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**Transient Techniques for
Battery Impedance Measurements
Small-Amplitude Exponential Perturbation Technique**

Prepared by

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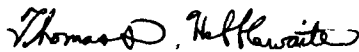
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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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.

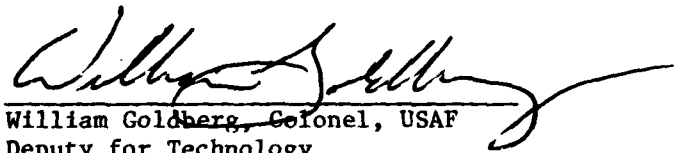


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I. INTRODUCTION

The proper operation of battery cells invariably depends on a number of internal physical and chemical reactions occurring at rates that are sufficient to sustain cell performance. These reactions typically involve charge transfer processes at the electrodes, as well as diffusional transport of materials to the active electrode surfaces. Kinetic measurements permit determination of the relative importance of these processes in controlling cell performance. The most general method for making these kinetic measurements is to measure the electrical impedance of the battery cell as a function of frequency. The rates of the various processes that affect the cell voltage are inferred directly from the frequency dispersion of the cell impedance.

A number of techniques have been used to measure the impedance of battery cells. The most commonly used is that of applying a sinusoidally varying ac signal to the battery cell and monitoring the cell response in terms of amplitude and ac phase shift. This ac method is relatively easy to use, but if data are required over a wide frequency range or at very low frequencies, it becomes somewhat cumbersome. Other techniques for impedance measurements of battery cells incorporate perturbing functions other than sinusoidal ac. For example, in the galvanostatic transient technique¹ a step change in the current passing through the cell is applied, and the response of the cell to the current change is measured. The relationship between the change in cell current and the voltage response gives the cell impedance. This technique is particularly useful when the cell contains appreciable stored capacity, since in this case controlling cell current is much easier than controlling cell voltage. However, when the cell contains very little stored capacity, any measurement attempted under conditions of constant current may change the cell voltage by a large amount and thereby appreciably alter the chemical state of the cell. In this situation, it is desirable to employ a potentiostatic

¹A. H. Zimmerman and M. R. Martinelli, Transient Techniques for Low Frequency Impedance Measurements, TR-0079(4970-10)-1, The Aerospace Corporation, El Segundo, Calif (6 October 1978).

technique that involves the application of a controlled perturbation to the cell potential.

We have developed and applied such a technique to battery cells. This technique is called small amplitude exponential perturbation (SAEP) and involves perturbing the cell voltage with a small amplitude (<5 mV) exponential signal while measuring the current response of the cell. Again, the cell impedance is obtained from the relationship between voltage and current. This technique can be used to measure the impedance of battery cells at any voltage or state of charge that is accessible to them, although very large currents (and power supplies) may be involved when the cell has appreciable active electrochemical capacity.

II. THEORY OF SAEP

Any potentiostatic transient technique for measuring impedance employs a transient potential function $V(t)$. This potential function is applied as a perturbation to a battery cell that has the initial potential V_0 . The cell current is initially $I_0 + I_N(t)$, where I_0 is the steady-state current at V_0 , and $I_N(t)$ is any change in current resulting from depletion of the stored electrochemical capacity of the cell at the initial voltage. After the perturbation $V(t)$ is applied, the current is $I_0 + I_N(t) + I(t)$. For this analysis to be correct, the amplitude of $V(t)$ must be sufficiently small that $I_N(t)$ does not change appreciably in response to $V(t)$. This means that typically $V(t)$ should be less than 5 mV in amplitude. In addition, the time constant associated with $I_N(t)$ must be much greater than that associated with $I(t)$ so that they can be separated in time.

The impedance as a function of time is then directly given by Ohm's law

$$Z(t) = \frac{V(t)}{I(t)} \quad (1)$$

However, the cell impedance is more conveniently analyzed in the frequency domain. Laplace transformation of $V(t)$ and $I(t)$ permits us to obtain the impedance as a function of frequency.

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} \quad (2)$$

where $V(\omega)$ and $I(\omega)$ are the Laplace transforms of voltage and current, respectively.

