ESTIMATION OF THE RESIDUAL CAPACITY OF MAINTENANCE-FREE LEAD–ACID BATTERIES
PART 1. IDENTIFICATION OF A PARAMETER FOR THE PREDICTION OF STATE-OF-CHARGE

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Summary

The ohmic resistance of maintenance-free lead–acid batteries has been identified as an ideal parameter for the prediction of the state-of-charge using the a.c. impedance technique. The ohmic resistance has been found to mirror the change in specific gravity of the battery electrolyte when charged or discharged.

Introduction

The total coulombic capacity of a cell depends on the electrochemical properties and on the quality and quantity of its components. In practice, the total capacity yielded during the useful life of a cell in a particular application may fall far short of the stored capacity owing to the type of discharge regime imposed on the cell. It depends on the magnitude of the load resistance, the discharge time, the time allowed between discharges for recuperation, and the value of the terminal voltage on load at the end of discharge.

Furthermore, there are always differences in the performance of cells which are nominally of the same type and have similar manufacturing, storage, and operational histories. To predict the residual capacity with sufficient accuracy for practical purposes, it is necessary to find a property of the cell that provides a good indication of its state-of-charge, which can be measured with ease, economy, and rapidity, and which causes negligible disturbance of the electrochemical condition of the cell.

The traditional methods of measurement of electrolyte density are no longer possible on maintenance-free lead–acid batteries since the battery

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unit is sealed and all the electrolyte is taken up in the plates and separator or, alternatively, immobilised with a gelling agent.

One of the simplest, and most widely used methods of residual capacity estimation in flooded batteries which could be applied to maintenance-free batteries is the loaded voltmeter test. Unfortunately, energy is withdrawn from the battery and more accuracy is obtainable only when energy is withdrawn over longer periods. Gates [1] claims that careful inspection of the open circuit voltage can reveal the residual capacity of its 'beer can cells' within 20% provided that the cell has not been charged or discharged for 24 h. The accuracy of prediction can be reduced to within 5% if a period of 5 days has elapsed since the last charge or discharge. Higginson and Peters [2] have described a similar relationship for sealed automotive and standby lead–acid batteries.

Hughes *et al.* [3, 4] have successfully used the a.c. impedance technique to predict the residual capacity of 2 V 2.5 A h and 2 V 25 A h lead–acid, sealed, recombination cells manufactured by Gates Energy Products. Their prediction was based on the correlation between the product of the charge transfer resistance and the double layer capacitance and, consequently, required isolation of the top of the charge transfer semi-circle.

Experimental

The following sets of impedance measurements were made at 25 °C on various batteries and individual cells:

(a) A.c. impedance measurements were carried out on maintenance-free Yuasa 6 V 2.6 A h lead–acid batteries at various states-of-charge. Two-terminal impedance measurements in the frequency range 60 kHz - 60 mHz were made in the potentiostatic mode as described by Karunathilaka *et al.* [5] for the measurement of cells with low impedances. All measurements were made after the batteries had been allowed to rest for 1 h following charge or discharge. The batteries were initially charged at a constant 7.5 V with a current limit of 260 mA, and subsequently all galvanostatic discharges were carried out at the 0.4 *C* rate to an end voltage of 5.1 V.

(b) Two-terminal impedance measurements were carried out on single 2 V cells from a 6 V 2.6 A h battery and 3-terminal impedance measurements were performed on single cells modified to include a reference electrode. One corner of the cell case was cut open and a lead foil (25 × 2 × 0.5 mm) was inserted into the microporous glass fibre separator between a positive and negative plate to provide a reference electrode. The cell was then resealed. This modification was carried out in a glove box with an oxygen-free environment to avoid oxidation of the negative plates.

(c) Two-terminal impedance measurements were carried out on a flooded lead–acid cell. The cell comprised a positive and a negative plate extracted from a 6 V 2.6 A h battery, spaced so as not to require the use of any separator, and flooded with new 1300 S.G. sulphuric acid after each discharge. A.c. impedance measurements were made at various states-of-charge allowing time for the system to stabilize before measurements were made.

