The prediction of the state-of-charge of some commercial primary cells

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Research carried out at Loughborough during the last five years on the impedance of Leclanché, alkaline Zn–MnO$_2$, alkaline Zn–HgO, Li–CuO, Li–SO$_2$, Li–SOCl$_2$ primary cells is briefly reviewed. The use of alternating current methods for the estimation of the state of charge of the cells is discussed. A search was made for properties of the impedance of each cell system which change in a marked and reliable manner when a prescribed amount of charge is withdrawn from the cell. It is concluded that simple tests based upon an assessment of these properties are adequate for the estimation of the state of charge of some of the systems studied. However, other systems are not so 'well-behaved'. The impedance of each cell changed significantly during discharge and, although making measurements of these changes would enable the state of charge to be estimated, the test techniques required would not necessarily be simple. Using the results obtained on the impedance of the cells, test sets have been constructed which provide a digital presentation of the open-circuit voltage and the state of charge of Leclanché cells (Ever Ready type SP11), mercury cells (Mallory, type RM502R) and lithium cells (Mallory, type L032S and SAFT, type LC01). The electronic techniques employed in these test sets are described in outline with reference in block-schematic diagrams. A proposal is made for the construction of a general-purpose tester for primary cells which would incorporate microprocessors and provide an indication of state of charge based upon data relating to impedance, temperature and discharge history. The tester might also be made self-calibrating for field use.

1. Introduction

The present investigation was initiated by the Ministry of Defence in 1977 in order to improve the then existing methods of primary cell status identification. For a very long time this has been a problem in connection with all electrochemical power sources, primary and secondary; however, with the former the problem appeared to be less convoluted. The reason for this is the primary cell is not subject to cycling 'wear' as are the secondary cells. Thus with secondary cells a 'state-of-health' aspect exists which is absent with primary cells.

The primary cell delivers energy as a consequence of the cell reaction but it starts to deteriorate from the moment that manufacture is complete. This deterioration may be quite significant, as with the ordinary commercially-produced Leclanché cell, or relatively insignificant, as

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observed with well-constructed Li–SiO$_2$ cells. The extent of the deterioration is a complicated function of temperature, possibly humidity and manufacturing technique and must be taken into account in any 'preparedness' assessment of time-stored battery-power electronic hardware.

As a first target it was decided to attempt the development of a device for the estimation of useful energy capacity in a primary cell in the range 100–90% of the fully-charged state. This was to be done using the impedance technique. Initial investigations were made on the commercial Leclanché cell which was chosen because of its popularity. Subsequently, the research was extended to the alkaline zinc–manganese dioxide and alkaline zinc–mercuric oxide aqueous cells. The lithium-based primary cells have also been examined. Lithium–copper oxide, lithium–sulphur dioxide, lithium–thionyl chloride and finally the lithium-thionyl chloride/bromine chloride cell have been studied. Reports on aspects of this work have from time to time been published. In this paper we wish to draw together all the results to date and assess the impedance technique in principle as a charge status indicator.

For the conventional impedance experiment a 3-electrode configuration is usually employed but, in the present experiments, only two-terminal devices are feasible. The inclusion of a third electrode inside the commercial primary cell is always a possibility but the incorporation of a third electrode materially alters the system and, to some extent, defeats the object of the research. On the other hand, a test of the state of charge of a cell, based upon parameters obtained from data on its impedance, would only be satisfactory, reliable and credible if sufficient kinetic interpretation could also be provided to justify the selection of those parameters for the test. In practice, this has meant that we have had to interpret impedance data obtained from the commercial cell in terms of the known cell reactions. For the classical primary cells, the electrochemistry was well established. With the more recently-developed cells the electrochemistry was less certain. In some cases this has resulted in the need to re-examine proposed cell discharge mechanisms and associated processes.

2. Experimental procedure

All the cells examined were available commercially and of sizes and types determined by Ministry of Defence requirements. Experiments were carried out to obtain the real and imaginary parts of the impedance of each cell poised at its rest potential over a range of frequencies from 1 mHz to 10 kHz. The equipment used was a Solartron frequency response analyser and electrochemical interface from which data were obtained for the production of graphical displays and for storage and processing in a PRIME 400 computer.