The digital Laplace transforms required are calculated from the voltage and current data,

$$F(\omega) = \int_0^{\infty} f(t) \exp(-j\omega t) dt = \sum_i \int_{t_i}^{t_{i+1}} f_i(t) \exp(-j\omega t) dt \quad (3)$$

which are digitized by computer into arrays having i data points, each corresponding to a given time. The function $f_i(t)$ fits the data for $f(t)$ in the interval t_i to t_{i+1} and may be any convenient function that fits the data. Functions used for $f(t)$ include linear, quadratic, and exponential forms as follows.

1. Linear: $f_i(t) = A_i t + B_i$

$$A_i = \frac{f(t_{i+1}) - B_i}{t_{i+1} - t_i}$$

$$B_i = \frac{[f(t_{i+1}) - t_{i+1}/t_i f(t_i)]}{1 - \frac{t_{i+1}}{t_i}} \quad (4)$$

2. Quadratic: $f_i(t) = L_i t^2 + M_i t + N_i$

$$M_i = \left[\frac{\Delta f_{12}}{\Delta t_{12}^2} \left(\frac{t_1^2}{t_{i+2}} - t_{i+2} \right) - \frac{\Delta f_{13}}{t_{i+2}} \right] \left[1 - \left(t_{i+2} \right) \frac{\Delta t_{12}}{\Delta t_{12}^2} + \frac{t_i}{t_{i+2}} \left(\frac{t_i \Delta t_{12}}{\Delta t_{12}^2} - 1 \right) \right]^{-1}$$

$$L_i = \frac{\Delta f_{12}}{\Delta t_{12}^2} - M_i \left(\frac{\Delta t_{12}}{\Delta t_{12}^2} \right) \quad (5)$$

$$N_i = f(t_i) - L_i t_i^2 - M_i t_i$$

where

$$\Delta t_{12} = t_i - t_{i+1}$$

$$\Delta t_{12}^2 = t_i^2 - t_{i+1}^2$$

$$\Delta f_{12} = f(t_i) - f(t_{i+1})$$

$$\Delta f_{13} = f(t_i) - f(t_{i+2})$$

3. Exponential:

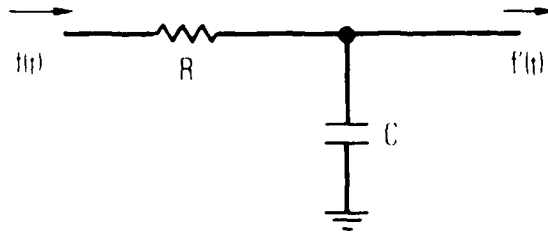
$$f_i(t) = C_i \exp(-a_i t) \quad (6)$$

$$a_i = \ln \left[\frac{f(t_{i+1})/f(t_i)}{t_i - t_{i+1}} \right]$$

$$C_i = f(t_i) \exp(a_i t_i)$$

The exponential function of Eq. (6) gave the best results for all data that were not near a point where $f(t)$ crossed zero. A listing of a Fortran program for doing the transformations that give the impedance is provided in the Appendix.

Actual experimental data contain noise; in particular, 60-Hz noise may pose a problem when small changes in voltage or current are being monitored. The simplest way to eliminate this kind of noise is with an RC filter.



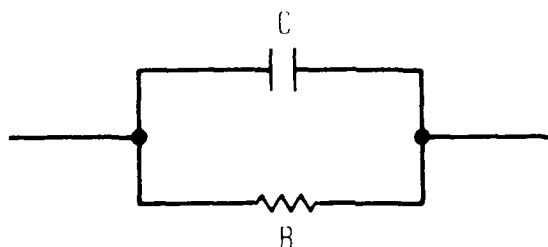
However, the transfer function of this filter must then be deconvoluted from the data. This is easily done in the frequency domain simply by multiplying the transformed function by the inverse filter function transform

$$f(\omega) = f'(\omega) (1 + j\omega\tau_F) \quad (7)$$

where $\tau_F = RC$ is the filter time constant.