(d) Two-terminal impedance measurements were performed on 6 V 3 A h Sonnenschein and 6 V 100 A h sealed lead–acid batteries at various states-of-charge.

Results and discussion

Figures 1 - 4 show the Sluyters and Randles plots of a 6 V 2.6 A h battery when fully charged and fully discharged, respectively. Figures 5 and 6 show the response of the battery at a 70% state-of-charge, which is typical of the response at all other states-of-charge. The inductive reactance gradually decreases from 100% state-of-charge to 0% state-of-charge. The ohmic resistance, *i.e.*, the resistance at which the impedance locus crosses the real axis, increases significantly from about 12 mΩ when fully charged to approximately 33 mΩ when fully discharged, though little difference is seen in the 100% - 70% range (Figs. 1, 5). Figures 1 - 6 reveal the highly porous nature of the battery plates, a characteristic highlighted by the 'flattened' semi-circles at the highest frequencies and by the 45° angle between

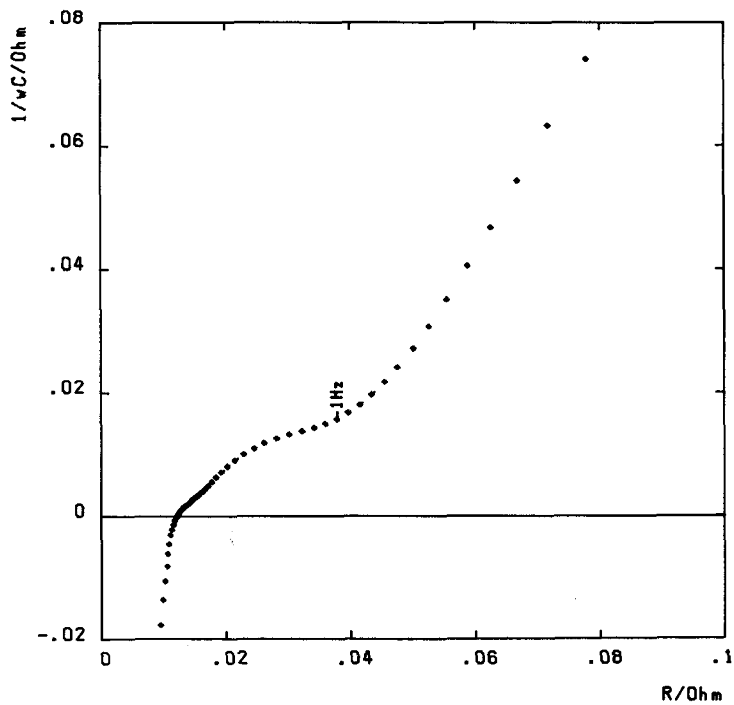
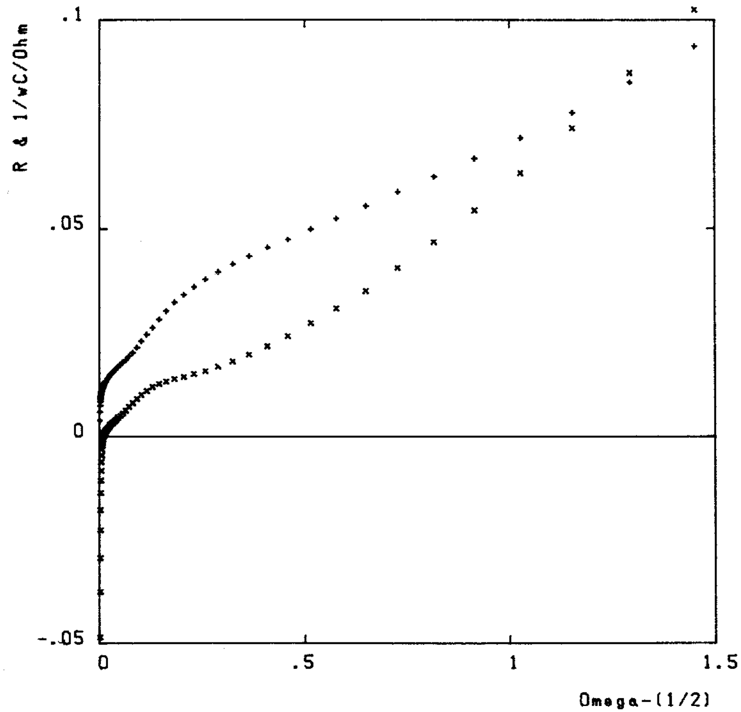


Fig. 1. Sluyters plot of a fully charged 6 V 2.6 A h maintenance-free battery.



