

## **NON-DESTRUCTIVE CHARACTERIZATION OF SEALED LEAD/ACID BATTERY CELLS WITH ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY**

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### **Summary**

The potential of using electrochemical impedance spectroscopy (EIS) as a routine testing technique for the characterization of sealed lead/acid batteries was investigated with several generations of Gates 'J' type cells sampled from batteries with known histories. It was found that EIS measurements are sensitive to many fundamental cell characteristics such as cell design and standing time or shelf period but more importantly they were also very sensitive to temperature variations. For this reason and for the considerable effort required to standardize such a technique it is believed that EIS measurements are not a practical technique for a battery shop environment. In a controlled laboratory environment the same sensitivity to a multitude of parameters becomes very valuable for studying the internal mechanisms of these sealed systems.

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### **Introduction**

The poor operation of 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

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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 to cell performance [1]. 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 cell impedance spectrum.

The development of the hermetically sealed lead/acid battery has led to the introduction of lead/acid power systems into critical areas of application. Moreover, the characterization of sealed lead/acid batteries as to their state of health or charge is greatly hampered by the inaccessibility of the electrolyte for traditional density measurements. These conditions have created a need for alternate techniques and procedures to screen sealed lead/acid batteries before putting them into service.

The early use of a commercial milliohmeter (Hewlett Packard) to successfully detect potentially defective batteries was later found to be an unreliable method unless the major changes in the cell design were constantly taken into consideration [2]. Since the milliohmeter measurements are essentially impedance measurements at a fixed frequency (1 kHz), an investigation of this technique was carried out in parallel with broader-spectrum a.c. impedance measurements.

a.c. Impedance and capacitance measurements have been demonstrated to be very effective in assessing the quality of inactivated reserve battery cells during fabrication [3 - 5]. More recently electrochemical impedance spectroscopy (EIS) has been successfully applied to a thorough study of the factors that determine Na/S cell characteristics [6, 7].

Several papers on the specific use of and calculations involved in the application of EIS to the study of lead/acid battery cells are referenced [8 - 12]. The potential of using EIS as a routine screening technique for the detection of defective lead/acid batteries was investigated with similar Gates 'J' type cells spanning a few generations of development and progress.

## Experimental

Prior to any measurements the Gates 'J' type cells were discharged at 7.5 A (*C* rate) down to 1.75 V and recharged at constant current (0.6 A) for 24 h. This conditioning cycle was repeated three times to make sure that all available active material was fully charged before making subsequent measurements. It was experienced that the end of charge profiles provided useful information not only on the gas evolution reactions but often on the changes brought by the manufacturer to the internal design of these cells. The end of charge profile measurements have been standardized by following one procedure: a cell would first be discharged at 1 A for 1 h, left on open circuit for 24 h and then recharged at 1 A. At the completion of the end of charge measurements, a reference cadmium rod was introduced in the mandrel of the

cell and the respective capacity of the positive or negative plates was evaluated during a forced discharge by monitoring the changing voltage at each electrode.

The a.c. impedance measuring set-up is illustrated in Fig. 1. Galvanostatic perturbations (60 mA) were achieved by using a 1250 Solartron generator/analyzer and a 1186 potentiostat/galvanostat from the same company. A Hewlett Packard 86 microcomputer served to store and analyze data generated. A high-pass filter connected to the cell terminals allowed the alternating voltage to be amplified without interference from the d.c. voltage itself. Resistor  $R_2$  and  $R_3$  controlled the amplification factor of the differential operational amplifier (Intel 07276). The low cut-off frequency of the filter (0.005 Hz) allowed measurements to be made down to 0.1 Hz without any contribution to the cell impedance. A high frequency limit of 500 Hz was imposed by the operational amplifier. An oscilloscope was used to monitor and calibrate the a.c. amplified voltage *versus* the small probing a.c. current.

A temperature study was made on fully charged cells that had been left on open circuit at room temperature for one day prior to being equilibrated in a water bath to  $\pm 0.1$  °C for 24 h. The range of temperature used for this study (20 - 40 °C) was similar to the internal temperature a cell can develop during its normal operation.

