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# Test cells for the investigation of battery reactions at high internal pressures

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## Abstract

Beginning with a construction based on a C-size (LR-14) battery container ('can'), encased in a strong PMMA-support and fitted with a removable cell top equipped with a manometer and a gas-outlet valve, a second and, finally, a more refined third generation cell was developed. The final (3rd generation) design provides additional options for experimental work. For example, the system can be flushed with inert gas; a regulating gas-flow valve has been fitted to feed precisely a gas chromatograph with the gaseous reaction products and a reference electrode to measure anode and cathode potentials individually has also been incorporated. Since AA cells (LR-6) are the dominant monocell battery size, test cells of the second generation were fitted with an adapter to accomodate either a C- or an AA-size. However, the most recent system was designed exclusively for AA-sized cans. The different cell designs are described and examples of their practical application (e.g., overcharge experiments) are given.

## 1. Introduction

Many battery reactions have side-reactions evolving gases as minor by-products. However, undesirable irregular battery reactions, occurring upon overcharging and overdischarging (cell reversal), produce gases as the major outcome [1]. Thus the development of a suitable test-unit, based on a standard cell container (stamped steel) supported by a hollow PMMA-cylinder and equipped with a regular anode and cathode as well as being fitted with an alternative top closure supplied with (at least) a manometer and a gas valve (tap), is desirable [2].

One major objective is the determination of the shelf-life of batteries at different discharge levels (DOD) by recording the time-dependent pressure rise inside the cells due to the evolution of hydrogen from the slowly corroding zinc anode. The suitability of the home-made pressure cells employed for the measurement of the variables described above soon led to the adaptation of these cells for additional purposes. With respect to these and other experimental applications, a number of modifications were found to be useful and/or necessary leading to the development of a second and third generation of cells realized in cooperation with a professional high-precision mechanical workshop [3].

## 2. Experimental details

### 2.1. *Construction of first generation C-size pressure cells*

Four C-size pressure cells were constructed using polymethylmethacrylate (PMMA). Each cell was made up of two main parts, namely the upper cap and the lower case. A cross sectional view of these is shown in Figure 1 (detailed drawings in [1, 2, 4]).

At the centre of the upper cap a specially designed brass current collector was fitted. This had, as shown in Figure 1, a lower end consisting of a C-size 'nail' current collector which was hot welded using tin solder to the middle section (extension). The middle section serving as anode current collector was threaded and fitted into the threaded hole made through the centre of the cap. All fittings, that is the current collector, manometer and tap, were screwed into position after initially wrapping PTFE-tape around each threaded part in order to ensure a firm and gas tight fitting. Due to the lack of

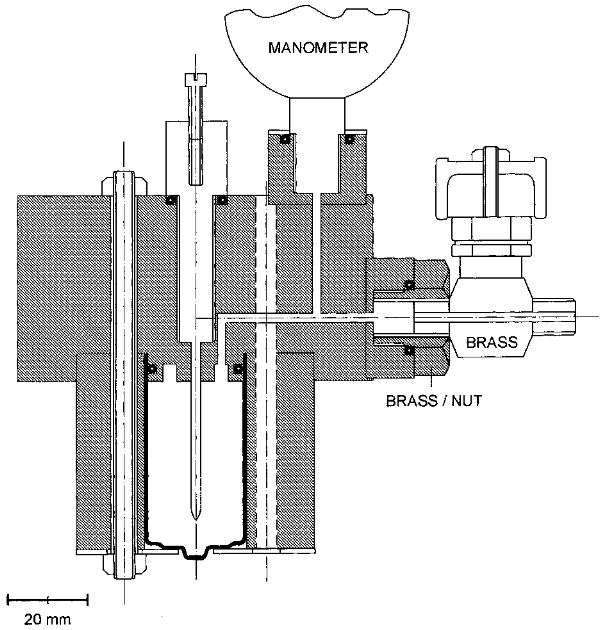

*Fig. 1.* Cross-sectional view of the original C-size pressure cell.

precision in fabrication, hot-melt glue and epoxy resin had to be used in the final stage in order to make the cells useable. Consequently, the manometer and tap could no longer be removed or exchanged.

The lower case housed the C-size cell container. At the bottom of the upper cap of the 'cell house' a seat for an O-ring which fitted into the standard C-size steel container was made. This provided the gas-tight connection of both parts. When the cell was assembled, the brass current collector rested in the centre of the anode mass filling the hole inside the staple of cathode rings. These were held in position by the steel can in the same way as in conventional cells. Cathode pellets and anode mass were separated by a laminated double-layer separator. The positive end was provided by the bottom of the steel can. All assembled cells were tested for pressure stability by filling with hydrogen up to a pressure of 15 bar and monitoring pressure for 24 h.