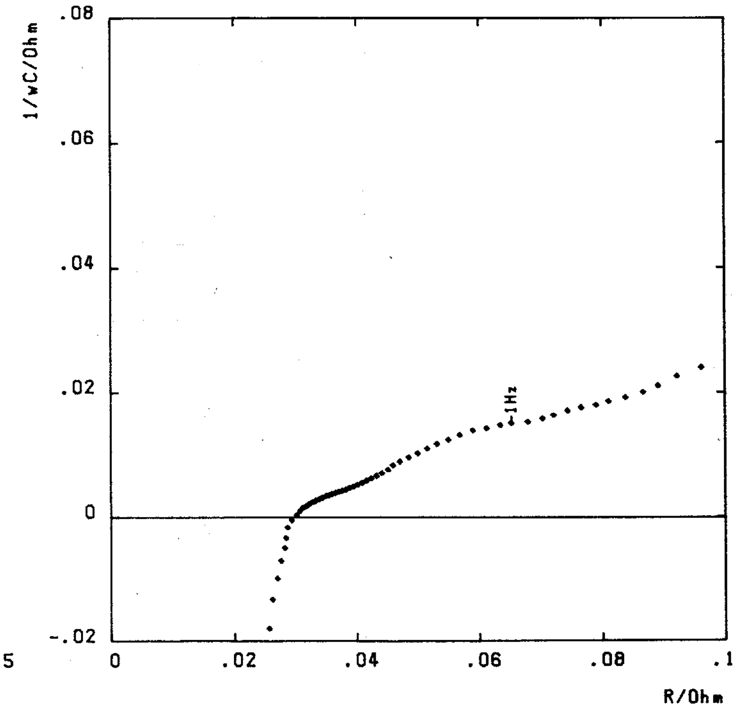
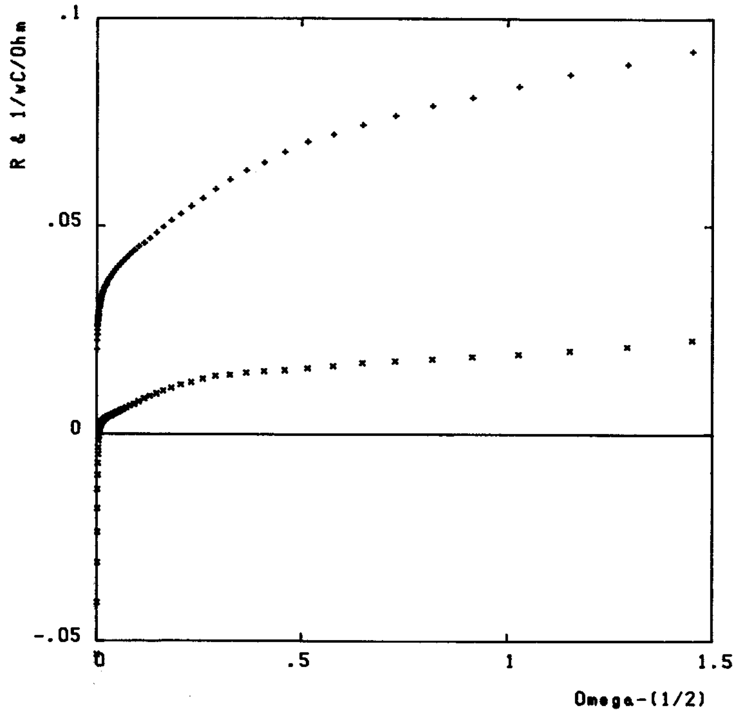


Fig. 2. Randles plot of a fully charged 6 V 2.6 A h maintenance-free battery. +, Resistive component; ×, capacitive component.

Fig. 3. Sluyters plot of fully discharged 6 V 2.6 A h maintenance-free battery.