The impedance data were matched to the most probable electrical circuit analogue using a mathematical technique perfected by us during the last four years. The mathematical technique involves an iterative process in which approximate values of circuit components are first postulated and then improved upon until the best fit is obtained between the locus of the impedance found by experiment (Sluyters plot) and that yielded by the circuit analogue. The experimental data was also derived in the form of Randles plots (real and imaginary parts of the impedance plotted against $\omega^{-1/2}$) and sometimes component values could be found from these. However, the Sluyters was preferred to the Randles type of plot for the purpose of curve fitting.

Our technique differs from the one sometimes used in electrode kinetics of writing all the component kinetic, diffusion, migration and conduction process equations and solving for the impedance via the Laplace technique. For a primary cell, this latter process is too complicated to be solved owing to the large number of indeterminate quantities within the cell and the fact that, with many contemporary primary cell systems, the kinetic processes occurring in the cells have not yet been precisely elucidated. The method used here will, at least, always provide the best available match to the experimental results. Due account has been taken of the currently-available theory for each cell system examined. Where these have proved inadequate, the modifications used have been those considered most likely in the light of the known chemistry.

Each cell was discharged in stages in a pre-scribed manner and the locus of the impedance was obtained at each state of charge. The circuit
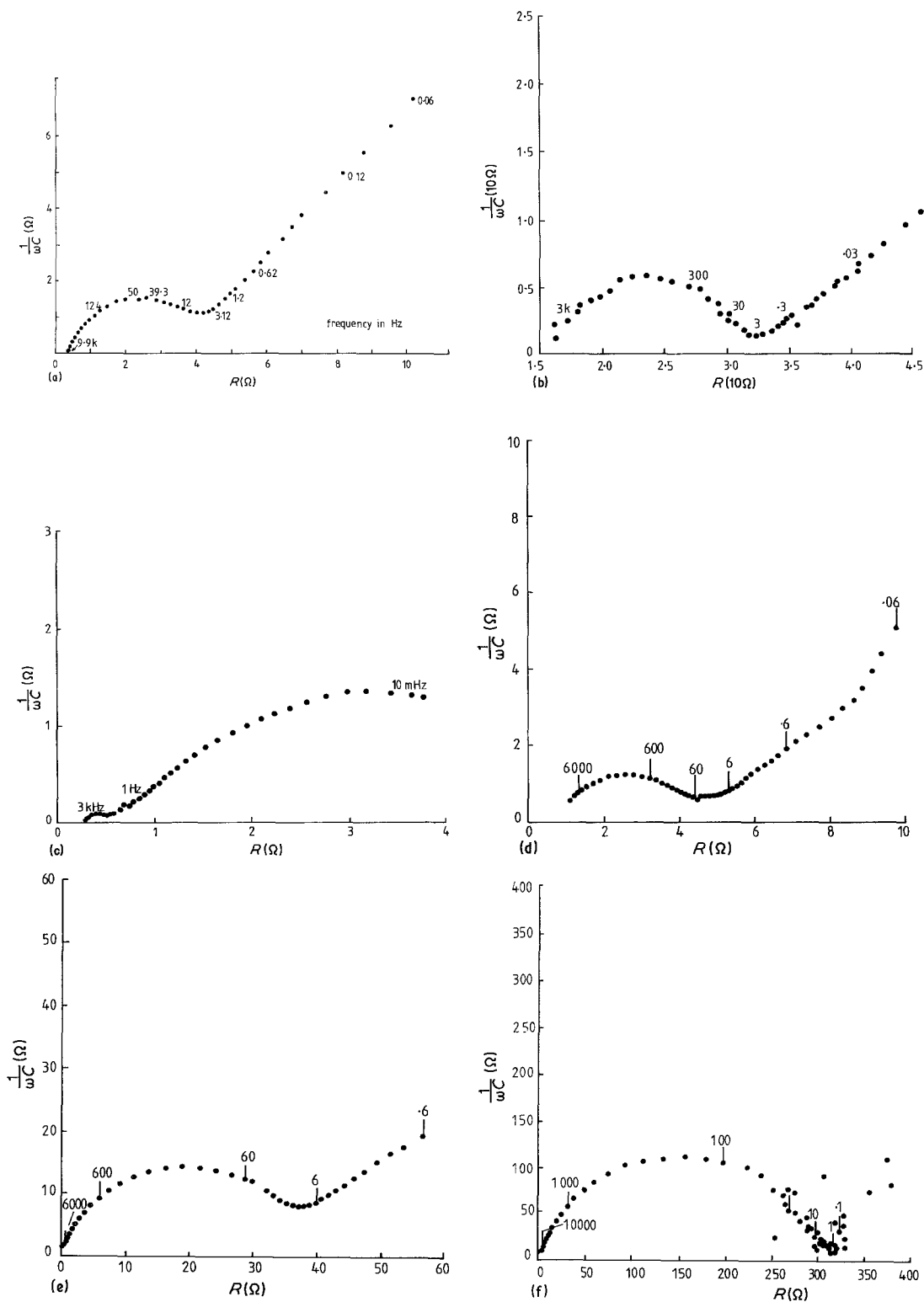
Fig. 1. Complex plane plots at high states-of-charge for some primary cells; (a) Leclanché (SP11, Ever Ready), (b) Alkaline Zn–MnO$_2$ (MN 15O, Duracell), (c) Alkaline Zn–HgO (RM 502R, Mallory Batteries Ltd.), (d) Li–CuO (LC01, SAFT Sogea), (e) Li–SO$_2$ (LO32S, Mallory Batteries Ltd.), (f) Li–SOCl$_2$ (LA30944 LAA-1, G.T.E. Products Ltd.).