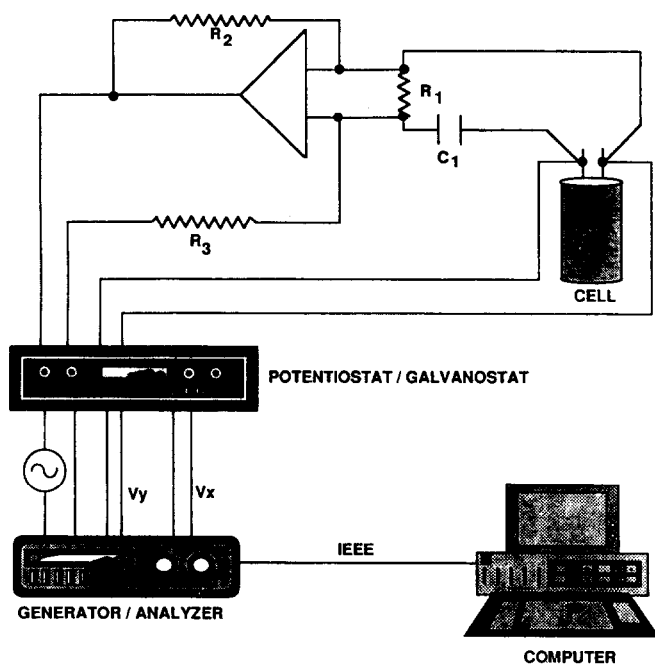


Fig. 1. Experimental set-up used to make impedance measurements on low impedance systems;  $R_1$  ( $10\text{ M}\Omega$ ) and  $C_1$  ( $30\ \mu\text{F}$ ) are the filter components;  $R_2$  and  $R_3$  determine the amplification factor of the differential Op-amp.

## Results

In order to evaluate the potential of using EIS as a routine testing technique six cells (three pairs) were chosen from three 12 cell batteries having different histories; the first pair was chosen from a healthy battery (grade A) while the other pairs were sampled out of two batteries rejected for early failure (grades B and C). Their general characteristics, when fully charged, are summarized in Table 1 where the results represent an average of the measurements made on all twelve cells of each battery. While the open circuit voltage (*OCV*) of fully charged cells is practically constant, it can be observed that both the internal resistance and the practical capacity of all the cells studied vary considerably.

Grade A cells, typical of early years of production of Gates cells, often delivered 120% of the nominal capacity (7.5 A h) at the 1 *C* rate. Grade B cells are from later production batches and demonstrate somewhat less capacity. Various modifications in the manufacturing processes throughout the years have brought the 1 *C* rate capacity to lower values and have also resulted in an increase of the internal resistance measured at 1 kHz. The grade C cells were from batteries that had failed the internal resistance test practiced in the field and taken out of service for lack of performance. Their effective capacities were often under 2 A h.

Different characteristics of these sealed lead/acid battery cells are revealed by plotting their end of charge profiles (Fig. 2) after overcharging them beyond gas evolution. Grade A cells normally show a sharp and well defined rise in the voltage at the end of charge with the potential rising rapidly to at least 2.75 V, corresponding to the onset of gas evolution [13]. The stability of the overvoltage observed after this rapid rise in voltage varies greatly. For some of the grade A cells the overvoltage plateau is stable and remains high until the end of testing while for some others the voltage would drop off after a specific overcharging period indicating the formation of soft short circuits. For grades B and C cells the overcharging voltage would always increase smoothly before sloping back to smaller and smaller values of charging potential.

