-measurement technique consisting of applying a step change to the battery current as being most suitable for automatic, computer-controlled operation. When a current step is applied to a battery cell [which may be regarded as an equivalent parallel resistance-capacitance (RC) circuit], the resulting exponential cell voltage change can be used to calculate the capacitance, by the following equation:

$$C = \frac{\Delta I}{\left(\frac{dV}{dt}\right)_0} \qquad (1)$$

where ΔI is the current step and $(dV/dt)_0$ is the initial slope of the exponential voltage response. For the capacitance calculated by Eq. (1) to correspond to a true battery capacitance, the initial slope must be constant. In applying this technique (or any technique) to an electrochemical system, the cell voltage must not be permitted to change more than about 5 mV during the measurement time, because the capacitance is generally a sensitive function of voltage.

For the instrument to apply Eq. (1) to a battery cell, it must know what ΔI to apply, and for how long to apply it, without departing from the linear region of the exponential response. To determine those parameters, the instrument makes an initial guess ΔI_i, using a 5% decrease in the charge or discharge current. The computer monitors the voltage response* to evaluate its amplitude A and time constant τ, then it computes ΔI and t based on allowing ΔV to be 10% of A and not exceeding 3 mV, as follows:

*The voltage response to a current step recorded in this fashion can, of course, be used to determine cell impedance as a function of frequency.[8]

$$\Delta I = \Delta I_i \left(\frac{0.0030}{0.1\ A}\right) \tag{2}$$

$$t = \tau\ \ln(1.11) \tag{3}$$

The instrument then modulates the current with ΔI for the interval t with seven pulses, waiting 8 times t between each pulse for the cell to return to a steady state. For each pulse, the instrument acquires 2000 voltage points equally spaced over the interval t, fits those points to a linear function by means of a least-squares routine, and determines the capacitance with Eq. (1). The results of the first two pulses are discarded because the voltage response may not have fully stabilized, and the calculated capacitance from the last five pulses is averaged to get the final cell capacitance value.

To improve signal to noise, digital signal processing is performed on the voltage function to reduce the noise level to about 20 to 50 µV or about 1 to 2% of the total voltage change. The signal processing consisted of averaging 2^N voltage readings acquired at 1-msec intervals, where 2^N is given by the greatest integer less than or equal to T/0.03, i.e., $N < \log(T/0.03)/\log 2$. In the processing algorithm, 2^N may not exceed 512 and T is the total elapsed time in seconds since the beginning of the transient. The minimum time between data points is 1 msec; however, by eliminating the real-time digital signal processing, the resolution could be increased to 50 to 100 µsec.

A diagram of the capacitance-measuring instrument is given in Fig. 1. All the instrumentation can be built into the microprocessor input/output; however, increased noise immunity is achieved if the three signal-processing amplifiers are located as close as possible to the cell. The instrument can plot capacitance versus time and capacitance versus voltage functions on an X-Y recorder, as well as store the data on disk for later examination or processing.

