Impedance characteristics of sealed lead/acid cells during galvanostatic charge

J. Jindra, M. Musilová and J. Mrha
J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 182 23 Prague 8 (Czechoslovakia)

A. A. Taganova
All-Union Accumulator Institute, 197137 Leningrad (USSR)

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Abstract

The electrochemical impedance of a model hermetic lead accumulator and its electrodes was measured during continuous or interrupted charging either in potentiostatic (at 10^4–10^{-3} Hz) or in galvanostatic (at 0.1 Hz) mode. The impedance characteristics of the negative electrode changed considerably during the second half of charging and during overcharging. The impedance curve at 0.1 Hz measured during continuous galvanostatic charging can be used to indicate the state of full charge of the cell.

Introduction

Several authors have considered the possibility of estimating the residual charge of lead/acid batteries, including those of the sealed type, from their impedance characteristics. The ohmic resistance of the electrolyte and of the electrode active mass was proposed to serve as a characteristic parameter [1]; other authors recommended for this purpose the impedance characteristics in the kinetic control region, namely the charge transfer resistance, the double-layer capacitance, or the frequency corresponding to the maximum on the high-frequency semicircle of the Nyquist diagram [2, 3]. Still other authors [4] considered the low-frequency region below 1 Hz as most informative and presented impedance diagrams of both accumulator electrodes in the charge state showing considerable differences. The low-frequency impedance of the accumulator is mainly given by the capacitance of the negative electrode. Impedance diagrams of this electrode were studied recently in both the charged and discharged states [5] and it was found that the influence of the state of the active mass on the capacitance was considerable, especially at frequencies 0.1–0.3 Hz.

The mentioned impedance studies were carried out in the potentiostatic regime after various storage times elapsed after discharge to ensure a pseudostationary state of the system. Several authors, however, observed a dependence of the impedance characteristics of the lead accumulator on the storage time and temperature of the environment. Therefore, the experimental conditions including the preparation of the battery for the measurement should be standardized if the impedance measurements are to be more widely used.

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On the other hand, an interesting problem is the evaluation of the state-of-charge during charging, representing a continuous process which is standardized by itself. Studies of the impedance characteristics of sealed Ni/Cd accumulators of various types [7] revealed characteristic changes of the diagrams during charging, which make it possible to check the state-of-charge in a wide range of charging currents and temperatures. This is based on an increase of the imaginary component of the low-frequency impedance during intensification of oxygen evolution at the positive electrode at the end of charging.

It can be expected that analogous effects will occur during charging of sealed lead/acid accumulators. The aim of the present work is therefore to find out whether their state-of-charge can be checked in a similar manner without a substantial increase of the internal pressure, and to select the most suitable impedance characteristic.

Experimental

Cell design

The electrodes were placed in a cylindrical test cell [8] shown schematically in Fig. 1. Dry-charged electrodes with Pb/Ca grids of dimensions 85×48×2 mm were used. The glass fibre mat separator of type MF4 (IRAPA, Czechoslovakia) was 2 mm thick, its square density was 264 g/m^2 and porosity 95%. The cell was assembled in the dry state and a solution of 5 M H_2SO_4 was added into it after evacuation. The degree of acid filling was approximately 75–80% and the capacity of the cell (5 h discharge rate) was 1.2 A h.

Impedance measurements

The impedance characteristics were measured by means of a Solartron 1250 frequency response analyser coupled with a Solartron 1286 electrochemical interface. The measurements were carried out either potentiostatically in a steady state in the frequency range 10^4–10^{-4} Hz with an a.c. voltage amplitude of 1 mV, or galvanostatically with an a.c. amplitude of 3 mA at constant frequency of 0.1 Hz during continuous charging with 200 mA. These measurements were made at 3 min intervals and at the same time the potential of the electrodes, the cell voltage and overpressure were

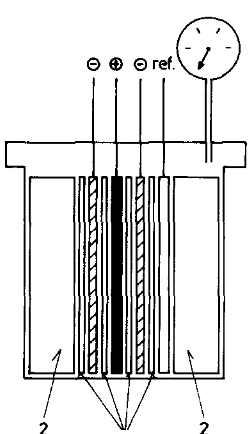

Fig. 1. Scheme of a model sealed lead/acid cell: 1, separators; 2, spacers.

followed. The cell impedance was measured in the two-electrode arrangement while the electrode impedance was measured in the three-electrode arrangement.