analogue proposed for each cell contained some component values which changed more markedly than others due to the discharge. Using the data stored in the computer, a search was made for parameters whose values were reliably and consistently linked with the least scatter of the state of charge of each cell.

3. Discussion of results and parameters suitable for state-of-charge tests

The results of the investigations made to date have been reported [1–10] in detail. Figure 1 shows Sluyters plots for the most common of the 'aqueous' primary cells together with similar data for some lithium non-aqueous primary cells. Here only high states-of-charge have been chosen in order to illustrate the common feature observed in our work so far with primary cells. This is that the locus of the impedance follows a semicircular shape at the higher frequencies and becomes mainly resistive when the highest frequency used is approached (10 kHz). The resistive character observed as the frequency becomes infinite clearly corresponds to the ohmic resistance of the cell electrolyte, electrodes and current conductors. This is due to the fact that the double layer capacitance and the faradaic processes act in parallel and, as the capacitive reactance falls when the frequency is raised, the reactance of the parallel combination as a whole tends to zero. The high-frequency semicircular shape respresents the faradaic process which controls the current in the high frequency range and is generally to be identified with the electrode that forms the negative terminal of the cell, namely the anode. This electrode has a nominally planar configuration whereas the depolarizer (the cathode) is usually of large surface area and may contain carbon as a conducting support (e.g., in the $Li-SO_2$ cell) or as a conductor (e.g., in the Leclanché cell). The depolarizing reaction is quite often the slowest of the two electrode reactions in the kinetic sense; however, the limitation imposed by the anode electrode area is sufficient to provide the major current control at the higher frequencies. The geometry of the semicircle is determined by the electrode area, the electroactive concentrations and the state of roughness of the electrode and might be expected to provide a useful guide to the state-of-charge.

As charge is drawn from the cell, the effective anode area may change and both the concentrations and quantity of electroactive species within the cell are bound to change. The smooth change in the geometry (diameter) of the semicircle which occurs when charge is delivered by the cell is clearly an attractive parameter for examination. We have found that a relatively simple relationship exists in only two cases of the 6 cell types examined, namely the alkaline Zn–HgO cell [5] and the $Li-SO_2$ cell [9].

For the alkaline Zn–HgO cell, the relationship between the diameter of the semicircle, θ, and the discharge, D, expressed as a percentage of full rated capacity, is

$$\theta^{-1} = (8.84 \pm 0.36) - (0.76 \pm 0.04)D. \quad (1)$$

Equation 1 may alternatively be expressed as a difference, M, between the resistances (in ohms) at frequencies of 10 kHz and 31.2 Hz plotted against percentage state of charge, S.

$$S(\%) = 107.3 - 66.6M. \quad (2)$$

Equation 2 yields the straight line relationship shown in Fig. 2.

