Journal of Power Sources, 16 (1985) 285 - 291

QUALITY ASSESSMENT OF UNACTIVATED CELLS BY A.C. IMPEDANCE TECHNIQUES

J R DRISCOLL*

Altus Corporation, San Jose, CA 95112 (U S A)

S SZPAK**

Naval Ocean Systems Center, Code 633B, San Diego, CA 92152-5000 (U S A)

(Received October 1, 1985, in revised form November 25, 1985)

Summary

A.C. impedance measurements are demonstrated to be very effective in assessing the quality of reserve activated battery cells during fabrication. The impedance of four-cell bipolar batteries was measured over the frequency range 0.1 - 20 kHz. A parallel *RC* circuit was determined to be a good model for the unactivated cells. Capacitance is a sensitive measure of cell spacing consistency. Uniform and defect-free cells have a variation of ±3% in capacitance, and a sensitivity analysis of capacitance to cell spacing shows that this is equivalent to a ±1.5% variation in cell spacing. Bode plots identify defective cells with high resistance shorts not detectable through capacitance measurements.

Introduction

The development of high energy and high power batteries has received a great deal of attention in the last few years, particularly with the emergence of lithium-based systems. One design for high power applications is a bipolar reserve activated construction in which the basic unit contains a large number of series-connected cells. The final battery configuration may contain as many as 1000 or more cells with individual cell thickness in the submillimeter range. With this number of closely spaced cells, there is a clear need for a method of assuring cell quality both during and after fabrication in order to meet both electrical performance and safety goals. The requirement for cell quality assurance is not limited to systems of this design for it can be extended to other systems as well

*Present address Lockheed Palo Alto Research Laboratories, Palo Alto, CA 94304, U S A

**Author to whom correspondence should be addressed

0378-7753/85/$3 30

One measure of cell quality during fabrication is the d.c. resistance of the dry cell. While this procedure will detect some defects, primarily internal shorts, it is not sensitive to other potential problems such as incorrect cell spacing or incorrect components. On the other hand, capacitance measurements [1, 2] have been used successfully as a measure of cell quality. In general, cell capacitance is sensitive to both low resistance internal shorts and cell spacing, but is insensitive to intermediate-level shorts.

Given the complimentary nature of the resistance and capacitance data, it was decided to explore the possibilities of using the more general a.c. impedance methods where both can be determined simultaneously in order to improve further the techniques of cell quality assessment. Should this prove useful, a computer based data aquisition system would make cell quality assessments reliable, rapid, and routine. This communication presents the results of an initial exploration.

Experimental

Test vehicle

Impedance measurements were made as a function of frequency on four-cell bipolar stacks. The nickel bipolar plates were 0.114 m in diameter and 5.1×10^{-5} m thick. Porous cathodes were fabricated from Shawinigan carbon black. In place of an active anode material stainless steel sheets were used. These were cut to the same dimensions and were 7.6×10^{-5} m thick. In the results reported here two separator systems were examined. a single layer of ceramic paper and a composite of three layers consisting of a layer of fibrous hemp against the cathode, a layer of 2.5×10^{-4} m unwoven glass fiber paper, and a layer of microporous polypropylene. Only three of the four cells in any one stack could be measured since one end of the stack had a plastic plate used for visual observations in other experiments.

Instrumentation

An Hewlett-Packard 4276A LCZ analyzer was used for the measurements. This instrument has a frequency range of 0.1 - 20 kHz Spring clip probes were connected to small tabs spot welded onto the individual bipolar plates. The magnitudes of the impedance and phase angle were recorded at 13 frequencies between 0.1 and 20 kHz.

Results and discussion

Discussion of the experimental results will be in terms of the relation between cell capacitance and cell uniformity and the effect of cell defects on the overall impedance characteristics. The determination of these depends on the equivalent electrical circuit which, in turn, can be estimated from the frequency dependent behavior of the cell.

Equivalent circuit

An unwetted cell would be expected to behave as a parallel *RC* combination, since, in essence, it consists of two electronic conductors separated by a dielectric. Data from defect free cells confirm this expectation. Figure 1 is a plot in the admittance plane of the data for three defect-free cells and shows a linear correlation between the imaginary and real components with the angle of the lines to the real axis slightly less than 90°. This is in accordance with the frequency response of a parallel *RC* circuit. There is some departure from ideal *RC* behavior in the system. The admittance plots have a slight curvature at low frequencies and the angle of the lines to the real axis is not exactly 90°. This non-ideal behavior can be attributed to frequency dependent energy loss mechanisms in a real system which are not due solely to d.c. resistivity [3 - 5].

All the cell data showed similar behavior and thus, initially, a simple parallel *RC* network was taken as a reasonable basis for further analysis of the data.