Some typical EIS measurements made on individual cells at room temperature after specific standing periods (1, 5 and 20 days), following the con-

TABLE 1

Cell characteristics: open circuit voltage (*OCV*), impedance at 1 kHz and capacity with limiting electrode

Grade	<i>OCV</i> (V)	1 kHz (m $\Omega$ )	Capacity <sup>a</sup> (A h)
A	2.17 $\pm$ 0.02	2.3 $\pm$ 0.2	9(+) $\pm$ 0.5
B	2.19 $\pm$ 0.03	3.1 $\pm$ 0.5	7(-) $\pm$ 1.0
C	2.19 $\pm$ 0.03	4.3 $\pm$ 0.7	3(-) $\pm$ 1.4

<sup>a</sup>At the *C* rate.

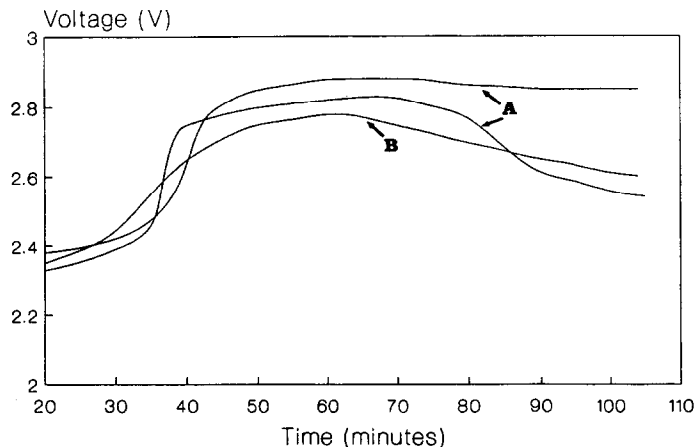


Fig. 2. End-of-charge profiles (at 1 A) obtained after having removed 1 A h of capacity from the cells.

ditioning cycles, are presented in Figs. 3, 4 and 5. The values for the charge transfer resistances calculated for these curves by using a computerized geometric analysis described elsewhere [14] are presented in Table 2. The double layer capacitance values of both positive and negative electrodes, also presented in Table 2, were evaluated by plotting the imaginary and real

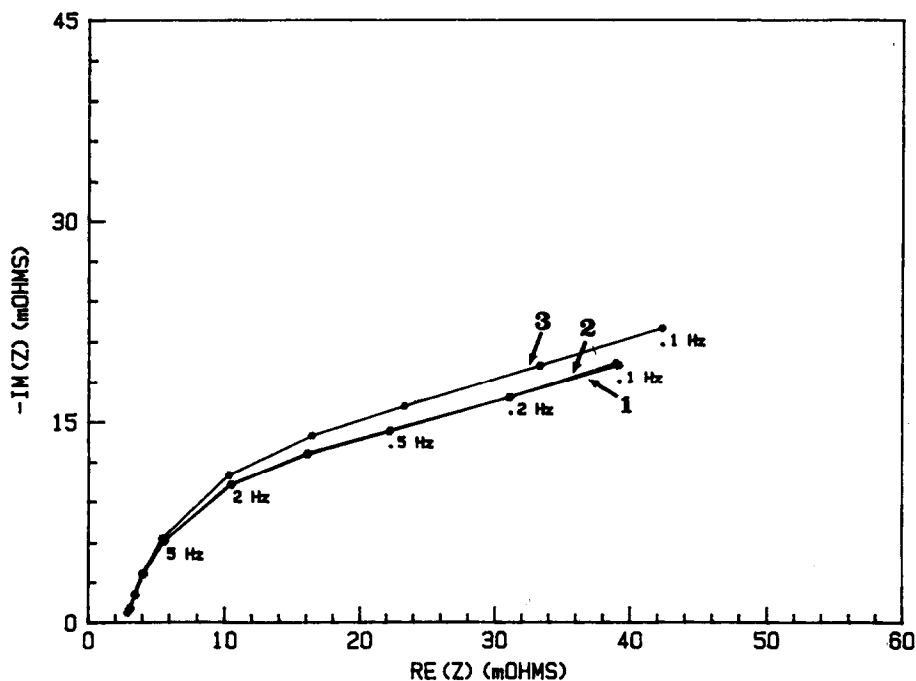


Fig. 3. Impedance patterns obtained with a grade A cell after three standing time periods: 1, 1 day; 2, 5 days; 3, 20 days.

