

## Short Communication

---

### Quality Analysis of Reserve-type Silver Oxide/Zinc Batteries by Capacitance and Phase-angle Measurements

HSING-YAW HU and HSIEN-WEN KO\*

*Electrochemical Section, Materials R & D Center, Chung-Shan Institute of Science and Technology, Lung-Tan, Taiwan 32500 (Republic of China)*

(Received February 15, 1987; in revised form April 6, 1987)

Capacitance and phase-angle measurements have proved effective in the quality analysis of reserve-type silver oxide/zinc batteries during fabrication. The dry-charged cell is taken to have an equivalent  $RC$  parallel circuit. A Bode plot has verified that the cell behaves like a pure capacitor. A simple digital multimeter with a fixed frequency can be used to measure the capacitance; values for ten incorrectly assembled cells have been analyzed. Nine cases have shown deviations in capacitance of more than 10% from that for a normal cell assembly; this is significant compared with the estimated 3% error of the measurements. The a.c. technique is considered to be valuable for diagnostic testing in cell production lines.

Reliability is one of the most important requirements of reserve-type batteries. The systems are intended to be used only once (so called "one-shot" batteries). The only definite way of confirming that a battery will function properly is to conduct a discharge test, but obviously this will terminate the useful life of a reserve battery. Therefore, every effort must be made to achieve high quality control in the production line. Capacitance measurements have been examined [1, 2] as a method of non-destructive quality analysis for reserve and dry-charged cells. Instead of employing elaborate equipment, the efficacy and accuracy of a simple instrument has been tested so that the technique can be applied readily on the production line. The characteristics of a reserve-type silver oxide/zinc cell have been used in this investigation.

In an unactivated state, the silver oxide/zinc cell behaves like a capacitor with the electrodes serving as the plates, and the air-separator space as the dielectric. The capacitance,  $C$  (in pF), is represented by:

$$C = KE_oAN/d \quad (1)$$

---

\* Author to whom correspondence should be addressed.

where  $K$  is the equivalent dielectric constant of the air-separator space,  $E_0$  is the electric permittivity under vacuum,  $8.9 \times 10^{-2}$  pF cm<sup>-1</sup>,  $A$  is the electrode area in cm<sup>2</sup>,  $N$  is the number of capacitors in parallel ( $N = 10$  in this case), and  $d$  is the spacing of electrodes in cm. Equation (1) demonstrates the usefulness of capacitance measurements for assessing cell quality. In practice, the cell is not an ideal capacitor; instrumental analysis showed that it is a combination of  $R$ ,  $L$ , and  $C$  components. This could lead to a misinterpretation of data when capacitance is determined by a digital multimeter or other types of measuring method. More appropriately, impedance, rather than capacitance, should be used to analyze the data. Phase-angle analysis can determine the inherent qualities of the cell capacitance. The phase angle,  $\theta$ , is defined as:

$$\theta = \tan^{-1} (Z''/Z') \quad (2)$$

where  $Z'$  and  $Z''$  represent the real and imaginary parts of the impedance,  $Z$ , respectively.

For an RC parallel circuit:

$$\theta = -\tan^{-1} (\omega CR) \quad (3)$$

where  $\omega$  is the radial frequency. Equation (3) shows that  $\theta$  is a function of the a.c. frequency. An unknown network can be treated as a pure capacitor when  $\theta$  is equal or close to  $-90^\circ$ . Clearly, it is essential to understand the nature of the cell capacitance before meaningful conclusions can be reached.

### Experimental

Silver oxide electrodes were prepared by powder sintering and electroformation; each electrode had dimensions of 5 cm (height)  $\times$  3.2 cm (width)  $\times$  0.23 mm (thickness). The Ag<sub>2</sub>O and AgO contents were determined by thermal gravimetric analysis. Zinc electrodes were prepared by high-current electrodeposition; each electrode had dimensions of 5.3 cm (height)  $\times$  3.5 cm (width)  $\times$  0.31 mm (thickness). The unit cell consisted of 5 silver and 6 zinc electrodes arranged in parallel and interleaved with cellulose-based separators. The cells were sealed so that only the positive and negative electrode tabs protruded outside the unit. The cells were kept overnight in an oven at 60 °C in order to reduce the moisture content.

A Hewlett-Packard type 4194A impedance/gain phase analyzer was used to analyze the electrical characteristics of the unit cell, namely,  $Z$ ,  $\theta$ , and  $C_p$ ,  $R_p$ , (for the RC parallel circuit) or  $C_s$ ,  $R_s$  (for the RC series circuit) as a function of a.c. frequency. For in-line quality control, a simple digital multimeter (DM728, Shampo Co. of Taiwan) was used to obtain capacitance data. The test frequency was 356 Hz.

### Results and discussion

A Bode plot for a typical defect-free cell is shown in Fig. 1. Test frequencies ( $f$ ) were set in the range 100 - 500 Hz to coordinate with the frequency (356 Hz) of the multimeter. The plot shows that a linear

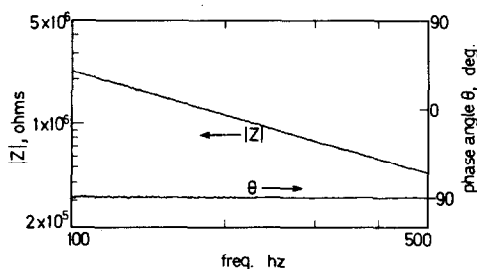


Fig. 1. Bode plot of a normal silver oxide/zinc cell.

relationship exists between  $\log |Z|$  and  $\log f$ . The slope has a value of  $-1$ , which indicates that the phase angle is close to  $-90^\circ$ . From a physical point of view, however, an  $RC$  parallel circuit is more appropriate, where the parallel resistance,  $R_p$ , represents a leakage between electrodes. The  $R_p$  value was found to be  $121 \text{ M}\Omega$  and was much larger than the capacitance impedance of the frequency range. These results verified that the cell could be treated as a pure capacitor, and that a simple digital multimeter could be used for determining its capacitance. This is essential for quality control in the production lines.