III. RESULTS

The impedance of battery cells below 1 kHz is generally capacitive in nature, behaving as an equivalent parallel RC circuit where the values of R and C may have a complicated dependence on frequency. The results of an SAEP experiment on a simple dummy cell consisting of the RC circuit



where $C = 1 \text{ F}$ and $R = 10 \Omega$ are examined first. For simplicity, let us assume that $V_0 + V_N(t)$, the initial cell voltage, is zero. An increasing exponential perturbation having amplitude α and time constant τ is applied to the cell

$$V(t) = \alpha(1 - e^{-t/\tau}) \quad (8)$$

$V(t)$ and the current response of the dummy cell $I(t)$ are indicated in Fig. 1 for $\tau = 2\text{s}$, $R = 10 \Omega$, and $C = 1 \text{ F}$. $I(t)$ is given by the relationship

$$I(t) = \frac{\alpha}{R} \left[1 - \left(1 - \frac{RC}{\tau}\right) e^{-t/\tau} \right] \quad (9)$$

Note that the values of R and C do not influence the time constant for current decay, but only control the amplitude of the current transient. From the time-dependent voltage and current functions, the impedance is calculated, with the results shown in Fig. 2 in the complex plane. The results in Fig. 2 agree with the theoretical result for the impedance

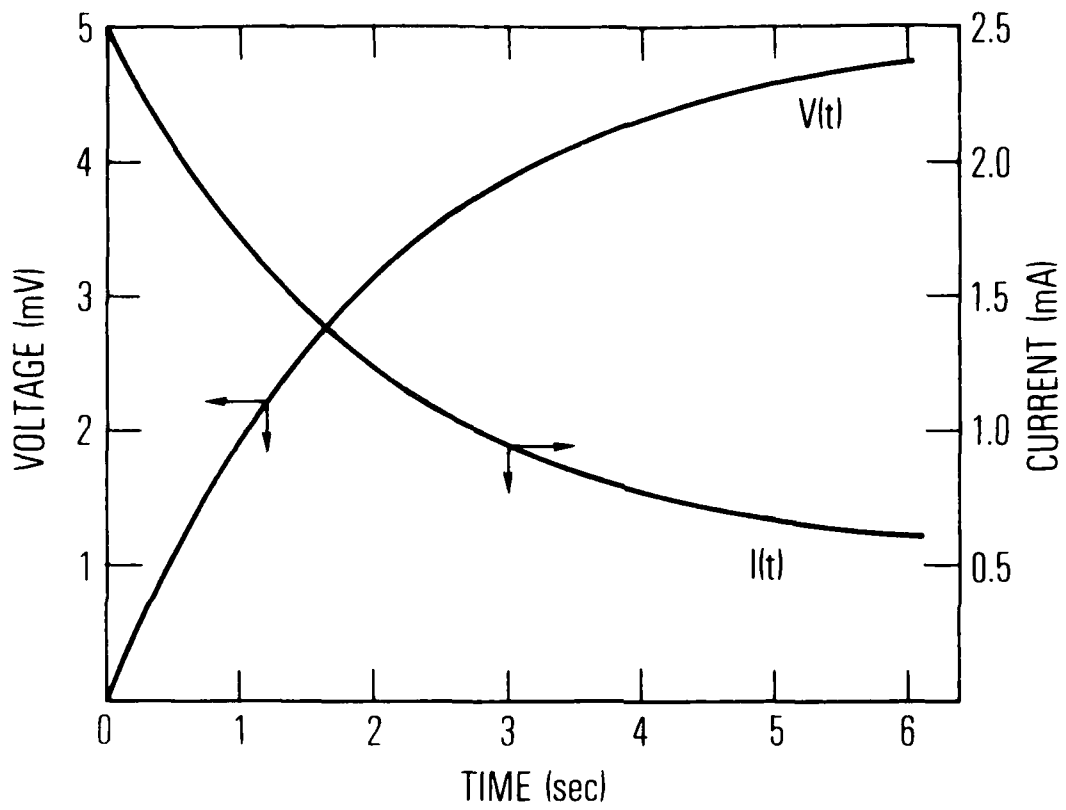


Fig. 1. Voltage Perturbation and Response Current for Dummy Cell

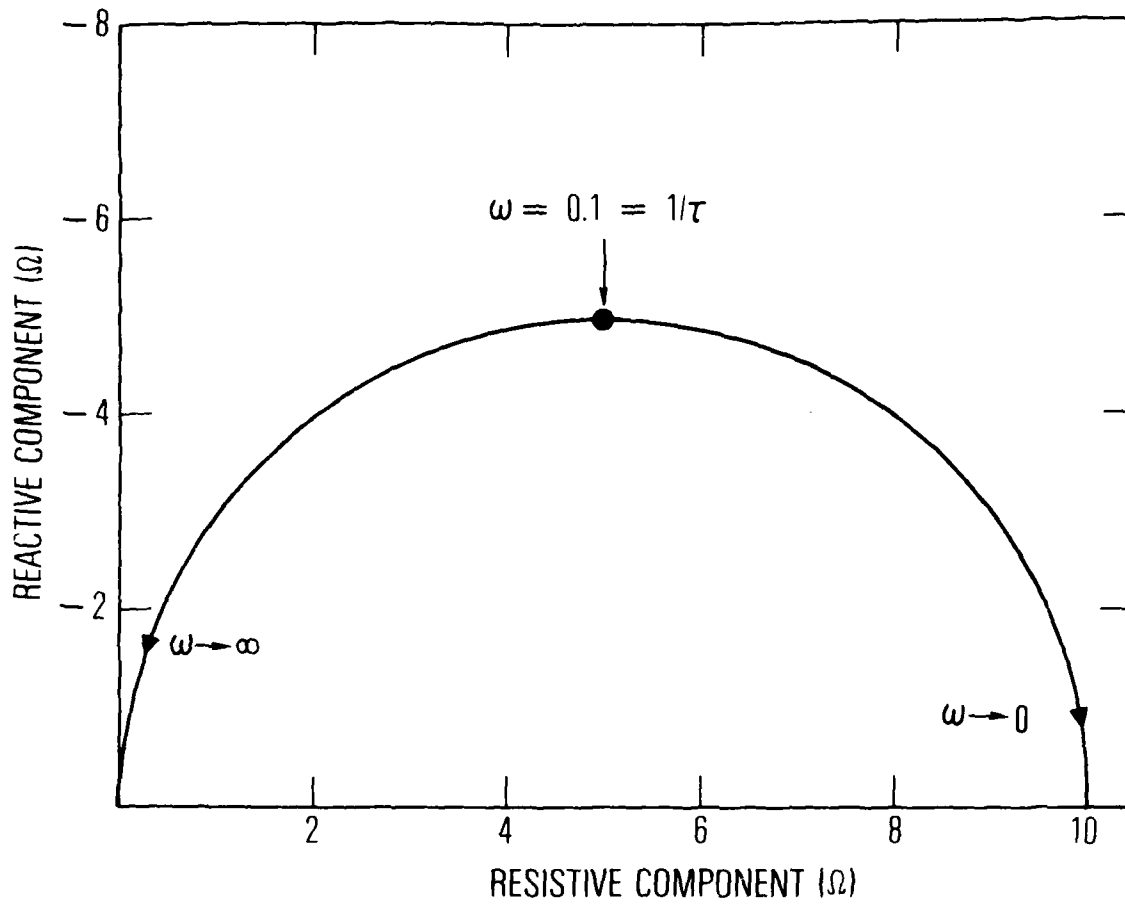


Fig. 2. Impedance of Dummy Cell from Data of Fig. 1

$$Z(\omega) = \frac{R}{1 + j\omega RC} \quad (10)$$

This simple example illustrates that the expected current response for a battery cell consists of a rapid rise to a maximum, followed by a decay to a steady-state current that is different from the initial current by the amount α/R . The magnitude of the peak current is controlled by the relative time constants of the exponential perturbation and the cell, and is given by $\alpha C/\tau$ in the preceding example. Thus, the experimental maximum transient current can be controlled simply by controlling the perturbation time constant.