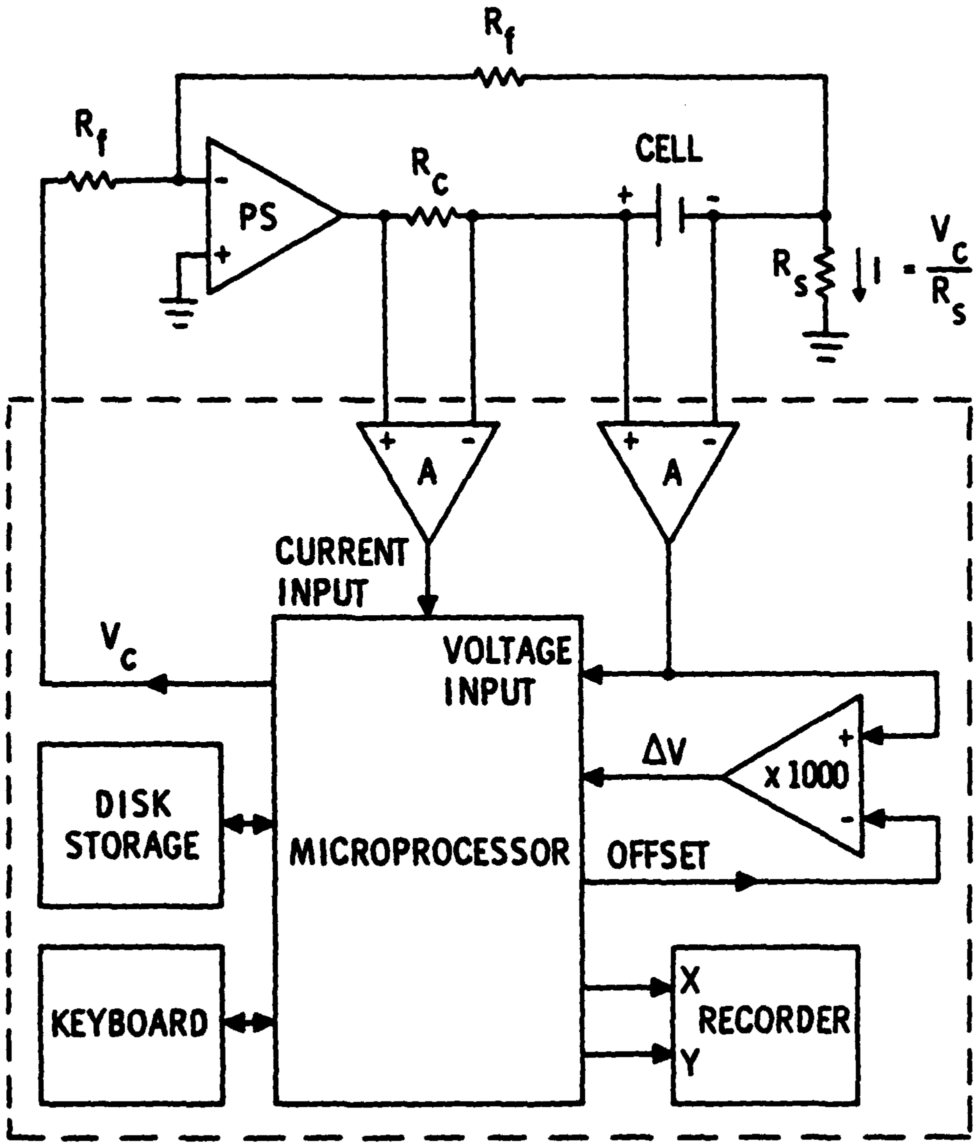

Fig. 1. Diagram of instrumentation. All instrumentation within dashed portion can be made part of computer assembly.

III. EVALUATION OF INSTRUMENT PERFORMANCE

Instrument performance was evaluated by means of a dummy cell consisting of the parallel combination of a variable resistor and a 0.02-F electrolytic capacitor with a 10% tolerance. The capacitance was measured as a function of t/τ for several values of ΔI and for several values of the voltage across the capacitor. The measured capacitance *should* be independent of ΔI as long as the ΔV induced by ΔI is small, but may show a slight dependence on the voltage across the capacitor. The accuracy of the capacitance measurement is expected to be best at the smallest values of t/τ. The results of those measurements are given in Figs. 2 and 3.