For the $Li-SO_2$ cell the correspond equations were

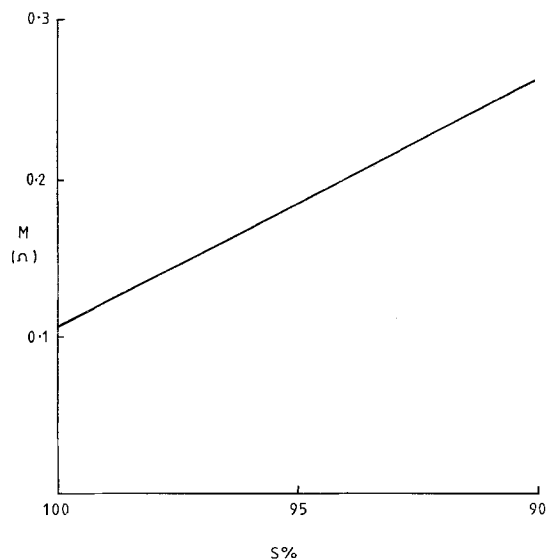$$\theta^{-1} = (0.048 \pm 0.016) + 0.163D \quad (3)$$

Fig. 2. Relationship between the percentage state of charge (S) and the difference in resistance (M) for the alkaline zinc–mercuric oxide cell, type RM502R.

and the design equation for the Mallory L032S cell

$$S(\%) = 82 + 1.47 M' \qquad (4)$$

where M' is the difference in resistance component at the two frequencies 6 Hz and 10 kHz.

It was considered that the use of a subtractive procedure in order to estimate the state-of-charge might be inadequate due to unassessed high resistances (poor contacts, etc.) within the cell. An examination of the high-frequency cell resistance (effectively R_Ω) indicated that a suitable acceptance test for the cell would be that the value of this resistance should be less than a specified upper limit.

With the Leclanché cell it was not found possible to devise a simple method for the isolation of θ due to the way the Warburg line and the semicircle merged at low frequencies. In the range from 100% to 90% of full rated capacity, a numerical examination of the impedance data led to a quite sensitive test for the state-of-charge which has proved to be very satisfactory for the commonly used SP11 (Ever Ready) cell. On the low-frequency side of the semicircle, the in-phase impedance component (R_X) contains contributions from double-layer, charge-transfer and infinite-frequency cell resistance (R_Ω). It was found that, at the frequency corresponding to this point (31.2 Hz), R_X was a linear function of the percenta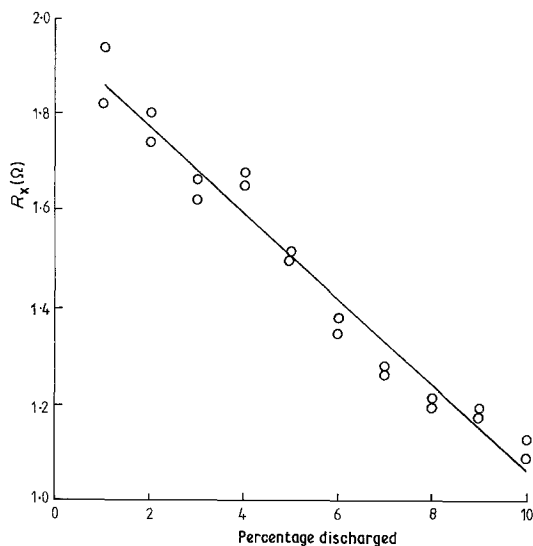ge state of charge, with a conclation coefficient approaching unity, and fell from a value of about 2 Ω at 100% to 1 Ω at 90%, as shown in Fig. 3. This R_X parameter turned out to be the best and most readily assessed state-of-charge indicator [3]. (The use of R_X clearly obviates the need for a cell conductivity test since R_X contains R_Ω.) State-of-charge indicators employing this principle have been working satisfactorily with MoD testing programmes during the preceeding 2 years and to date three generations of Leclanché testers have been built. Recently a tester for mercury cells was also delivered to MoD for routine test purposes. Another tester for lithium Li–SO$_2$ cells has recently been constructed and is working satisfactorily. A tester for LiCuO cells is now being made.

4. The design of a satisfactory state-of-charge meter

The basic principles for a state-of-charge indicator that we have used are set out as follows:

(i) Cell holder; this is accurately made with minimum tolerances, defines the geometric size of the cell and ensures that cell polarity is correct.