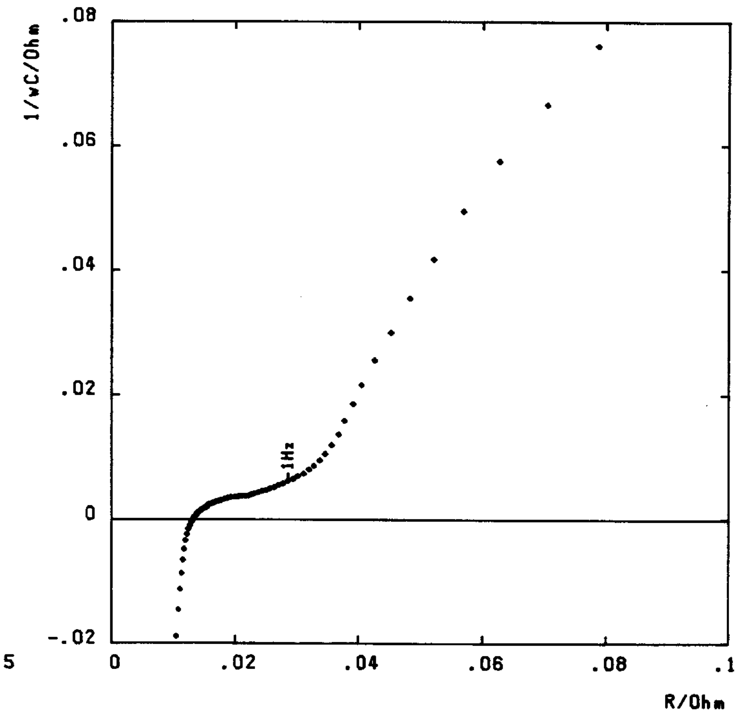


Fig. 4. Randles plot of a fully discharged 6 V 2.6 A h maintenance-free battery. +, Resistive component; ×, capacitive component.

Fig. 5. Sluyters plot of a 6 V 2.6 A h maintenance-free battery at 70% state-of-charge.

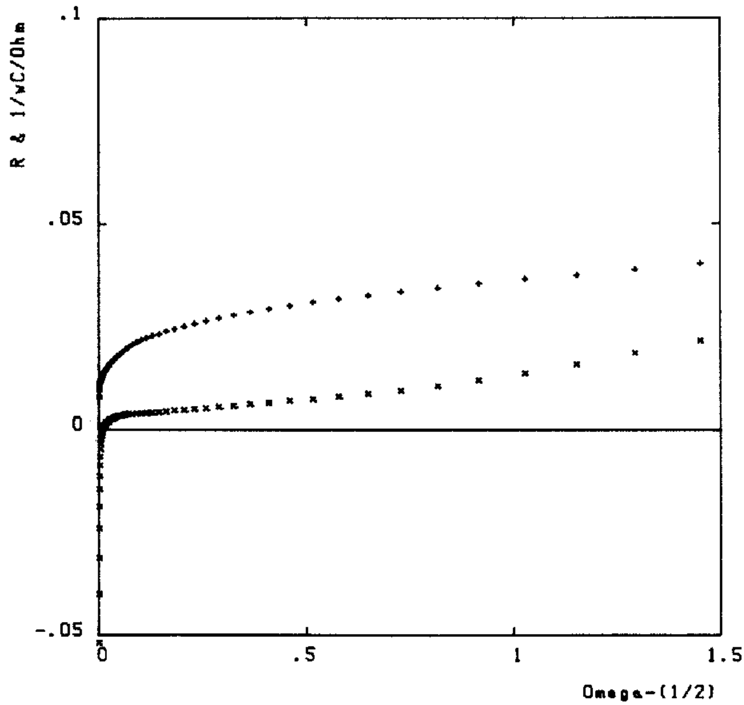


Fig. 6. Randles plot of a 6 V 2.6 A h maintenance-free battery at 70% state-of-charge. +, Resistive component; ×, capacitive component.

impedance locus and the real axis. At frequencies less than 1 Hz the diffusion tail subtends an angle of 60° when fully charged, and this angle gradually decreases over the various states-of-charge below 70% to less than 22° when fully discharged, with a general tendency to return to the real axis at the lowest frequencies. At 100% and 0% state-of-charge two semi-circles are clearly seen at frequencies greater than 1 Hz, followed by a relaxation to a diffusion process at frequencies less than 1 Hz. These observations are confirmed by the three distinct relaxation processes revealed in the corresponding Randles plots.