The small dependence on ΔI in Fig. 2 is probably the result of voltage changes induced by ΔI at 0.5 mA. It is difficult to check the accuracy of the results because they appear to be significantly better than any standard available in our laboratory. At low values of t/τ, the measurement accuracy should approach the precision, which is about ±0.05% and is essentially determined by the signal-to-noise ratio for monitoring the voltage data as a function of time. From the data in Fig. 3, the capacitor in the dummy cell appears to have a capacitance of 19,740 ± 20 μF at 0 volts and 20,010 ± 20 μF at 1 volt. The data also enable the percent error to be determined as a function of t/τ, as indicated in Fig. 4. Also plotted in Fig. 4 is the theoretical error based on the deviation of an exponential response from linearity as a function of t/τ. At $t/\tau = 0.05$ the accuracy is about 2%, which is adequate for most measurements. Better accuracy may be obtained by correcti[illegible]r such deviations. Precision is determined by signal to noise and rem[illegible] at about 0.05% in the measurements reported here, and is independent of t/τ. The difference between the experimental and theoretical errors in Fig. 4 is likely to be due to internal capacitor leakage, which causes appreciable deviation from an exponential response for the relatively long time constants used in the experiments in Figs. 2 through 4.

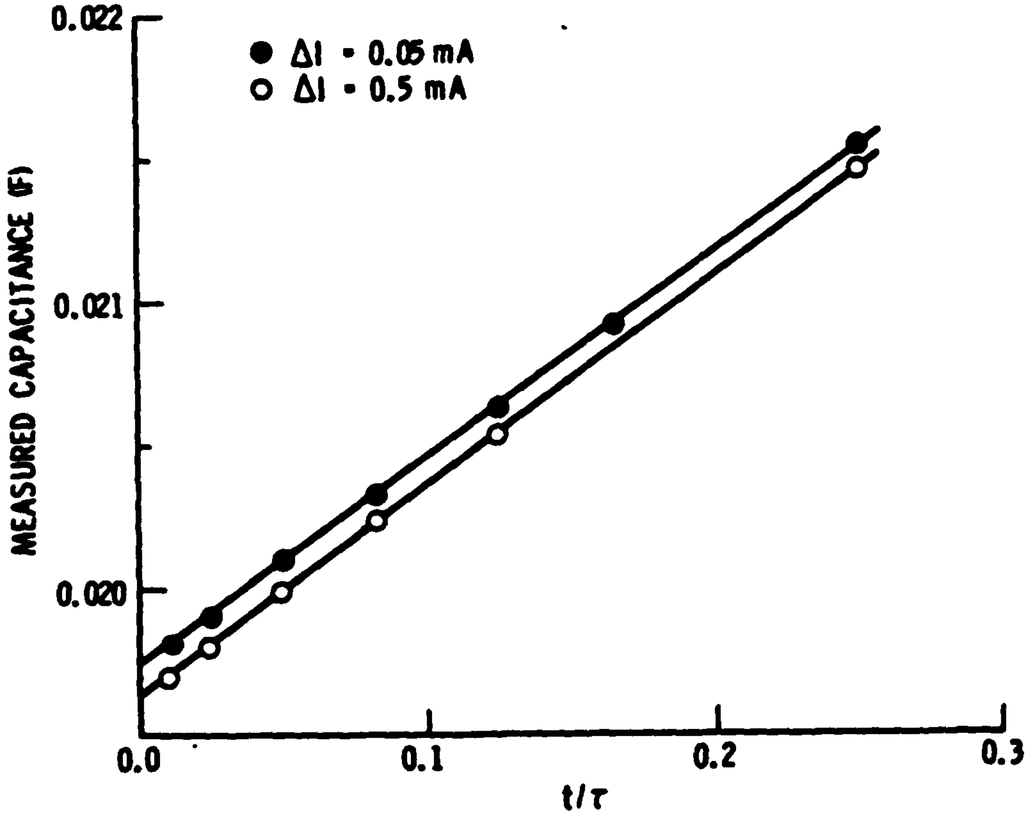

Fig. 2. Measured capacitance as a function of measurement time. Voltage across capacitor was initially zero.