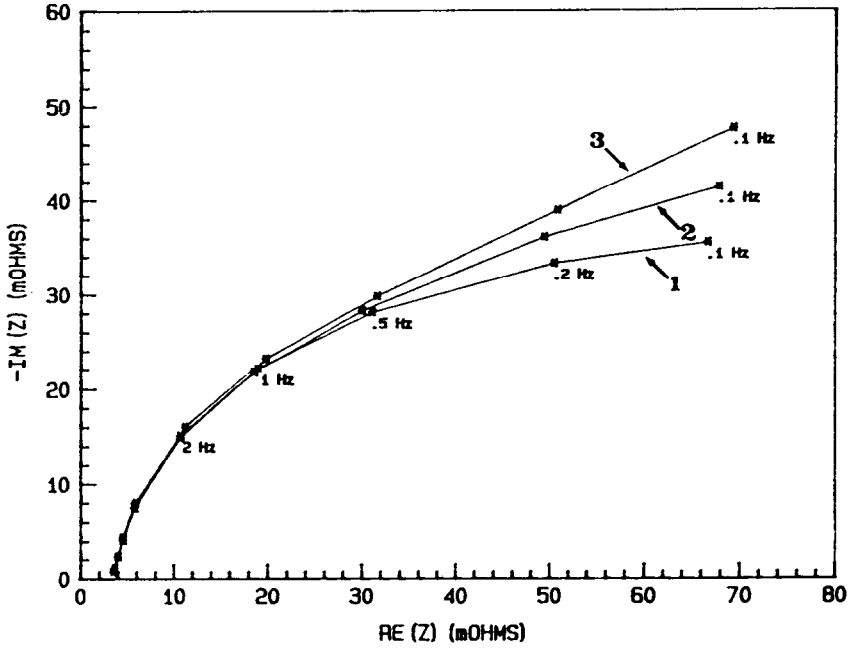


Fig. 4. Impedance patterns obtained with a grade B cell after three standing time periods: 1, 1 day; 2, 5 days; 3, 20 days.

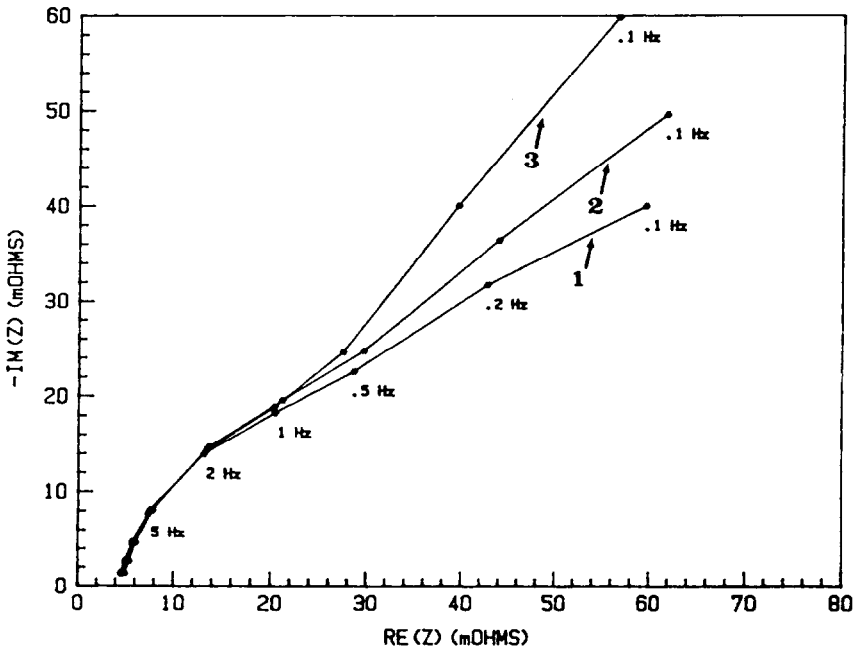


Fig. 5. Impedance patterns obtained with a grade C cell after three standing time periods: 1, 1 day; 2, 5 days; 3, 20 days.