One way to ensure good quality control of a reserve battery is, obviously, to assemble each cell correctly. In order to test the efficacy of capacitance measurements as a means of quality control, various types of incorrectly assembled cells were constructed. Of course, some of these could easily be detected by very simple methods. For example, a bright dot on the current tab of either the silver or the zinc electrodes should distinguish these electrodes clearly. Capacitance values for the cells are given in Table 1. It can be seen that, as expected, the phase angles are all close to  $-90^\circ$ . A properly assembled cell has an  $N$  value of 10. The values of  $N$  are 9 and 8 for cells 1 and 2-1, respectively, and this accounts for the capacitance values being lower than the normal value. In cell 2-2,  $N$  is 9: a misplaced zinc electrode exists that has a larger area than its silver counterpart. Consequently, there is a smaller capacity loss than that found for cell 1. In cells 3, 4-1, and 4-2, the situations are reversed. Since the space for electrodes inside the cell is fixed and the number of electrodes is increased by 1, the value of  $d$  is decreased. In addition, the value of  $K$  is increased because the separator is compressed and cellulose has a higher dielectric constant than air. Such possibilities occur in cells 6 - 8 and result in increases in capacitance to varying degrees. Cell 5 has one less capacitor (because different kinds of electrode tabs are bundled together), and therefore the capacitance is decreased. Except for cell 2-2, all defects in assembling gave rise to deviations in capacitance of more than 10%, which made the quality analyses feasible because carefully assembled cells have an estimated error of 3%. The nature of the defects can be deduced from a higher or lower capacitance value than from that of the norm.

Table 2 shows the results for cells containing moisture and having internal short-circuits. The relationship of capacitive susceptance (reciprocal

TABLE 1

Data for defective silver oxide/zinc cells

Cell no.	Cell conditions	$ Z ^*$ (k $\Omega$ )	$\theta^{**}$	$R_p^*$ (M $\Omega$ )	$C_p^*$ (pF)	Meter reading C (pF)	Deviation** (%)
1	Normal assembly; N = 10	645.1	-89.4	121.5	692.6	691	—
	Missing 1 Zn: 5 Ag/5 Zn; N = 9, d $\uparrow$ ***	806.1	-89.7	132.0	554.0	554	-19.8
2-1	Missing 1 Ag, normal assembly						
2-2	4 Ag/6 Zn; N = 8, d $\uparrow$ Same as 2 - 1 except 1 Zn in Ag position; N = 9, d $\uparrow$	890.3	-89.4	126.5	502.2	501	-27.5
3	1 excess Ag: 6 Ag/6 Zn N = 11, d $\downarrow$	670.0	-89.5	78.6	663.2	664	-3.9
4-1	1 excess Zn, normal assembly 5 Ag/7 Zn; N = 10, d $\downarrow$	511.6	-89.3	57.0	869.4	871	+26.0
4-2	Same as 4 - 1 except 1 Zn in Ag position; N = 11, d $\downarrow$	543.5	-89.4	62.2	820.2	822	+19.0
5	Neighboring Ag and Zn tabs interchanged; N = 9	466.4	-89.4	41.9	953.4	954	+38.0
6	1 excess Ag missing 1 Zn: 6 Ag/5 Zn; N = 10, d $\downarrow$	718.1	-89.8	199.6	623	620	-10.3
7	Incorrect separator (ordinary filter paper)	557.2	-89.4	49.5	802.2	801	+15.9
8	1 excess separator, d $\downarrow$	569.7	-89.4	38.7	786.0	785	+13.6
		552.7	-89.6	54.5	810.7	810	+17.2

\*Determined from data at 356.6 Hz.

\*\*Calculated from digital voltmeter readings.

\*\*\*d $\uparrow$  shows increase in d; d $\downarrow$  shows decrease in d.

TABLE 2

Data for defective silver oxide/zinc cells

Condition	$ Z ^*$	$\theta^{**}$	$R_p^*$	$C_p^*$	Meter reading
Moisture in cell	467.2 k $\Omega$	-69.0	1.35 M $\Omega$	884.5 pF	980 pF
Short circuit	161.3 M $\Omega$	-2.0	0.16 $\Omega$	96.0 $\mu$ F	$\infty$ (>100 $\mu$ F)

\*Determined from data at 356.6 Hz.

of capacitive impedance)  $\gg$  conductance no longer existed, and the phase angle deviated from  $-90^\circ$ . The simple multimeter method could no longer be used. These cases can easily be detected by a d.c. method due to insufficient insulation resistance.

### *Conclusions*

D.c. resistance measurements have been used for detecting defects in a silver oxide/zinc reserve battery. This method is adequate for detecting internal short-circuiting or moisture-contaminated cells. An a.c. impedance technique is found to be suitable for detecting cell defects such as missing electrodes, incorrectly assembled electrodes, and incorrect selection of the separator. It is also demonstrated that, instead of elaborate equipment, a simple digital multimeter is capable of displaying deviations in capacitance for these defective cells. Although most of these defects have been designed for testing purposes, and are unlikely to occur with proper quality-control procedures, the a.c. impedance technique is believed to be valuable for early testing when the production lines are first commissioned and unexpected mistakes may occur. The technique can be extended to other battery systems.

### *References*

- 1 K. L. Hampartzumian, in J. Thompson (ed.), *Power Sources* 9, Academic Press, New York, 1982, p. 39.
- 2 J. R. Driscoll and S. Szpak, *J. Power Sources*, 16 (1985) 285.