JOURNAL OF APPLIED ELECTROCHEMISTRY 16 (1986) 894–898

Influence of superimposed alternating current on capacity and cycle life for lead–acid batteries

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Received 25 November 1985; revised 3 January 1986

Capacity and cycle life have been measured for commercially available lead–acid batteries by superimposing an a.c. upon the charge and discharge d.c. to clarify the influence of an a.c. invasion into the d.c. system on battery performance in an electric power storage system. The current was controlled to be $I = I_0(1 + \sin \omega t)$ in all the experiments. The value of I_0 corresponded to 5 or 8 HR and the frequency range was 0.1 to 4000 Hz. No capacity change was observed for the a.c. superimposition on the charge current in this frequency range. When an a.c. was superimposed upon the discharge current the capacity of the battery increased by less than 1%. No effect on the cycle life caused by the a.c. superimposition on the charge and the discharge current was observed, as the inherent distribution of the cycle life of the batteries used was much greater than the change caused by the a.c. superimposition. Thus, it was clarified that the influence of the a.c. superimposition on battery capacity and cycle life is practically negligible for lead–acid batteries.

1. Introduction

The d.c. power of a battery electric power storage system is converted to a.c. power for load levelling of a utility electric power system by an a.c./d.c. converter. This converter also contains devices for protecting the batteries against various accidents or problems in the a.c. power system. The batteries must be protected against short circuit caused by a converting failure or external problem as well as against an invasion of high voltage, e.g. a lightning surge or a switching surge. In our previous papers [1, 2], we reported the measurement and prediction methods for the short circuit current which is necessary in the system design.

The converter fundamentally consists of a transformer and a multi-phase thyristor bridge. Since the rectification is not perfect, a residual voltage ripple cannot be avoided in the d.c. system. The voltage ripple factor is defined as

$$\delta = \frac{\left(\sum_i E_i^2\right)^{1/2}}{E_0} \qquad (1)$$

where E_0 is the d.c. voltage of the system, E_i is the amplitude of the a.c. component, i.e. fundamental tone or ith order higher harmonic, and the summation is carried out over all the a.c. components. The ripple factor is one of the most important values for the design of the converter. Even a small voltage ripple causes a large current, since the internal resistance of the batteries in the electric power storage system is fairly small and the output impedance of the a.c. system is also small. This large ripple current causes a small reduction of the energy efficiency of the storage system and there is the possibility that it may influence battery performance. In order to reduce the ripple factor, a large reactor and/or a capacitor are used in the circuit. However, in general, the large reactor and/or capacitor are of high cost and require a large space. Therefore, the reactor and/or the capacitor should be designed according to the balance between their cost and the allowable ripple of the batteries.

Thus, it is important to understand the influence of the voltage ripple on battery performance. However, no report on the influence of a.c. superimposition has been found. Only the results of a capacity test using a pulsing discharge was available for lead–acid batteries for vehicular application [3]. Hence, we have investigated the influence of a.c. of various frequencies superimposed on d.c. charge and discahrge currents on the capacity and the cycle life of lead–acid batteries.

2. Experimental details

In an electric power storage system the batteries are usually charged and discharged at constant d.c. power. At the same time a.c. voltage ripple, including higher order harmonics, invades the batteries. The batteries in our experiment were charged and discharged conventionally at constant d.c., and an a.c. instead of the voltage ripple was superimposed on the d.c.