TABLE 2

Charge transfer resistance ( $R_{CT}$ ) and double layer capacitance ( $C_{DL}$ ) as a function of standing time

Period (days)	Grade A		Grade B		Grade C	
	$R_{CT}$ ( $m\Omega$ ) $\pm 2$	$C_{DL}$ (F) $\pm 0.2$	$R_{CT}$ ( $m\Omega$ ) $\pm 4$	$C_{DL}$ (F) $\pm 0.2$	$R_{CT}$ ( $m\Omega$ ) $\pm 5$	$C_{DL}$ (F) $\pm 0.2$
1	59	2.2	97	2.2	99	1.2
5	56	2.1	102	2.1	116	1.0
20	60	2.2	112	2.1	110	0.6

admittance components, normalized by dividing them with the frequency, and projecting the linear portion of the low frequency data points onto the imaginary admittance axis [15].

For the grade A cells the standing time seems to have little or no effect since the measurements made after 1, 5 and 20 days almost overlap. For grade B cells a slight increase in the basic arc slope was observed as standing time was increased from 1 to 20 days (Fig. 4). Such an increase translates into a marginal increase of the calculated charge transfer resistance (Table 2).

When a poor performance cell (grade C) is tested as a function of standing time, the high frequency section of the impedance spectrum remains constant, while the lower frequency measurements become increasingly dominated by a Warburg component (Fig. 5). The cell's limited active surface area apparently causes the charge transfer mechanism to become diffusion controlled as the double layer capacitance breaks down with time.

From a practical point of view these subtle differences between a marginally acceptable cell (grade B) and a definitively worse one (grade C) are somewhat tenuous when the absolute values of the individual data points are compared. An additional handicap to the implementation of such testing procedures in a battery shop or in the field is demonstrated in Figs. 6 and 7 which illustrate two series of impedance measurements made on a grade A and a grade B cell over a range of temperatures. The calculated charge transfer resistances and double layer capacitances corresponding to these measurements, presented in Table 3, confirm the strong effect temperature variations have on impedance values.

The calculated  $RC$  parameters indicate a levelling off of the differences between grade A and grade B cells which, at lower temperatures, differ mostly in their charge transfer resistances. The gradual decrease of the cells' capacitance with increasing temperature is accompanied by an increased control of a diffusion-limiting Warburg component which is by nature very insensitive to cell characteristics.

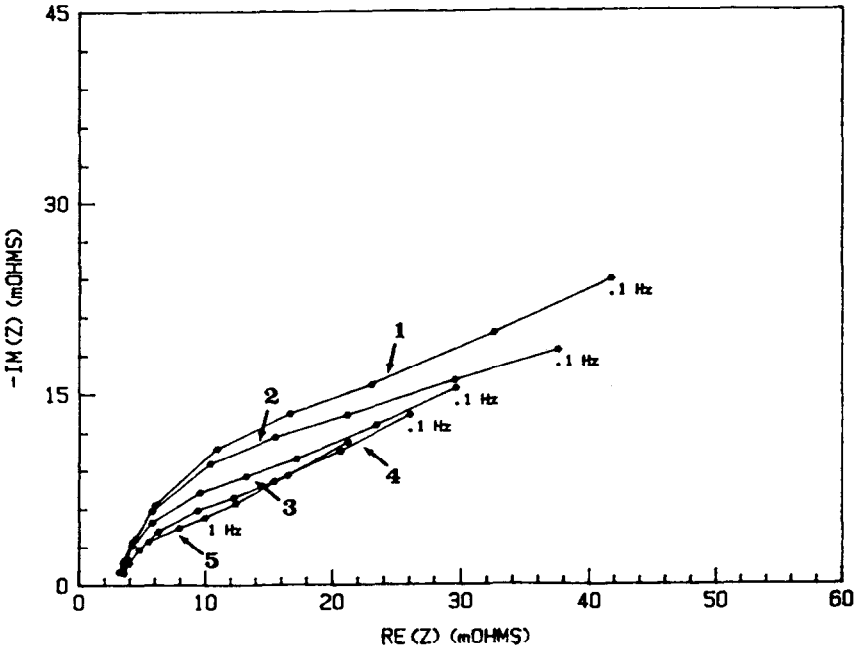


Fig. 6. Impedance patterns obtained with a grade A cell after at least 10 days on open circuit and at: 1, 20; 2, 25; 3, 30; 4, 35; 5, 40 °C.