(ii) Open circuit voltage test; this ensures that the unit is an electrolytic cell of approximately correct potential range, this voltage is displayed.

(iii) High frequency resistance test; this ensures that the conductivity of the cell is sufficiently low for the cell manufacture to have been satisfactory.

(iv) Prescribed frequency test; this provides sufficient data to characterize the charge-transfer semicircle geometry and hence the state-of-charge; alternatively the test (iii) is not used and the state-of-charge parameter determination implies a suitable check of the cell manufacture.

(v) Setting-up procedure; this enables the calibration of the indicator to be carried out so that its proper working and accuracy are maintained. Access to appropriate controls must be provided.

All the above features have been incorporated into the design of the battery testers constructed in the Department of Electronic and Electrical Engineering at Loughborough University of Technology. The full circuit diagrams and descriptions of their manner of working have been given and described in reports submitted to MoD. However, the basic principles of operation may be

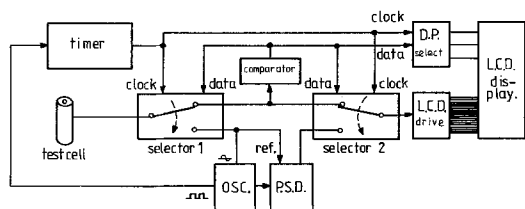Fig. 3. R_X parameter against percentage discharge at 31.2 Hz for the cell, type SP11.

Fig. 4. Block schematic diagram of circuits for the Leclanché cell tester.

outlined with reference to the block schematic diagrams given in Figs. 4 and 5 for the circuits contained in the Leclanché and zinc–mercuric oxide battery testers, respectively.

Photographs of the Leclanché tester are given in Fig. 6. On insertion of a battery (type Ever Ready SP11) into the specially-shaped recess, a microswitch is closed and the circuit is activated. The liquid crystal display first indicates the open-circuit voltage of the cell and, if this voltage is less than a prescribed minimum value, an arrow flashes to recommend rejection of the cell. However, if the voltage is satisfactorily large, its value is presented on the display for three seconds to enable it to be manually recorded. After the three seconds pause, the circuit automatically proceeds to pass a very small test current of accurately controlled size at a frequency of 31.2 Hz through the cell. The resistance of the cell is measured and compared by electronic means with the value given on the curve shown in Fig. 3. The percentage state of charge is then presented on the display. In order to carry out these functions, the processes indicated in the diagram shown in Fig. 4 are performed. The essential part in the open-circuit

voltage measurement is an internal reference voltage provided by a semiconductor. The voltage of the cell is switched by a timer to a comparator which is also connected to the internal reference. After a suitable delay, during which the voltage of the cell may be recorded, the timer switches an oscillator signal current into the battery and the voltage across the cell is resolved into in-phase and out-of-phase components by a phase-sensitive detector (psd). Since the resistance of the cell but not its reactance is involved in this test, only the in-phase component is required. This component is smoothed and has a voltage of accurately stabilized magnitude subtracted from it. The difference of the two signals actuates the drive to the display. The oscillator is also used to obtain the necessary timing signals. The tester is battery operated and portable and the batteries used for the power supply may be either the same as those being tested or of the nickel-cadmium re-chargeable type.

The basic principles of operation employed in the testers for mercury and lithium batteries are the same as for the Leclanché tester with respect to the measurement of open-circuit voltage by comparison with an internal reference and for the measurement of resistance using phase-sensitive detectors. In addition, however, the resistance (R_Ω) of a cell is measured at 10 kHz and, if this resistance is larger than a prescribed maximum, an indicator flashes to recommend rejection of the cell. A perusal of Equations 1 and 2 and the curve in Fig. 2 indicates that the difference of resistances at two frequencies has to be measured and, as regards the mercury cell, this difference is rather
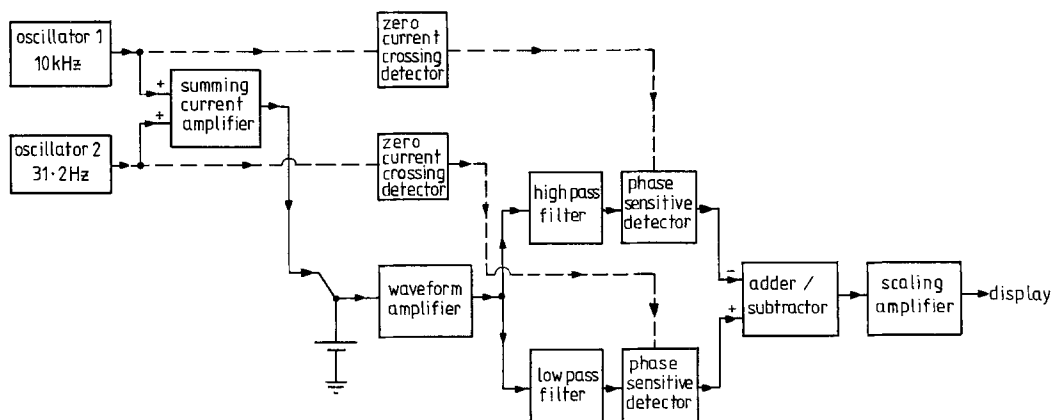