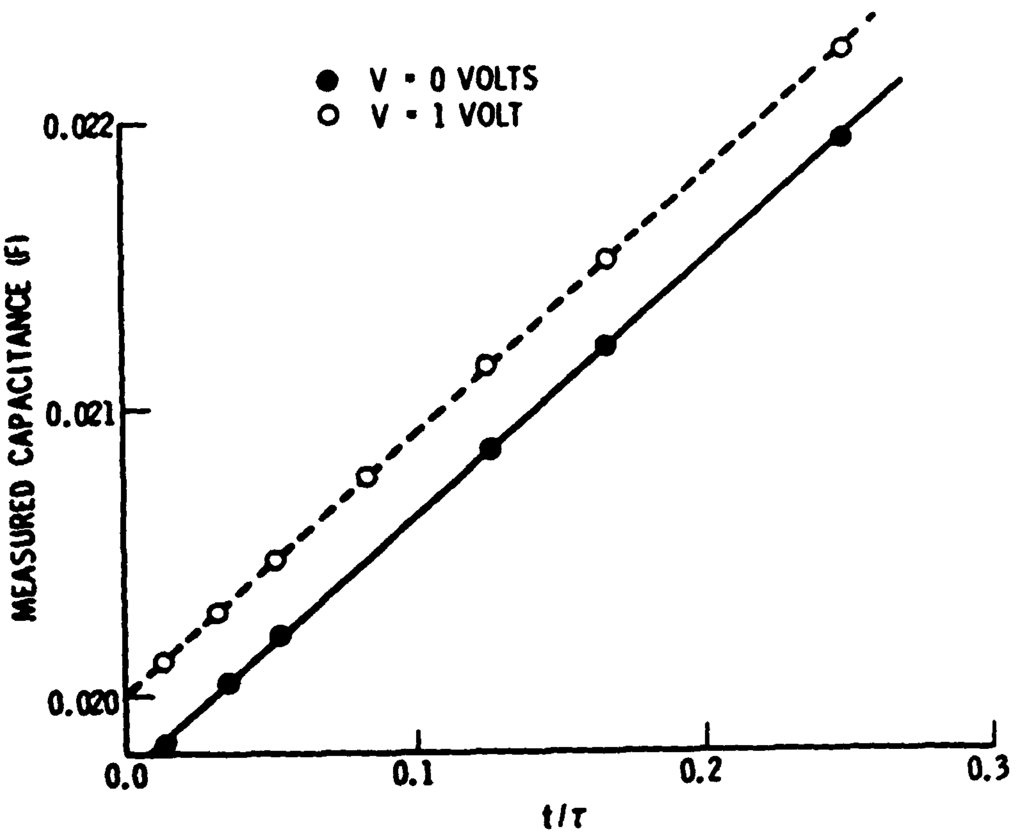

Fig. 3. Measured capacitance as a function of measurement time using a 0.05-mA ΔI.