The results obtained when an exponential perturbation is applied to a nickel cadmium cell are shown in Fig. 3. The nickel cadmium cell used was a 10-Ah prismatic cell, and the initial cell voltage was 0.5 V. The impedance is indicated in the complex plane in Fig. 4. In making these measurements, it was found that signal to noise became relatively poor unless the time constant of the applied perturbation was the same order of magnitude as the relaxation time for the battery cell. With this general requirement satisfied, the SAEP technique provides a convenient method for making impedance measurements on battery cells over an extremely wide range of frequencies, under conditions of battery operation for which potential control is acceptable.

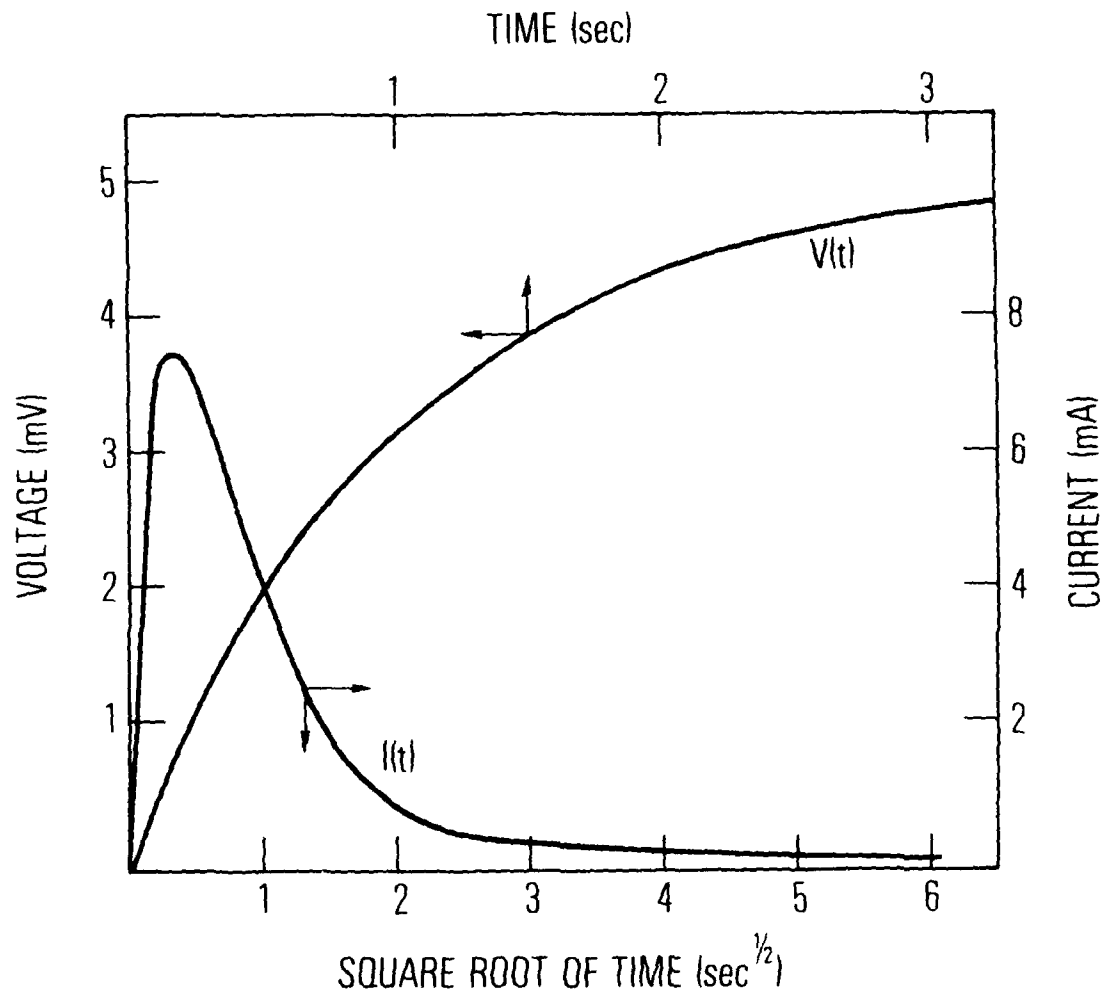


Fig. 3. Voltage Perturbation and Current Response for Nickel Cadmium Cell at 0.5 V