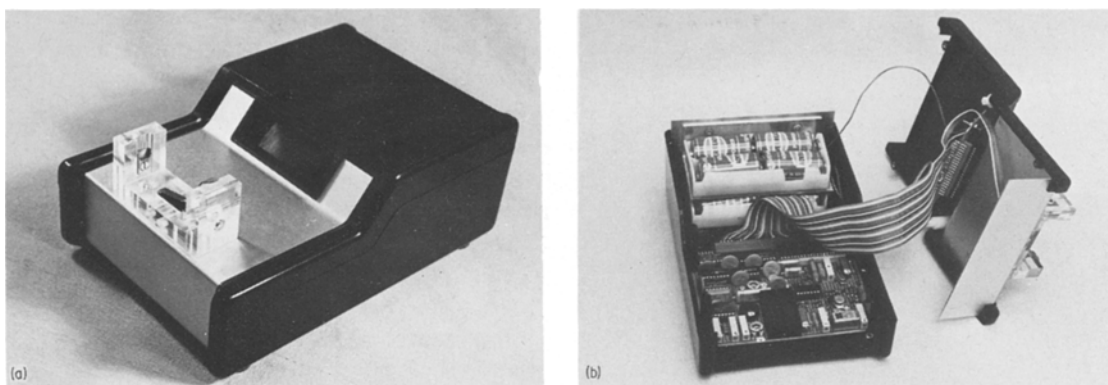Fig. 5. Block schematic diagram of circuits for the mercury cell tester.

Fig. 6. Photographs of Leclanché cell tester.

small (0.1 to 0.3 Ω). Since the test current which may be passed through the cell is restricted to a small value so that the electrochemistry is not disturbed, the test signal which has to be processed is also small. The circuitry devised for the mercury cell tester is therefore superior in sensitivity to that of the Leclanché tester. As depicted in Fig. 5, two oscillators are employed and a current from each is switched in turn through the battery. The voltage across the battery is amplified and sorted by filters before being passed to the appropriate psd. The outputs from one psd is subtracted from that of the other and scaled to obtain a voltage, proportional to the quantity, M, as shown in Fig. 2, suitable for application to the display. Photographs of the mercury cell tester are shown in Fig. 7.

The testers which perform at two frequencies contain oscillators of the quadrature type so that signals are available for making an assessment of

both the reactance and the resistance of a battery, should this be required. In fact, since the reactance of the Leclanché and mercury cells is much less than the resistance at each test frequency, it would be possible to make very simple testers for these cells which measure the magnitude of the impedance at each frequency so that resolution into quadrature components is rendered unnecessary: the accuracy of such a tester would, however, be less than that provided by the testers we have built which also contain circuitry of a more versatile capability.