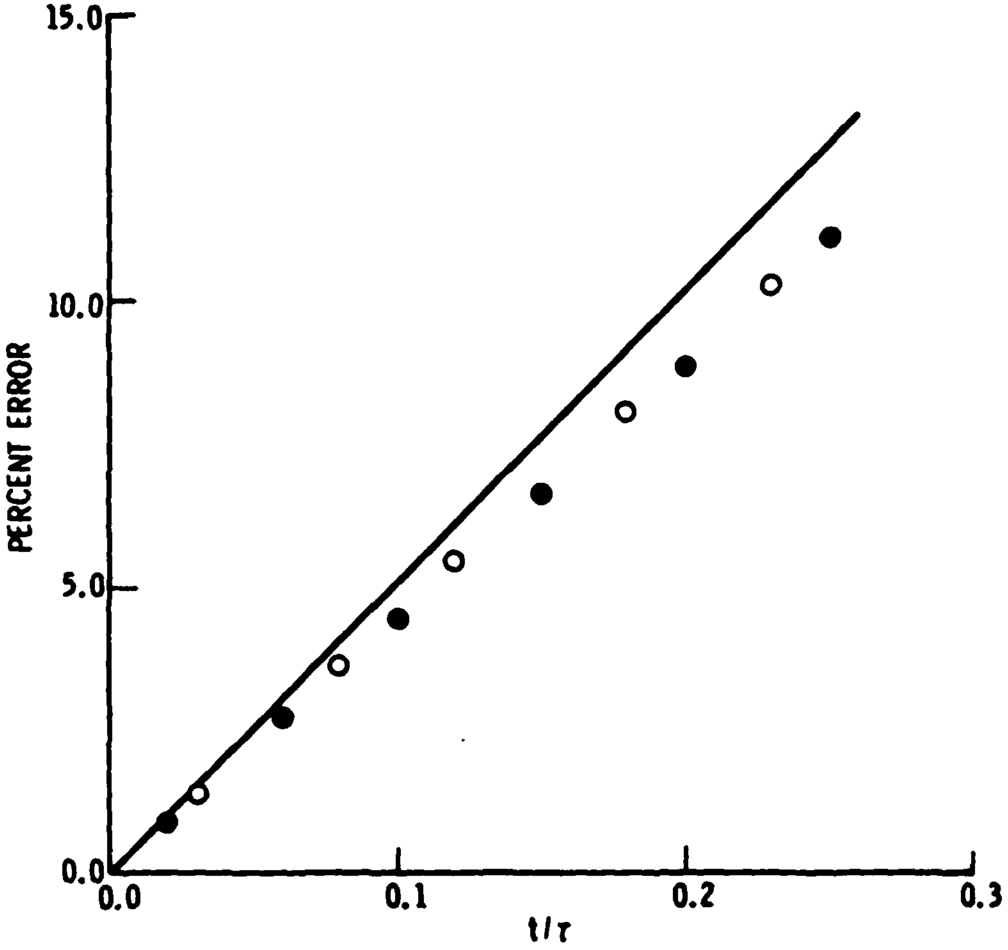

Fig. 4. Percent error in capacitan as a function of measurement time. Solid line is theoretical error for an ideal exponential transient; points are experimental errors for data indicated in Fig. 3.

The nickel and cadmium electrodes in the NiCd cell may not exhibit exponential voltage responses over their normal operating range in batteries, but may instead exhibit voltage responses governed by diffusional mass transport in the electrodes or electrolytes,[8] which initially follow a square root of time dependence and for which Eq. (1) does not apply. For this reason the capacitance of the Ni electrode only was determined by measuring the voltage response of the Ni electrode relative to a mercury-mercuric oxide (Hg-HgO) reference electrode rather than the Cd electrode. Furthermore, the measurements had to be made for a Ni electrode that was nearly discharged, because only at low states of charge does the Ni electrode behave as a parallel RC-equivalent circuit and diffusion processes do not govern the current-versus-voltage (I-V) behavior. Figure 5 indicates that a typical transient voltage response does indeed closely follow an exponential time dependence. The instrument will provide capacitance values when nonexponential transient behavior is observed; however, the capacitances thus obtained will depend on both the ΔI and t values selected by the instrument, and the capacitance will not correlate with an RC-equivalent circuit.