Results and discussion

The impedance diagrams of a test cell measured in the frequency range 10^4 to 4×10^{-3} Hz are shown in Figs. 2 and 3. The measurements were made for 16 h after

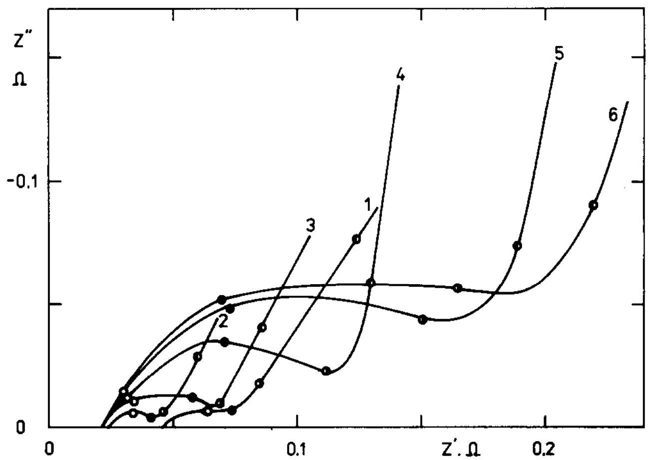

Fig. 2. Impedance characteristics of a model sealed lead/acid cell at different applied charges, C_c/C_d, equal to: 1, zero; 2, 0.6; 3, 0.9; 4, 1.15; 5, 1.45; 6, 1.95. The following symbols denote frequencies: ○, 10 Hz; ●, 1 Hz; ◑, 0.1 Hz; ◐, 0.01 Hz. Symbols C_c and C_d denote charge and discharge capacity, respectively.

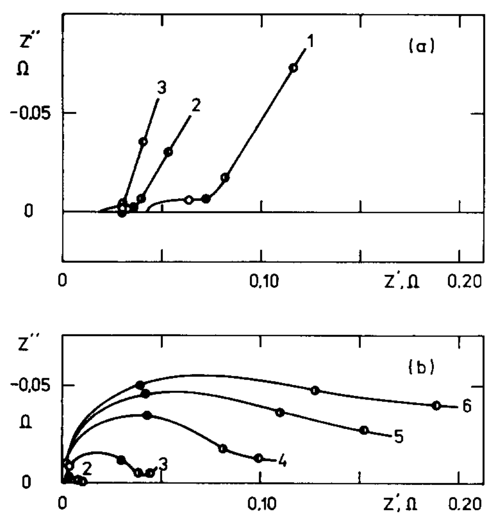

Fig. 3. Impedance characteristics of (a) positive and (b) negative electrodes of a model sealed lead/acid cell at different applied charges. Notation as in Fig. 2.

the state-of-charge had been changed. It can be seen from these diagrams that the ohmic resistance of the cell is due mainly to the resistance of the positive electrode. At frequencies below 1 Hz, when the accumulator is only partially charged (up to 50%), the impedance of the positive electrode constitutes the essential part of the cell impedance and also its changes are most marked, as the charging progresses and also during overcharging the impedance of the negative electrode becomes the controlling factor, especially its real component. The impedance diagram of the charged positive in the region of low frequencies is similar to that observed earlier [4]. The diagrams corresponding to the negative electrode in both the charged and discharged states are in accord with the concepts presented in ref. 5.

Analysis of the impedance data at 10, 1, 0.1 and 0.01 Hz revealed that the sum of the real or imaginary impedance components for the particular electrodes was practically equal to the corresponding component for the complete cell, the deviations not exceeding ±10%. Larger deviations were found during overcharging at 0.1 and 0.01 Hz, which may be due to instability of the measurement in connection with the interfering oxygen cycle.