So far, a separate battery tester has been made for each type of battery but a general-purpose tester of compact form could be made which would incorporate microprocessors. In addition to carrying out the functions described above for the presentation of open-circuit voltage and the results of an assessment according to a one- or two-frequency test, it would be possible to take
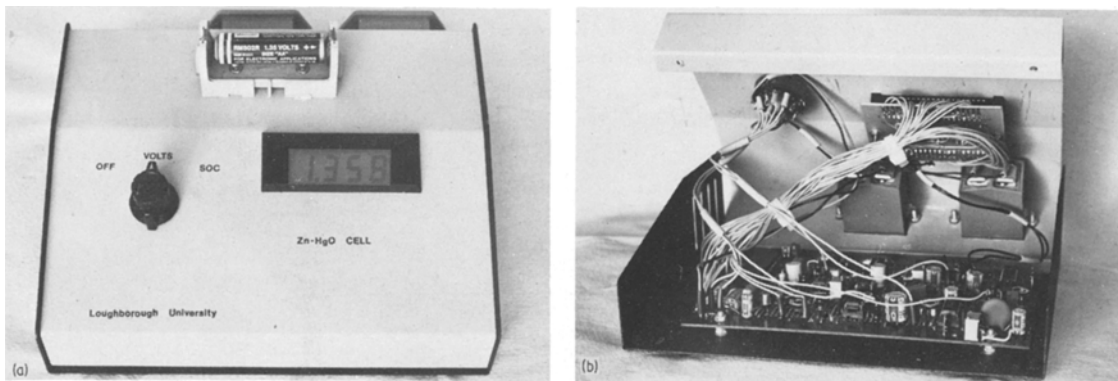

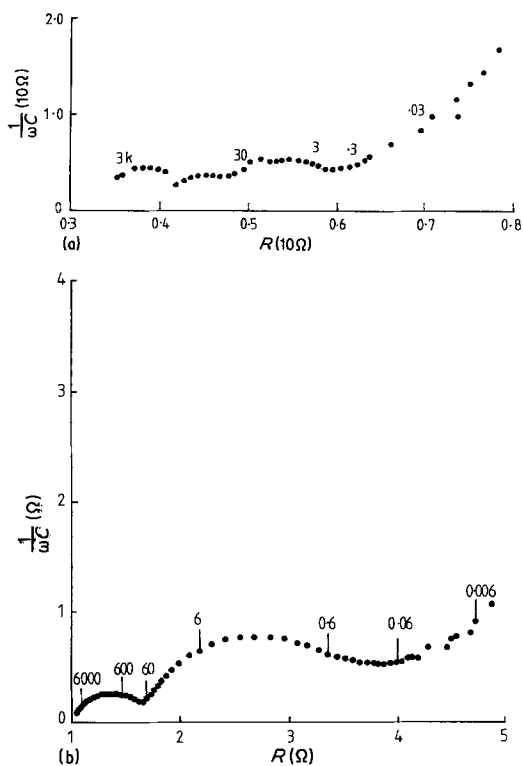Fig. 7. Photographs of mercury cell tester.

Fig. 8. Complex plane plots for partially discharge cells: (a) alkaline $Zn-MnO_2$ (MN 1500 — Duracell) with 50% of its rated capacity remaining, (b) Li–CuO (LC01 — SAFT Sogea) with 70% of its rated capacity remaining.

into account by electronic means data concerning temperature, storage and discharge history. Also, where necessary, more elaborate test signals might be applied to the battery, as discussed in the next section.

5. Cases where the simple test was inadequate

The alkaline zinc–manganese dioxide cell [4, 7, 11] and the lithium–copper oxide cell [10] have both proved to be very difficult systems for state-of-charge estimation. Figure 8 shows the impedance plots for cells of these types after some charge has been removed. The salient point to notice here is that the simple picture of the Randles-type behaviour (modified by porosity) is complicated by other effects. These are mainly due to the cathode. We have discussed the theoretical frequency response of two terminal cells in which both electrodes exert comparable current control [6]. Comparison of the theoretical and actual