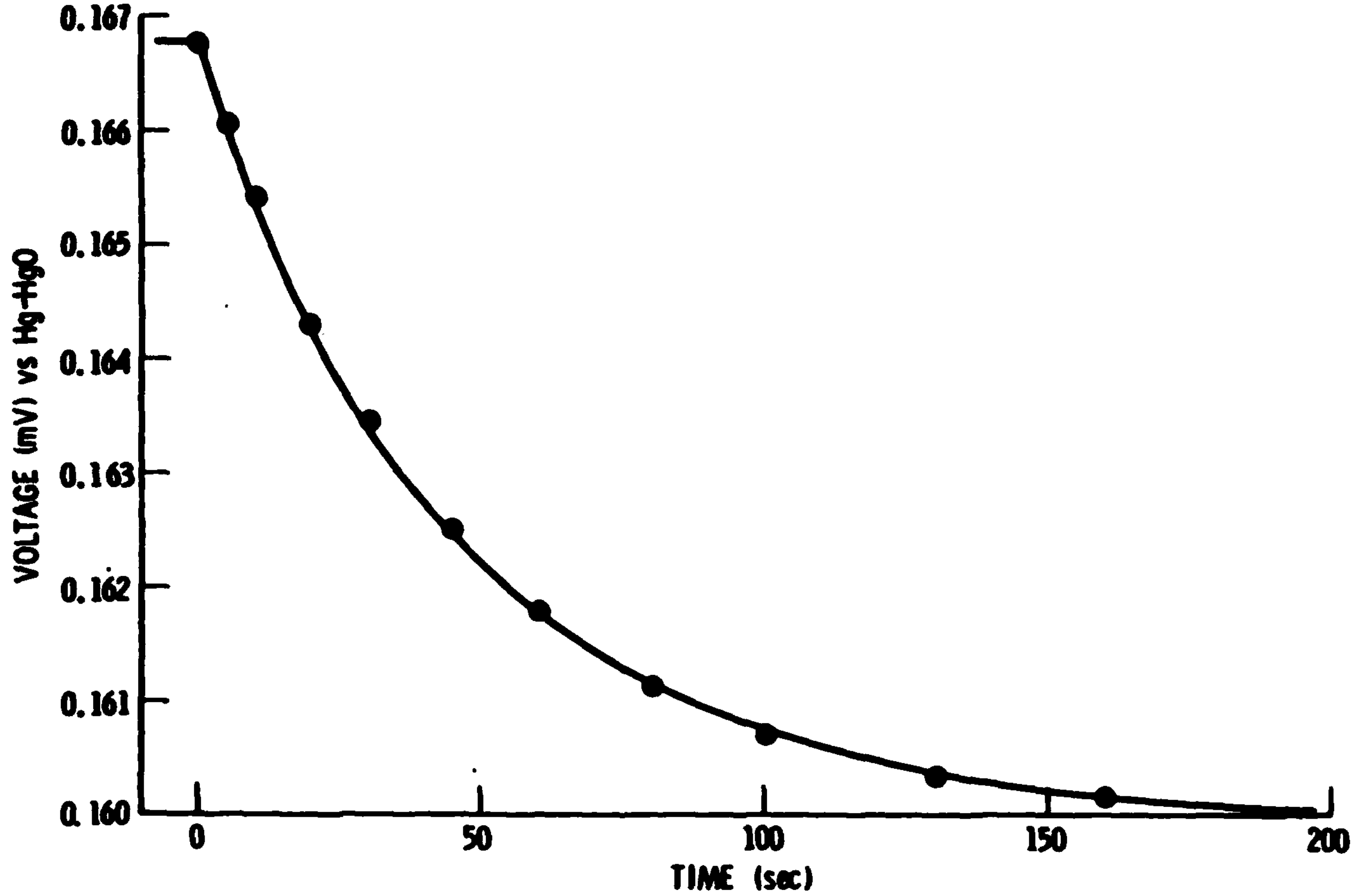

Fig. 5. Transient voltage response function (solid line) for a nickel electrode during a C/100 discharge in response to a C/12,000 current step (1.8 μA). Points indicate a true exponential response.

IV. CONCLUSIONS

The instrument permits the capacitance of battery electrodes to be automatically measured as a function of state of charge or voltage, as indicated in Figs. 6 and 7, respectively, for discharge of residual capacity from the nickel electrode. The sharp decrease in capacitance in Fig. 6 occurs at a state of charge where the nickel electrode voltage drops to a voltage plateau at about 0 volts versus Hg-HgO. Figure 7 indicates the Mott-Schottky dependence of capacitance on voltage in the lower voltage plateau region. Capacitance measurements for a NiCd or NiH_2 cell at low states of charge should produce similar results as long as the cells are positive limited.

Taking together its capabilities for automatically cycling and for measuring the impedance of cells and electrodes, the instrument described here can fully characterize the electrical properties of an electrolytic cell.