Figures 7 and 8 show the Sluyters plots of the positive and negative plates produced by the 3-terminal impedance measurements of the modified 2 V cell. These plots clearly show that the impedances of both positive and negative plates are of the same order of magnitude, and that the first semi-circle, *i.e.*, at the highest frequency, in Figs. 1 and 3 is consistent with the negative plate and the second semi-circle with the positive plate. To ensure that no detrimental effects were suffered by the modified cell, impedance measurements were performed on a single, unmodified cell for comparison; these showed no difference in the impedance response.

Earlier work by Hughes *et al.* [3, 4] on a maintenance-free lead–acid cell with unalloyed lead grids demonstrated a relationship between the

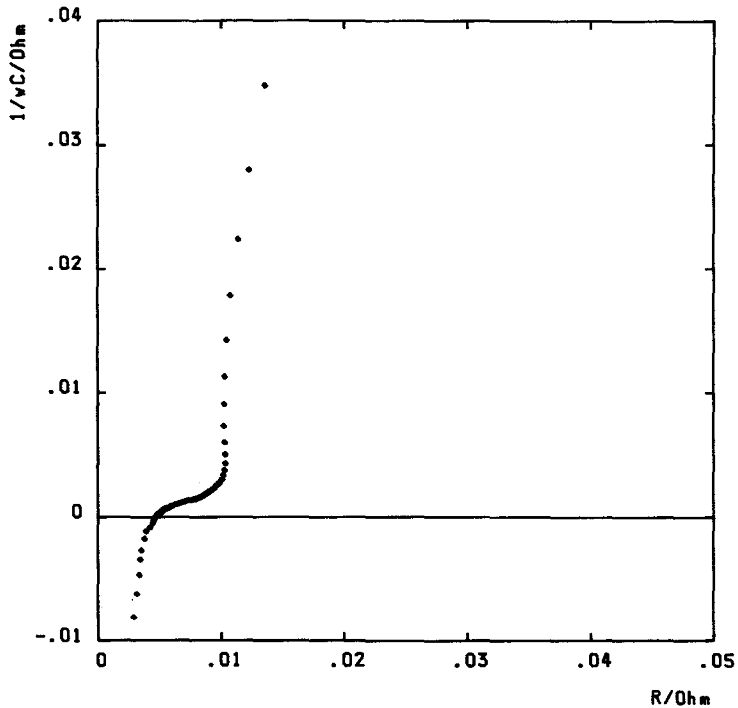


Fig. 7. Sluyters plot of the positive plates in a modified 2 V cell.

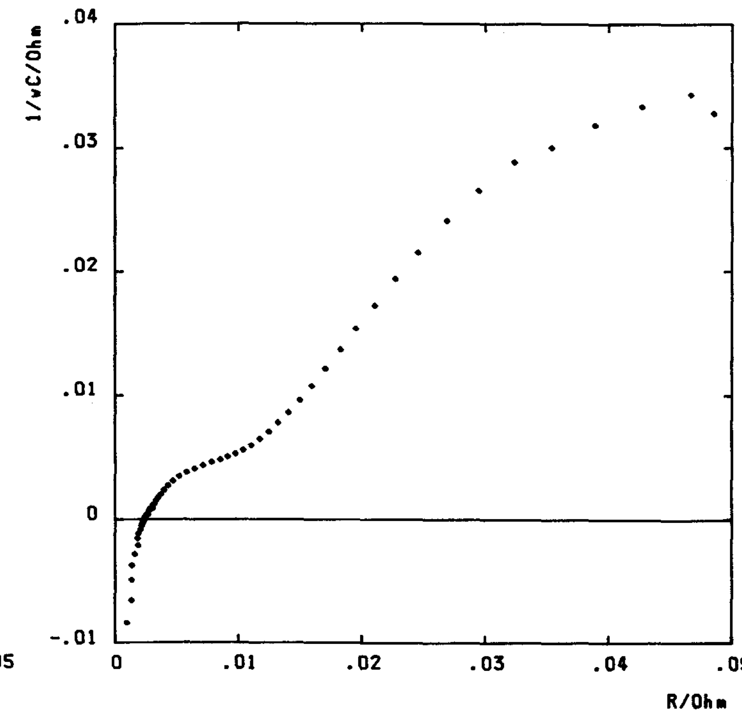


Fig. 8. Sluyters plot of the negative plates in a modified 2 V cell.