Since the d.c. charge and discharge current, $I^{C}_{d.c.}$ and $I^{D}_{d.c.}$, respectively, were constant and equal, they were written as

$$I^{C}_{d.c.} = I^{D}_{d.c.} = I_{d.c.} = I_0 \qquad (2)$$

Then the superimposed a.c., $I_{a.c.}$, was taken to be

$$I_{a.c.} = I_0 \sin \omega t \qquad (3)$$

where $\omega(= 2\pi f; f$, frequency) is angular velocity. Thus, the total current, I, was controlled to

$$I = I_0(1 + \sin \omega t) \qquad (4)$$

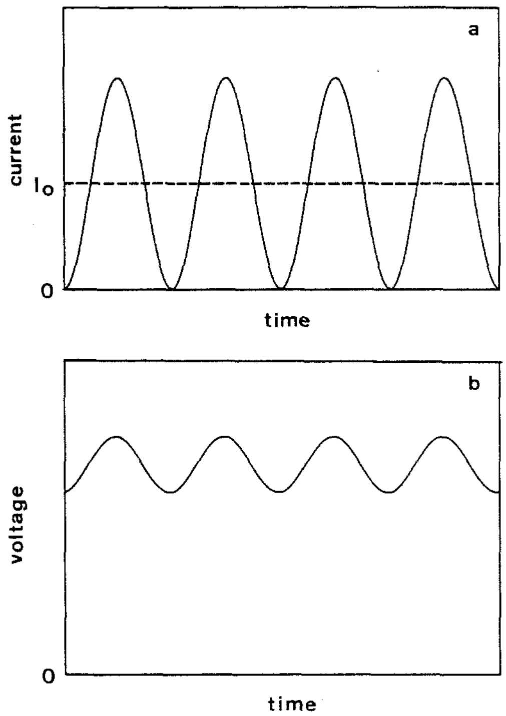

Fig. 1. A model profile of the current (a) flowing in the batteries used to produce a voltage ripple (b) similar to one from an a.c./d.c. converter. Amplitude of the voltage response is expanded.

A profile of the current is shown in Fig. 1. Though this current does not include the polarity inversion, it should be one of the most harmful conditions for the battery. In this experiment the voltage ripple factors were as small as 1% for the 6 V and 15 A h tubular-type lead–acid battery, 0.4% for the 6 V and 6 A h pasted-type lead–acid battery, and 0.2% for the 6 V and 12 A h pasted-type lead–acid battery, since the internal resistances of the batteries used here were small.

The higher order harmonics in the distorted voltage ripple are also interesting. For example, the amplitude of the 24th order harmonic is still significantly large in a 12-phase self-commutation converter. Hence, a frequency up to 4000 Hz which corresponds to the 66th or the 80th order harmonic for the 60 or 50 Hz fundamentals, respectively, was adopted. The low frequency range is also interesting, extending the concept of the voltage ripple in the storage system to the a.c. itself. Hence the a.c. current expressed as Equation 3 was superimposed on the d.c. charge and discharge currents using the frequencies of 0.1, 1, 10, 100, 1000 or 4000 Hz.

The voltage responses to the superimposed a.c. were observed for the 6 V and 6 A h pasted-type lead–acid battery, which was charged and discharged with $I_0 = 1.2$ A(5 HR). The voltage distortion was measured by a Spectral Dynamics Corp. SD335 spectrum analyser. The amplitude was read from a Nicolet 1090A digital memory scope.

Capacity was measured for the 6 V and 15 A h tubular-type lead–acid battery because the capacity is generally considered to be more stable than that of the pasted-type battery. The I_0 was 3 A, i.e. 5 HR, the charge rate was fixed to be 120%, and a cut-off voltage of discharge of 5.25 V was adopted. The frequencies of the a.c. superimposed on the charge and the discharge currents were 0.1, 1, 10, 100, 1000 or 4000 Hz, and 10, 100, 1000 or 4000 Hz, respectively.

Two kinds of cycle life tests were carried out:

some using only the d.c. charge and discharge currents and some using the d.c. with the a.c. superimposed. The frequency of the a.c. was 0.1, 100 or 4000 Hz. The battery used was a 6 V and 12 A h pasted-type lead–acid battery. The I_0 was 1.5 A(8 HR), the depth of discharge was 60% of the nominal capacity and the charge rate was 120%. Three 6 V sample batteries were connected in series. Since the battery consisted of three 2 V single cells, a total of nine cells were available for one frequency and a statistical treatment of the results was possible. Thus a total of 36 (9 × 4) single cells were used. They all belonged to the same production lot and the root mean square percentage deviation of their initial capacities was only 0.4%. The cycle life was defined to be ended when the terminal voltage of the battery reached 90% of the nominal voltage (2 V) in the discharge.