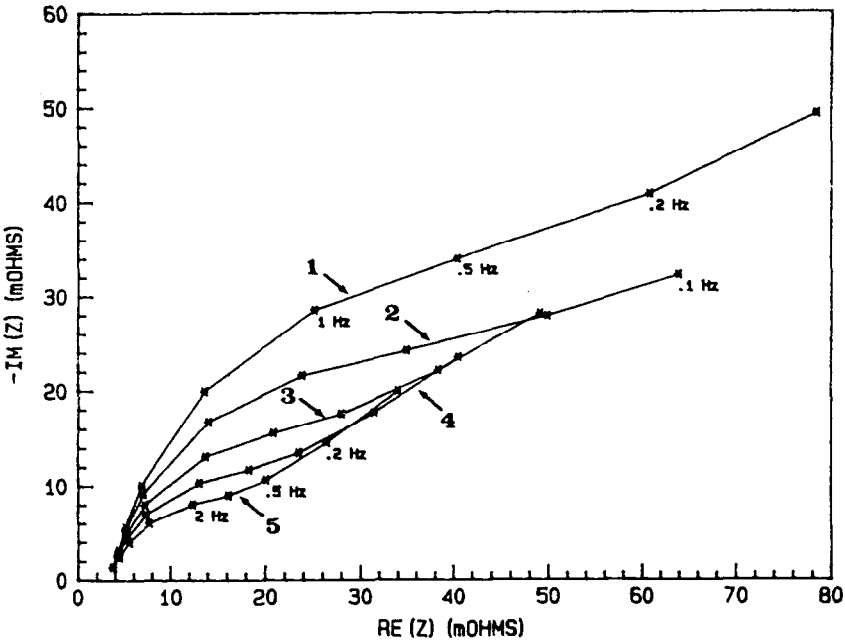


Fig. 7. Impedance patterns obtained with a grade B cell after at least 10 days on open circuit and at: 1, 20; 2, 25; 3, 30; 4, 35; 5, 40 °C.



TABLE 3

Charge transfer resistance ( $R_{CT}$ ) and double layer capacitance ( $C_{DL}$ ) as a function of temperature

Temperature (°C)	Grade A		Grade B	
	$R_{CT}$ (m $\Omega$ )	$C_{DL}$ (F)	$R_{CT}$ (m $\Omega$ )	$C_{DL}$ (F)
	$\pm 2$	$\pm 0.2$	$\pm 4$	$\pm 0.2$
20.0	62	2.0	132	1.9
25.0	58	2.0	91	1.7
30.0	42	1.6	69	1.6
35.0	39	1.0	58	1.3
40.0	32	0.7	44	0.9

## Conclusions

It can be concluded from this study that EIS measurements are moderately sensitive to sealed lead/acid cell design and period of shelf time but this sensitivity is marginal compared to what even a few degrees change in temperature can do to impedance patterns. At the elevated temperatures often encountered in batteries during charging the impedance patterns became quite extensively dominated by a Warburg diffusion-control mechanism making it difficult to distinguish quality and state of health of various cells.

For real-life situations, where each cell is often one in a series of six or twelve cells in a sealed battery, the EIS measurements would reflect the overall behaviour and thus be even less sensitive to individual cell patterns. On the other hand, the sensitivity of EIS measurements to a multitude of cell characteristics is a great asset if such a technique is applied in a controlled laboratory environment where the power sources internal mechanisms can be studied at length.

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