product of the charge transfer resistance, the double layer capacitance, and the state-of-charge of the cell, although only one semi-circle was evident from their results at all states-of-charge. The change in resistivity of the sulphuric acid electrolyte with concentration has been described in detail by Bode [6] and Vinal [7], and the specific gravity of the battery acid is known to change in a corresponding manner with charge or discharge. Figure 9 shows how the ohmic resistance changes with state-of-charge and is consistent with the change in resistivity of the sulphuric acid, mirroring the response described by Bode and Vinal. We have confirmed this behavior by measuring the ohmic resistance of a flooded cell in which the plates were at various states-of-charge, but the sulphuric acid concentration was held constant at 1300 S.G. The ohmic resistance remains unchanged at all states-of-charge.

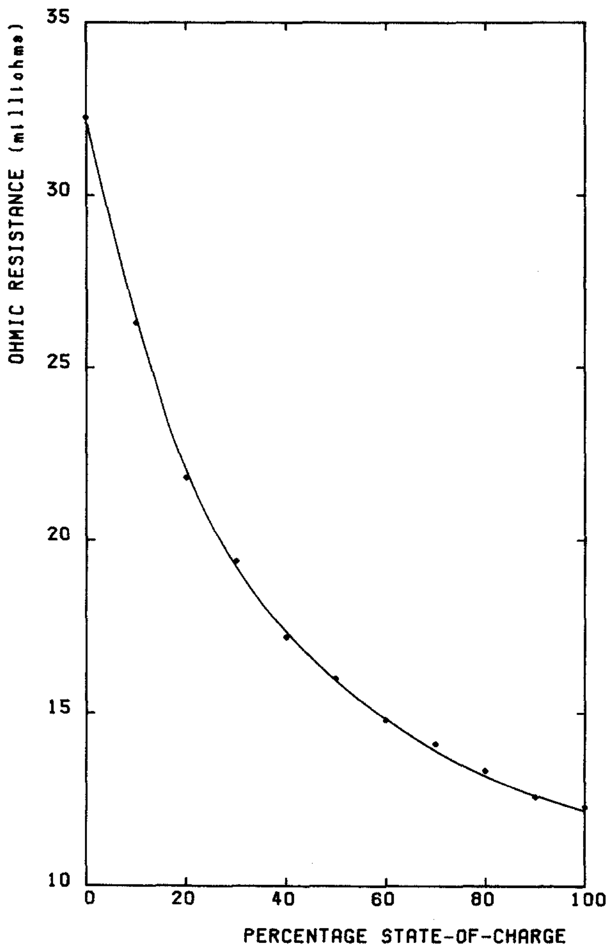


Fig. 9. Change in ohmic resistance of the 6 V 2.6 A h battery with state-of-charge.

The results of impedance measurements on the Sonnenschein and 6 V 100 A h batteries have, as expected, revealed different ohmic resistances. The overall change in ohmic resistance was found to be approximately 0.1 Ω - 0.2 Ω for the Sonnenschein batteries and 1 mΩ - 5 mΩ for the 6 V 100 A h batteries. Both types, however, reveal the same characteristic response to that shown in Fig. 9.

Conclusion

The ohmic resistance of maintenance-free lead–acid batteries, which correlates with the specific gravity of the battery electrolyte, has been found to be an ideal parameter for the prediction of the state-of-charge. The method does not draw current from the battery, and is an ideal technique for flooded batteries where access to the battery is difficult and remote sensing would be more convenient. Work is continuing on this project and a subsequent paper will describe the usefulness of this method when used in a dynamic mode.

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