The batteries were immersed in a water bath controlled at 25 ± 1° C in all of the experiments stated above. The charge and the discharge of the batteries were controlled by a sequencer which was specially constructed for this experiment and connected with a Hokuto Denko HA305 potentio/galvanostat and a Wavetek 175 function generator.

3. Results and discussion

3.1. *Battery response*

In the high frequency region, i.e. 10, 100, 1000 and 4000 Hz, the battery showed a linear voltage response even to the large a.c. Higher harmonics were detectable but they were negligibly small for both the charge and discharge current. On the other hand, the response included the second, the third and the other higher order harmonics in the low frequency region, i.e. 0.1 and 1 Hz, and the response wave form was slightly distorted [4]. Remarkably large higher order harmonics were observed especially in the final stage of the charge. This may be related to the competitive reaction of hydrogen generation.

The absolute value of the impedance, $|Z|$, was obtained from the amplitudes of the superimposed a.c. and the a.c. component of the voltage, assuming linear response. The results are presented in Figs 2 and 3 for the charge and the discharge, respectively. The abscissa represents the ratio of charged or discharged coulombs, Q, to the capacity of the battery, Q_0. The right side in Fig. 2 and the left side in Fig. 3 correspond to a fully charged state. It is possible to estimate the current ripple by using these figures from a voltage ripple. Even a small battery like this has a comparatively low impedance. Since the batteries for electric power storage systems are

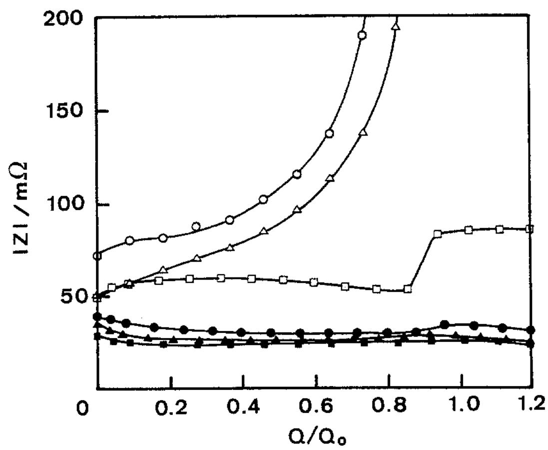

Fig. 2. The absolute value of the impedance, $|Z|$, in the voltage response to the superimposed a.c. on the d.c. charge current as expressed in Equation 4 for the 6 V and 6 A h pasted-type lead–acid battery as a function of the ratio of charged coulombs, Q, to the capacity, Q_0. ○, 0.1 Hz; △, 1 Hz; □, 10 Hz; ●, 100 Hz; ▲, 1000 Hz; and ■, 4000 Hz.

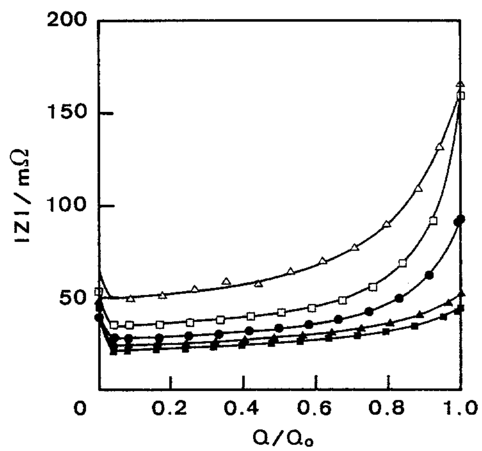

Fig. 3. The absolute value of the impedance, $|Z|$, in the voltage response to the superimposed a.c. on the d.c. discharged current as expressed in Equation 4 for the 6 V and 6 A h pasted-type lead–acid battery as a function of the ratio of discharged coulombs, Q, to the capacity, Q_0. ○, 0.1 Hz; △, 1 Hz; □, 10 Hz; ●, 100 Hz; ▲, 1000 Hz; ■, 4000 Hz.

designed to have extremely small internal resistance, the voltage ripple must be treated carefully in the converter design.