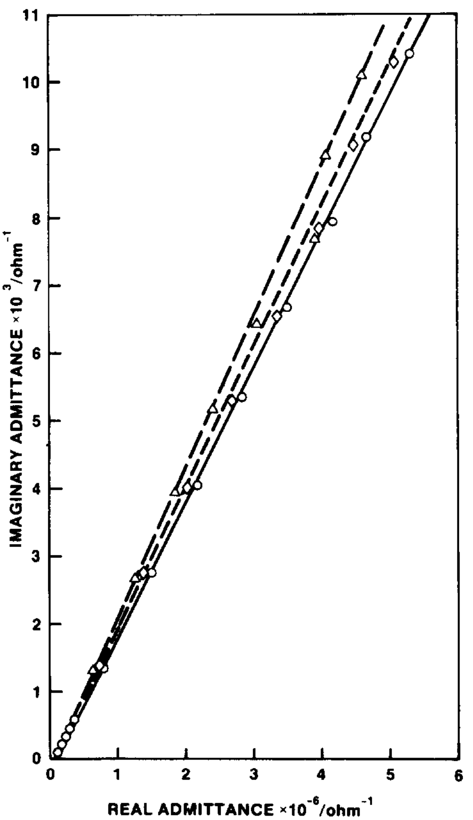

Fig 1 Data for 3 identical cells plotted in the admittance plane The nearly vertical lines indicate the cell can be modelled with a parallel *RC* circuit (Note scale change between ordinate and abscissa) ○, Cell 25-1, △, cell 25-2, ◇, cell 25-3

Capacitance and cell uniformity

Given the parallel *RC* network model, capacitance is directly calculated from the impedance and phase angle as

$$C = \sin\theta/\omega Z \qquad (1)$$

where C is the capacitance in farads, θ is the phase angle, ω is the radial frequency and Z is the magnitude of the impedance in ohms. The capacitance for a set of defect-free cells of the same design is quite consistent at all frequencies, with a standard deviation of about 3%. This is shown in Table 1 for data measured at 20 kHz. The excellent capacitance reproducibility for identically constructed cells is encouraging as a measure of consistency. This alone is important, but it is also important in establishing the sensitivity of the method to anomalous cell spacings.

An estimate of the sensitivity of capacitance to total cell spacing is obtained from the basic equation for capacitance and the cell data. Assuming the dielectric constant of the separator and the cell area remain constant as a function of cell thickness, the capacitance is given by the standard equation.

$$C = \epsilon_0 \epsilon A/(t - m) \qquad (2)$$

where C is the capacitance in farads, ϵ_0 is the permittivity of free space, ϵ is the insulator dielectric constant, t is the total cell thickness, m is the thickness of the electrodes, and the term $(t - m)$ represents the dielectric thickness. The sensitivity of capacitance to changes in total cell thickness is given by eqn (3), which is derived from eqn (2) by taking the derivative of capacitance with respect to total cell thickness, dividing by eqn (2) and rearranging

$$\mathrm{d}C/C = [-t/(t - m)]\,\mathrm{d}t/t \qquad (3)$$

The magnitude of the term $-t/(t - m)$ establishes the sensitivity of capacitance to cell thickness. The value of m was not experimentally measurable in these cells but was determined, on the assumption that the electrodes are incompressible at the specified cell dimensions, by rearranging eqn (2) to eqn. (4) and performing a linear regression analysis.

TABLE 1

Capacitance of unwetted cells with composite separator

Cell spacing ($m \times 10^4$)	Capacitance (nF)	Standard deviation	Number of cells
4 70	0 641	0 017	6
4 45	0 717	0 017	9
4 19	0 828	0 019	6
3 94	0 915	0 020	7
3 68	1 02	0 039	5

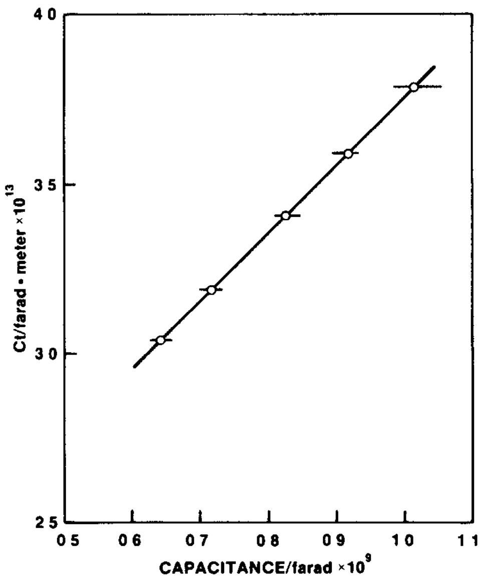

Fig 2 A plot of the capacitance–thickness data according to eqn (4) in the text for the determination of m and $\epsilon_0\epsilon A$ The correlation coefficient of the linear fit is 0 986

$$Ct = mC + \epsilon_0\epsilon A \tag{4}$$

The values of m and $\epsilon_0\epsilon A$ were calculated from the 33 data points of capacitance *versus* cell spacing summarized in Table 1. The result shows a good correlation, as illustrated in Fig. 2, with the values of m and $\epsilon_0\epsilon A$ of 1.98×10^{-4} m and 1.77×10^{-13} farad-meter, respectively. These values are reasonable for the system. Since the anode thickness was 7.6×10^{-5} m, the cathode thickness in the compressed cell is the difference between this and m — 1.22×10^{-4} m. The dielectric constant of the compressed separator calculated from the value of $\epsilon_0\epsilon A$ is 2.97, based on the electrode area of 6.7×10^{-3} m^2 and ϵ_0 equal to 8.9×10^{-12} farad/m.