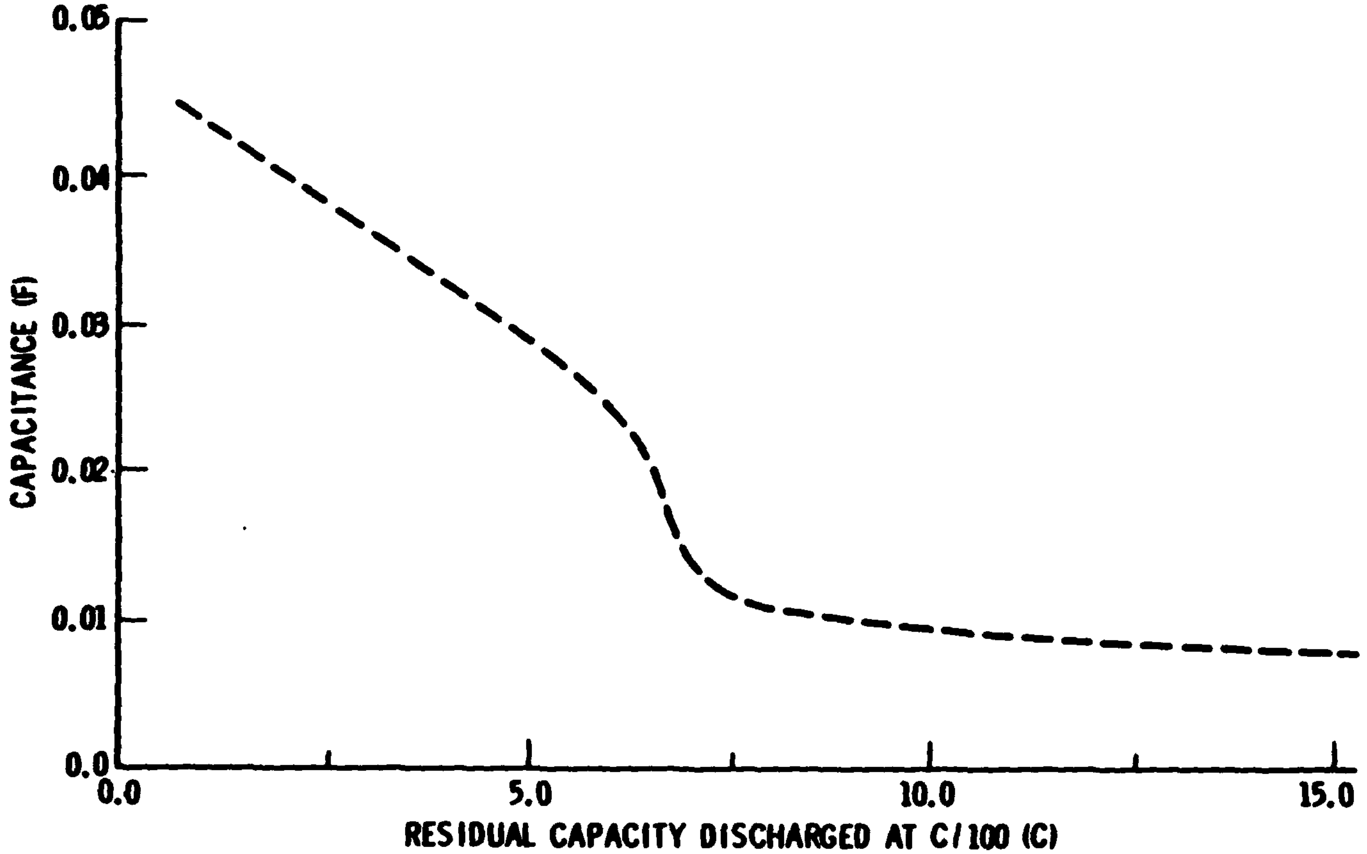

Fig. 6. Capacitance of 20-mAh nickel electrode during discharge of residual capacity at C/100 rate.