### 2.1.1. *Effect of depth of discharge on shelf life*

One of the discharge byproducts of the zinc anode is cathodic hydrogen gas. The quantity of hydrogen produced is, therefore, directly related to the extent of self-discharge of an unused cell. Subsequently, this determines the shelf-life of the cell. In a series of tests, the pressure build-up of test cells as a result of self-discharge has been used to determine shelf-life.

Reports on the shelf-life of batteries usually refer to batteries which have not been discharged after production. There have been no reports on how the depth of discharge of these batteries may affect their shelf-life. Part of the work reported here has been devoted to determine this relationship (see Figure 2 displaying data reported in [2]).

Additional tests have been conducted on mercury-free zinc cells as a standard for similar experiments carried out on mercury-free zinc cells which contain other doped inhibitors of an inorganic nature.

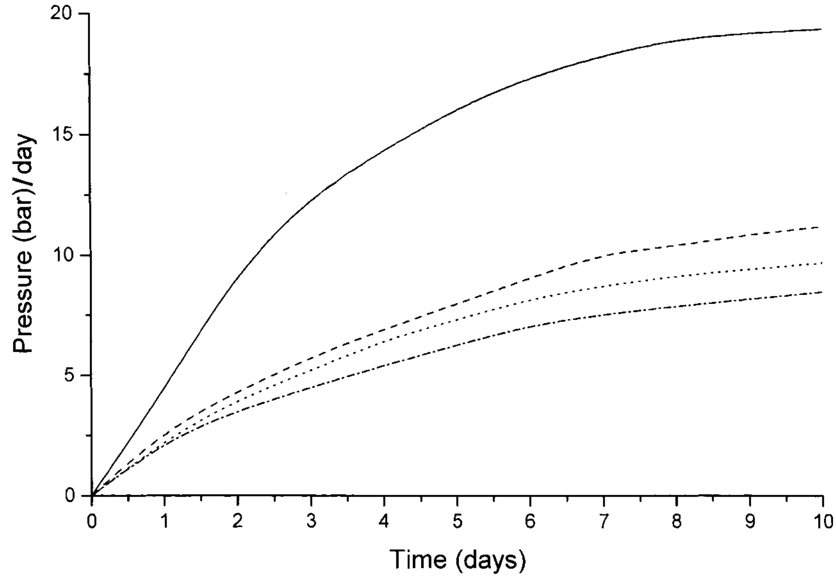

*Fig. 2.* Correlation between hydrogen evolution by anode corrosion and depth of discharge. DOD: (——)0%, (– – – –) 25% , (- - - - -) 50% and (–·–·–·–) 75%.

### 2.1.2. *Cell pressure control upon overcharging*

One of the major problems encountered with the use of the secondary alkaline $MnO_2$/Zn cell is how to recombine the hydrogen and oxygen produced during cell use. Hydrogen is the gaseous byproduct of the discharge reaction while oxygen is that of the charge reaction. Without adequate means of controlling gas build-up, cell pressure can reach catastrophic levels with cycling and this can give rise to cell leakage, closing failure and, in the worst case, explosion. With the recommended voltage controlled taper current charge method, 1.72 V is set as the upper voltage limit. This limit is suitable because oxygen evolution starts with the cathode normally at a voltage value of about 1.75 V, producing soluble manganates which cause capacity loss and corrosion problems [5]. When charging continues, the voltage increases slowly to 1.90 V, and even higher, which also gives rise to hydrogen gas evolution at the anode.

To guard against cell abuse, attempts have been made over the years to sufficiently curb the pressure build-up in the cell during each charge/discharge cycle. Prominent among these attempts are utilisation of fibrous nonwoven separators instead of gas impermeable membranes. This was with the aim of promoting oxygen permeability to the anode for reaction with the zinc. This approach has the disadvantage that dendrite penetration cannot be prevented and short circuits may occur.

Other attempts include substituting an ionic cycle for the oxygen gas phase recombination cycle [6]. This is feasible if a halogen salt having a low decomposition voltage, for example KI and KBr, is added to the electrolyte. The principle behind this method is that instead of oxygen gas being evolved, molecular iodine or bromine is produced. This dissolves and migrates through the separator in the form of an oxyhalogen compound.