Substitution of this value of m into eqn. (4) indicates that, for the range of cell thicknesses in these experiments, the relative change in capacitance is 1.7 - 2.2 times the relative change in cell thickness. Thus, capacitance is a sensitive measure of cell spacing uniformity. For example, the standard deviation of ±3% observed in the experimental cells translates to thickness deviations of about ±1.5%. It is clear, then, that anomalies which affect cell spacing, *e g* , the insertion of an extra component or the omission of a component, are detectable.

This analysis assumes an invariant dielectric constant for the separator, since variations in the separator, *e g* , porosity and composition, also will affect the measured cell capacitance. This implies that prior to cell fabrication the uniformity of the separators must be assured, which can easily be done with a.c. measurements in a standard test fixture.

Effect of cell defects

Determination of capacitance does not take full advantage of the information available with the a.c. method. High resistance shorts do not necessarily affect the capacitance but do affect the overall impedance behavior of the cell. This is illustrated in Fig. 3 where a Bode plot of the data from three cells with the ceramic paper are presented. The capacitance of all three cells was essentially identical, the average was 0.971 with an average deviation of ±0.020 nF. The Bode plots of the two defect-free cells have slopes of approximately −1 over the range of accessible frequencies, indicating that the impedance is dominated by the capacitive reactance down to at least 100 Hz. With no detectable contribution from the d.c. resistance, it is only possible to put a lower bound of approximately 3 MΩ on the actual cell resistance. If the cell resistance was less than this, the low frequency data points would begin to deviate from the linear relationship. This is illustrated by the behavior of the defective cell.

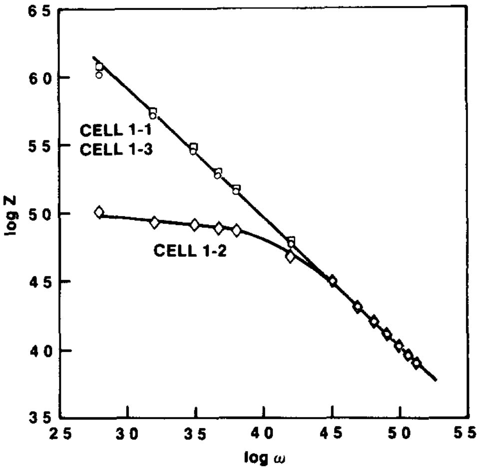

Fig 3 Bode plot of the impedance data for 3 cells from battery #1 Cells 1 and 3 are defect free, thus the plots are linear with a slope of −1 Cell 3 has a high resistance short of 0 1 MΩ which dominates at the low frequencies ○, Cell 1-1, □, cell 1-3, ◇, cell 1-2

The Bode plot of the defective cell has an initial slope of −1 at the high frequencies, which is identical to the behavior of other cells. At lower frequencies, however, the slope gradually changes to 0, indicating dominance by the d.c. resistance of 100 kΩ. Post-test examination of the defective cell revealed a small perforation in the separator allowing the formation of a carbon track between the cathode and anode. This procedure identified all cells which were defective due to an internal short.

Conclusions

This exploratory investigation has shown that a.c. impedance techniques are valuable tools for assessing the quality of dry cells. One of the advantages of the method is that it not only locates defective cells but also helps identify the nature of the problem. Moreover, it has been shown that capacitance is a sensitive function of cell spacing. Over the frequency range investigated, Bode plots of the data provide a good method of distinguishing shorted from unshorted cells. Unshorted cells have a slope of −1; deviations from this indicate a short in the cell which may not be indicated by the capacitance. Only lower bounds could be determined for the resistance of defect-free cells.

Acknowledgement

This work was funded by Naval Sea Systems Command (NAVSEA 63R3). We thank Mr Frank Romano for his interest and support.

References

1 K L Hampartzumian, in J Thompson (ed), *Power Sources 9*, Academic Press, New York, 1982
2 Final Tech Rep — Advanced Lithium Battery Program, *Contract N00024-81-C-6124*, Altus Corp , 30 May, 1984
3 A K Jonscher, *J Mater Sci*, *13* (1978) 553
4 K S Cole and R H Cole, *J Chem Phys*, *9* (1941) 341
5 J R MacDonald, *J Appl Phys*, *34* (1963) 538