complex plane plots together with a computer match of the impedance data has yielded sufficient kinetic information to show convincingly that our interpretations are the correct ones [7, 12]. However, when both electrodes make significant contributions to the total impedance of the cell, complications result which prevent a simple and reliable assessment being made of the state of charge based on properties of the first high-frequency semicircle. We have made repeated efforts to discover a relatively simple a.c. test by analysing, with the aid of a computer, the numerical test data at various states-of-charge over the whole of the frequency range. Although the impedance shapes have been satisfactorily interpreted in terms of processes generally accepted for primary cell systems, the accuracy with which the changes in the impedance occurred did not enable a very precise estimate of the state-of-charge to be made. It follows that a test based upon an assessment over a range of frequencies would be more accurate. A test signal of any shape and frequency composition may be stored electronically in the battery test equipment and applied to the cell. The component parts of this signal would be those which have been found by computer analysis of the impedance data to provide the most sensitive and reliable indications of the state of charge. It would be possible to apply a signal to the cell for a short time comprising a random selection of components in a particular frequency range and to determine the state of charge of the cell using correlation techniques. This would be an interesting development for the future. It can be concluded that state-of-charge tests are entirely feasible with the more complicated battery systems but not on the basis of simple one- or two-frequency measurements. However, simple test conditions may be specified which will guarantee that a cell is at least 90% fully charged, e.g., for the alkaline $Zn-MnO_2$ (MN 1500) cell these conditions are that the resistance of the cell at a frequency of 0.5 Hz should not exceed 0.30 Ω with an open-circuit voltage of at least 1.48 V. This type of test would be used when making a go/ no-go selection of stored $Zn-MnO_2$ cells.

6. Open-circuit variations of impedance

For the extraction of electrochemical kinetic

constants, it is customary to design an experiment so that mass transport problems are eliminated or, at least, simplified. For the case of commercial primary cells, especially those for which a storage requirement exists, cell deign is often arranged so that the establishment of conditions uncomplicated by mass transport are precluded. Some form of separator is always placed between anode and cathode, electrolyte solution is frequently contained within a static phase, restricted circulation of the solution is always a feature. The total resultant effect is to produce a pronounced time delay between the end of a discharge and the establishment of equilibrium on open circuit.

The three 'aqueous' primary cells became stable in an experimentally reasonable time. When there was a gap of 24 hours between the end of a period of discharge and the commencement of the gathering of impedance data, any errors introduced into the data due to instability became negligible. Of the three cells, the alkaline zinc–MnO_2 cell was the most readily stabilized unit (which confirms that the difficulty in identifying a state-of-charge test with the alkaline Zn–MnO_2 cell was not due to an insufficient stabilization time).

Much greater problems were encountered due to instability in the non-aqueous cells. This was particularly true of the Li–CuO cells which posed unsurmountable difficulties in the establishment of reliably stabilized impedance values for each state-of-charge. The impedance changed markedly as soon as any charge was withdrawn and thereafter changed continuously for as long as consecutive readings were taken. Even after 1 month, the impedance was still slowly changing. We must emphasize that the impedance of this cell was very temperature-sensitive and the ambient changes in temperature occurring over a 24 h period can materially affect the impedance. It would be preferable to enclose these cells in a small electronically-controlled temperature-stabilized enclosure fixed close to the terminals of the frequency-response analyser and, also, to store the cells at a known constant temperature between tests. The Li–SO_2 and Li–$SOCl_2$ cells were both much more satisfactory for experiment. We have found [9] that, for the Li–SO_2, equilibrium was established very rapidly after a discharge. Successive experimental determinations of cell impe-

dance immediately following a discharge yielded corresponding results which over the whole frequency range were within 1%. The Li–$SOCl_2$ cell [13] gave satisfactorily replicable results within an hour or so of a discharge being completed. In any case, for both these cells a settling-down period of 6 h after a discharge was sufficient to ensure that equilibrium was established.

In practical terms, as far as the present programme is concerned, this time dependence is not important (provided that time-stable results can be obtained under reasonable experimental conditions so that 'time infinity' data can be procured) since the aim is to specify a satisfactory test for a cell taken from store. However, in ideal circumstances, a test would indicate how much charge remains in a primary cell which is actually being discharged. Although this is a much more severe requirement, satisfactory appropriate test methods could be prescribed for certain cells but the alkaline Zn–MnO_2 and the Li–CuO cells present problems which appear to be insurmountable.

7. Conclusions

1. Certain cells are amenable to the formulation of a state-of-charge test which monitors the high states (down to ~ 90%). These include the Leclanché, the alkaline Zn–HgO and the Li–SO_2 cells.

2. State-of-charge tests for other cells can be formulated but those will be more complex than the simple one- or two-frequency tests.

3. The alkaline Zn–MnO_2 cell has a complex impedance locus which arises from the relatively equal contributions of each electrode to the cell impedance.

4. The Li–CuO cell has a very long time-stabilization requirement after discharge before equilibrium within the system is re-established.

Acknowledgement

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