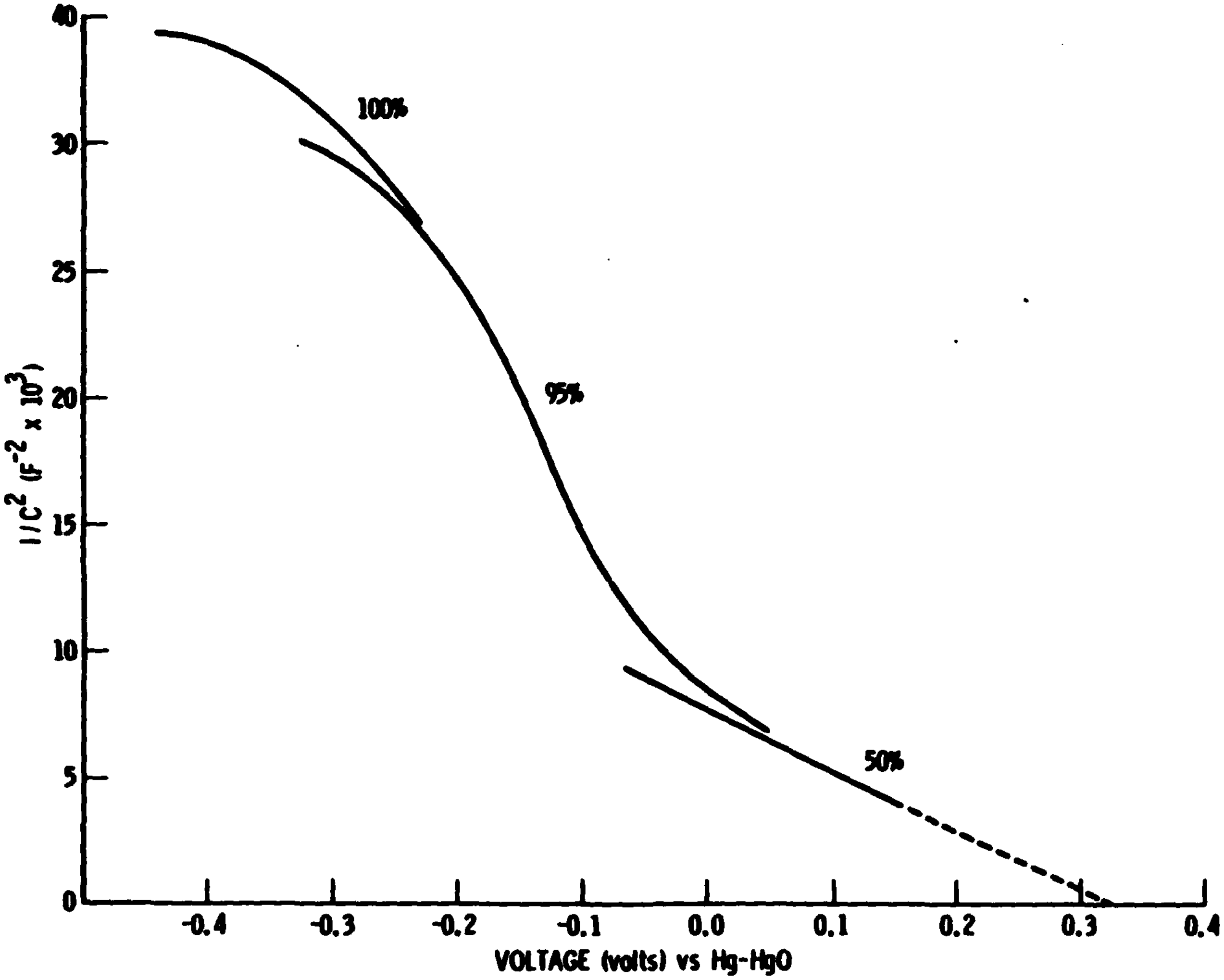

Fig. 7. Capacitance as a function of voltage at states of charge obtained after discharges of 50%, 95%, and 100% of capacity indicated in Fig. 6.

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