Analysis of the impedance characteristics of the lead/acid cell at various charge states revealed that during advanced charging and during overcharging the real impedance component at 0.1 and 0.01 Hz changes most profoundly. This is mainly caused by changes of the negative electrode, which may be due to decreasing coverage with $PbSO_4$ and increasing free Pb surface. These two regions are responsible for the reactions

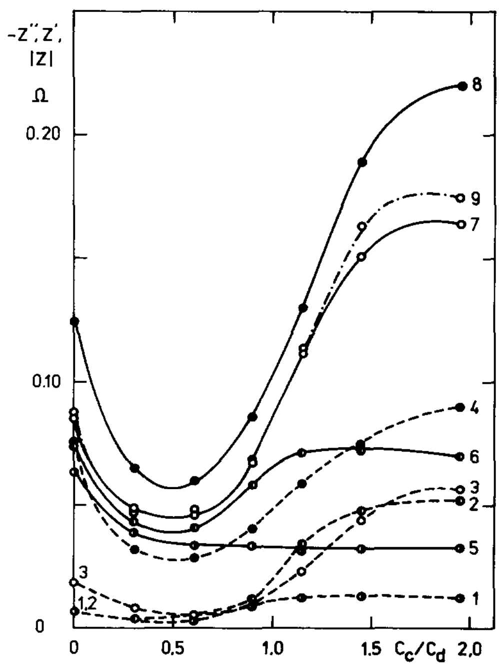

Fig. 4. Imaginary (1–4) and real (5–8) impedance components and impedance module |Z| (9) for a model sealed lead/acid cell at different applied charges. Measuring frequency: 1, 5 at 10 Hz; 2, 6 at 1 Hz; 3, 7, 9 at 0.1 Hz; 4, 8 at 0.01 Hz.

$PbSO_4 + H^+ + 2e^- = Pb + HSO_4^-$

$O_2 + 4H^+ + 4e^- = 2H_2O$

whose ratio controls the course and changes of the impedance characteristics of both the negative electrode and the complete cell.

The imaginary component of the cell impedance at low frequencies and various charge states amounts to 15–35% of the real components, and they both change in the same sense. This allows us to characterize the charge process by the impedance module, $|Z| = U_\sim / I_\sim$, which is more simply measurable than the components. Its changes at 0.1 Hz are illustrated by the curves in Fig. 4. We preferred this frequency to 0.01 Hz, which requires a longer time of measurement with similar results.

During continuous charging, the oxidation of lead proceeds at somewhat different conditions compared to the interrupted process with interposed storage periods. Therefore, measurements were also carried out during galvanostatic charging. Since an impedance spectrum in a wide frequency range can only be obtained after a longer time which is comparable to the time of charging, we limited ourselves to the frequency of 0.1 Hz. The cell of 1.1 A h capacity was loaded with 200 mA and the measuring a.c. current signal was 3 mA. The characteristics of the cell and electrodes were measured in three subsequent cycles after the internal overpressure had been lowered to zero.

The results are shown in Fig. 5. It can be seen that the imaginary component of the positive electrode impedance is practically constant during the whole charging process, while the real component decreases to 0.08 Ω after about 15% of the full

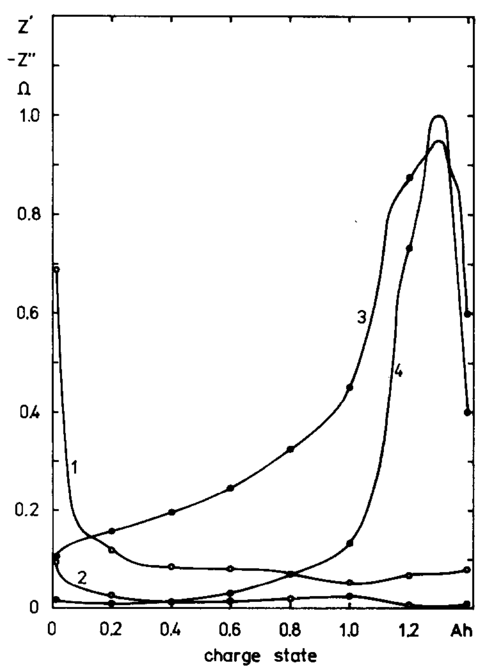

Fig. 5. Evolution of impedance characteristics of positive (1, 2) and negative (3, 4) electrodes of a model sealed lead/acid cell during galvanostatic charging. 1, 3 real and 2, 4 imaginary components at 0.1 Hz.