There appear to be three characteristics of the absolute value of the impedance for these frequencies. These are distinct, especially in the charge, i.e. Fig. 2. The absolute value of the impedance was large and its dependence on Q/Q_0 was also large for the frequencies of 0.1 and 1 Hz compared with those for the higher frequencies. In contrast, the absolute value of the impedance changes little and has relatively small values for the frequencies of 100, 1000 and 4000 Hz. These values and dependencies were in the intermediate situation for the frequency of 10 Hz. These characteristics should be closely related to the facts that the lower two, i.e. 0.1 and 1 Hz, belong to the Warburg region, that the higher three, i.e. 100, 1000 and 4000 Hz, are representative of charge transfer, and that 10 Hz belongs to the intermediate region in the conventional complex plane analysis of chemical impedance of lead–acid batteries.

3.2. *Capacity*

In order to examine the influence of the a.c. superimposition on the charge current and the discharge current separately, the battery was charged and discharged in three ways. First, the battery was charged with the a.c. superimposition, and immediately after the charge it was discharged with only the d.c. current to a fixed cut-off voltage of discharge. Second, the battery was charged with only the d.c. and discharged with the a.c. superimposition. Last, the battery was charged and discharged without the a.c. superimposition, this latter mode being used as a reference. The battery was cycled as follows.

$(n - 1)$th, charged and discharged with only the d.c.

nth, charged with the a.c. superimposition and discharged with only the d.c.

$(n + 1)$th, charged and discharged with only the d.c.; or

$(n - 1)$th, charged and discharged with only the d.c.

nth, charged with only the d.c. and discharged with the a.c. superimposition

$(n + 1)$th, charged and discharged with only the d.c.

Then the capacity change ratio, P, was defined as

$$P = \frac{2C_n}{C_{n-1} + C_{n+1}} \tag{5}$$

in order to reduce the error caused by the continuous capacity change along the cycles, where C_n is a capacity for the a.c. superimposition and C_{n-1} and C_{n+1} are capacities for the reference tests just before and after the cycle of the a.c. superimposition. At least two of the reference tests were placed between the tests concerned with a.c. superimposition. For example, a capacity test was carried out from the 23rd cycle to the 130th cycle for one of the three batteries used. The capacity then decreased from 14.38 A h to 12.21 A h along the cycles, which corresponded to about a 15% reduction of the capacity. The situations were similar for the other two batteries. This shows the necessity of dealing with capacity change as the ratio to those capacities before and after the cycle of the a.c. superimposition as defined in Equation 5.

The results are shown in Table 1, both for the charge and the discharge. The test using only the d.c. was a blank test, which was carried out in the same way as the a.c. superimposition except that the a.c. was not superimposed on the charge and the discharge current. The blank test was used as a measure of the error in the

Table 1. Capacity change caused by the a.c. superimposition on the charge or the discharge d.c. for the 6 V and 15 A h tubular-type lead–acid battery

Frequency (Hz)	P_{av}	
	Charge	*Discharge*
0.1	0.999	
1	1.002	
10	1.000	1.009
100	1.003	1.006
1000	0.997	1.008
4000	0.997	1.009
d.c.	1.002 ± 0.005[a]	

[a] Standard deviation.
P_{av} is an averaged value of the ratio as defined in Equation 5. Between two and nine measurements are made for each. The d.c. experiment is the capacity test without the a.c. superimposition and serves as a reference.

experiments. The value of P should then be unity. The result was 1.002 ± 0.005, and this shows a good accuracy in the experiments.