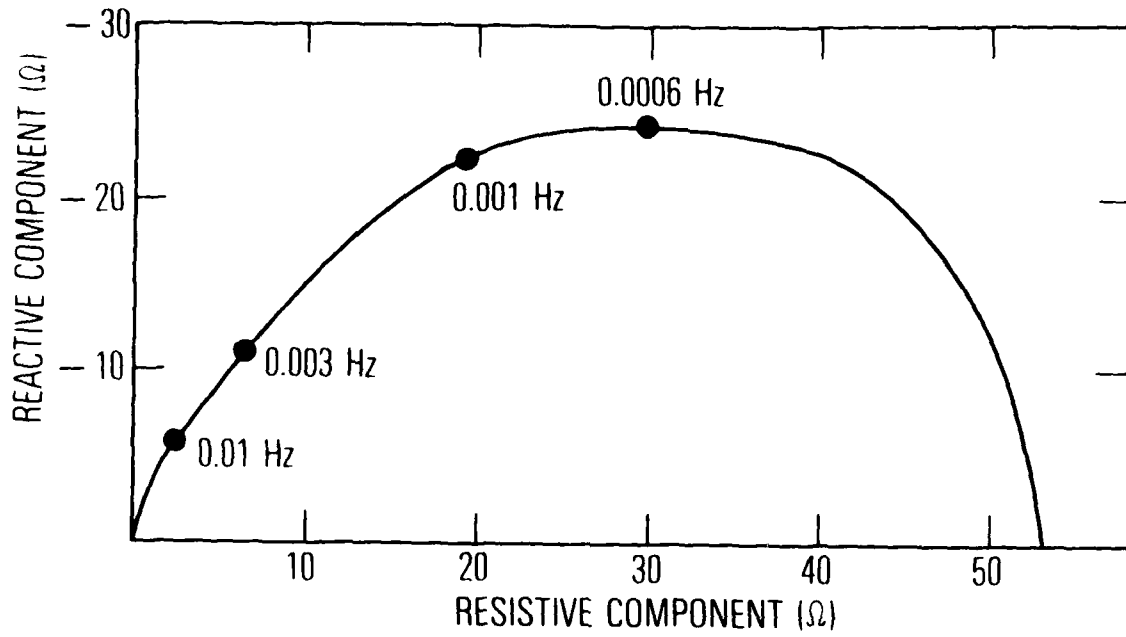


Fig. 4. Impedance of Nickel Cadmium Cell from Data of Fig. 3

IV. CONCLUSIONS

The SAEP technique has been developed and applied to measuring the impedance of battery cells under conditions of controlled potential. This appears to be the optimum method for measuring the impedance of battery cells that contain little stored electrochemical capacity.

APPENDIX

FORTRAN PROGRAM FOR SAEP IMPEDANCE CALCULATION

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```
COMPLEX FUNCTION CTANH(Z)  
COMPLEX UI,7  
DATA UI/0,1,1,  
IF (CABS(Z),GT,1.1) GO TO 1  
CTANH=-UI*CSIN(UI*Z)/COS(UI*Z)  
RETURN  
IF (CABS(Z),GT,39.1) GO TO 2  
CTANH=(1.-CEXP(-2.*Z))/(1.+CEXP(-2.*Z))  
RETURN  
CONTINUE  
CTANH=CMPLX(1.,0.)  
RETURN  
END
```

7
44
46
53
103
105
110
112

```
SUBPROGRAM LENGTH  
000143  
FUNCTION ASSIGNMENTS  
STATEMENT ASSIGNMENTS 2 - 000106  
1 - 000047  
BLOCK NAMES AND LENGTHS  
CTANH - 000143  
VARIABLE ASSIGNMENTS UI - 000141  
CTANH - 000137  
START OF CONSTANTS  
000115  
START OF TEMPORARIES  
000123  
START OF INDIRECTS  
000137  
UNUSED COMPILER SPACE  
011200
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