capacity has been supplied and afterwards remains stable. This is in accord with the course of the two components during stepwise changes of the state of charge.

The values of Z' and Z'' for the negative electrode increased from the beginning of charging up to 90% of the state-of-charge practically linearly at rates of 0.03 and -0.01 Ω per 10% increase of the state of charge, respectively. During further charging, the two components increase more rapidly, which is probably caused by blocking of the electrode pores with hydrogen. In contrast to the experiments with stepwise charging, the values of Z' and Z'' decrease during overcharging, this is accompanied by an increase of the cell overpressure. In this situation, the ionization of oxygen at the negative electrode becomes important and is apparently responsible for the observed decrease of the Z' and Z'' values.

The course of the cell impedance is shown in Fig. 6. Since the contribution of the positive electrode is relatively small, especially in the second half of charging, the curves reflect the processes at the negative electrode. It can be seen that the characteristic changes of the curves accompanying the overcharge and the internal pressure increase make it possible to indicate the state of full charge of the cell.

The observed changes of the impedance (mainly $|Z|$) of the sealed lead/acid cell are analogous to those of the sealed Ni/Cd accumulator. This enables us to establish a general method for indicating the state of full charge of sealed accumulators operating on oxygen cycle. Changes of the charging current and temperature cause changes of the peak on the impedance curve and its shift with respect to the charge capacity, but the character of the curve remains preserved [7].

The described method for indicating the state of full charge of sealed lead/acid accumulators is more sensitive than the classical method using the cell voltage and

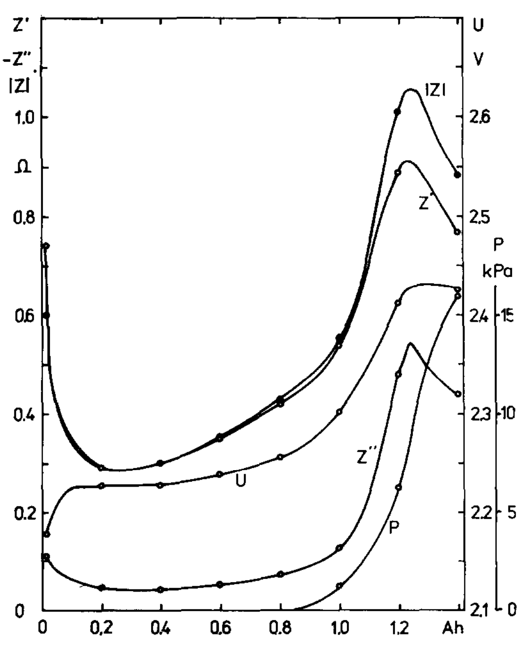

Fig. 6. Evolution of impedance characteristics ($|Z|$, Z', Z'') at 0.1 Hz, voltage U and overpressure P of a model sealed lead/acid cell during galvanostatic charging.

requires a rather simple equipment, provided that the impedance module is used as a source of information.

Conclusions

(1) The ohmic resistance of the sealed lead/acid cell is given mainly by the resistance of the positive electrode in the whole range of charge states. The cell impedance in the first half of charging is essentially controlled by the positive electrodes, while at higher charge states and during overcharging it is controlled by the negative electrode.

(2) During galvanostatic charging, the cell impedance measured at 0.1 Hz during advanced charging is controlled mainly by the negative electrode and it shows a characteristic course when the state of full charge is reached. This can be utilized to indicate the state of full charge of the cell.

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