The ratios were almost 1.000 for each frequency and were distributed around 1.000 within a negligibly small deviation for the a.c. superimposition on the charge current. No difference was observed compared with the value of the d.c. experiment. Thus the a.c. superimposition on the charge current did not affect the capacity of the battery. In this case the charge rate, 120%, which was sufficiently greater than 100% may have eliminated the effect of the a.c. superimposition.

The ratio P showed values greater than unity in all frequencies of the a.c. superimposed on the discharge current. These were 1.009, 1.006, 1.008 and 1.009 for 10, 100, 1000 and 4000 Hz, respectively. There is a statistically significant difference between the capacities with and without the a.c. superimposition. The effect of the small capacity enhancement has a good correspondence to the apparent capacity increase for the pulsing discharge in the electric vehicular system [3]. Thus, the a.c. current enhanced the capacity of the battery. However, the enhancement did not exceed 1%. Considering the large superimposed

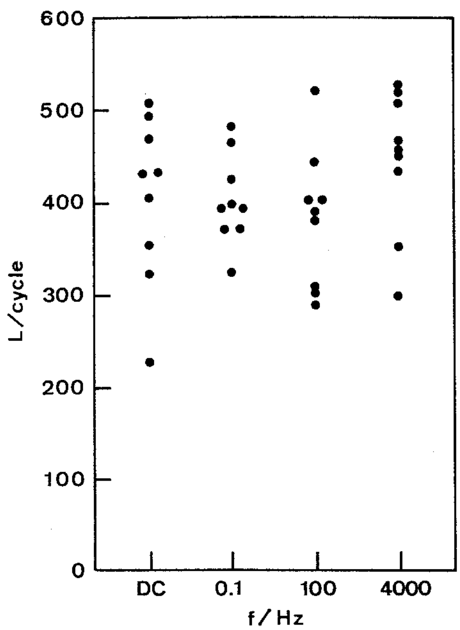

Fig. 4. Distributions of the cycle life of the 6 V and 12 A h pasted-type lead–acid battery for the d.c. experiment and the a.c. superimposing experiment with frequency, *f*.

Table 2. Averaged cycle life of the 6 V and 12 A h pasted-type lead–acid battery with and without a.c. superimposition

Frequency (Hz)	L_{av}(*cycle*)	ΔL(*cycle*)	σ(*cycle*)	σ_p[a]
d.c.	405		90	22
0.1	403	−2	49	12
100	382	−23	75	19
4000	446	41	76	17

ΔL is the difference between the averaged cycle life and that of the d.c. system. σ and σ_p are the standard deviation and the root mean square percentage deviation, respectively, of the cycle life.

$$^{a}\ \sigma_p = 100\left(\frac{\sum [(L_{av} - L)/L_{av}]^2}{n-1}\right)^{1/2}$$

a.c. used in this work, the influence is negligible for an electric power storage application.

3.3. *Cycle life*

Table 2 shows the averaged values and standard deviations of the cycle life of the batteries. The practical values of the cycle life are plotted in Fig. 4 against the frequency of the superimposed a.c. in order to display the cycle life distribution. It is remarkable that the root mean square percentage deviations are as large as ~10–20% of the averaged values. This could originate from the battery performance itself rather than from the experiment. The cycle life with the a.c. superimposition for the frequency of 100 Hz was less than that of the reference, i.e. the life test without the a.c. superimposition, by 23 cycles. The standard deviation of the distribution of the cycle life, however, was estimated to be as large as 75 cycles, which substantially exceeded the difference between the cycle life of the reference d.c. systems and that of the a.c. superimposition. This should be the same for the other frequencies. Thus, no influence on the cycle life was observed for the a.c. superimposition of these frequencies.

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