Recently, the problem has been considered differently. Specifically, catalysts have been incorporated to promote oxygen evolution in the cathode mass and fuel cell-type oxygen reduction auxiliary electrodes have been employed. Cobalt oxide ($Co_3O_4$), nickel oxide ($Ni_2O_3$) and vanadium pentoxide ($V_2O_5$) have been used as oxygen evolving catalysts [7]. These are meant to promote oxygen evolution and thereby prevent oxidation of the $MnO_2$ electrode to soluble manganates upon overcharging. These manganates subsequently undergo disproportionation to Mn(IV) and Mn(II). The Mn(II) cannot be re-oxidized to Mn(IV) under battery conditions, as previously mentioned [1], and is, therefore, inactive which leads to a loss of cathode material.

These catalysts were incorporated into the cathode mass. At the same time, a fuel cell type auxiliary oxygen reduction electrode was employed to reduce the molecular oxygen which facilitates the chemical reaction. The disc shaped auxiliary electrode was spot welded to the anode current collector; its surface was exposed to the anode but direct contact was avoided because this promotes zinc corrosion.

Another method of consuming the evolved oxygen by chemical reaction is the oxidation of highly dispersed metallic zinc in the anode gel (Figure 3) [1]. In this case, hydrogen evolution must be prevented and this is achieved by having zinc oxide in reserve in the anode.

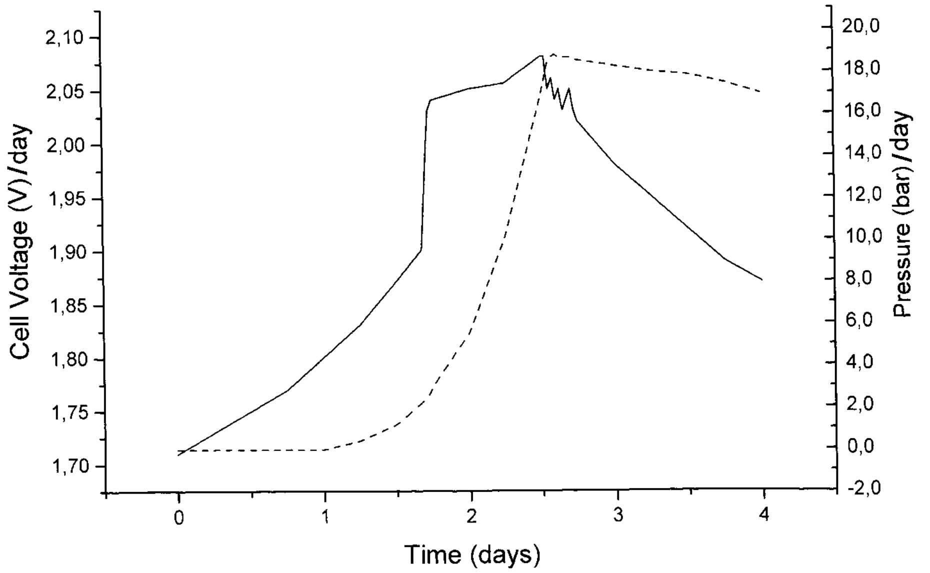

*Fig. 3.* Cell voltage and internal pressure as functions of galvanostatic overcharge. ($I = 25$ mA). Key: (- - - -) pressure and (——) cell voltage.

To allow close contact of the oxygen evolved at the cathode with the finely dispersed metallic zinc present in the anode compartment, the cell construction had to be modified by equipping it with a central rod made of a spongy polymer material which allows oxygen to penetrate to the bottom of the test cell [8].

### 2.1.3. *Investigating the hydrogen absorption of gas absorbing alloys*

The advent of hydrogen storage alloys, which reversibly absorb and desorb hydrogen, has opened the way to numerous research applications. A 'C-size' cell was 100% discharged under galvanostatic conditions with a current of 100 mA. The separator basket with the discharged zinc anode gel was discarded. A new separator basket was inserted into the discharged cathode, soaked with 9 M KOH and filled with KOH gel which contained starch (Farinex 267), $\alpha$-Cellulose, and 9 M KOH.

Except for the standard cell in which no alloy was incorporated, 1 g of each alloy (in a hydrogen-free state) was introduced above the respective cathode surface which was then covered with a PVC ring. During overloading the anode, the brass current collector nail was observed to corrode and decrease in size. Consequently, this problem was overcome when the nail was tin plated. The cell was discharged under galvanostatic conditions of 50 mA for six hours. Cell pressure was monitored at intervals of 30 min for 6 h. With reference to Table 1 [9], all alloys caused a reduction in cell pressure. Over the test period the most significant reduction in cell pressure was shown with the alloy $Ti_2Ni$ (6.6 bar).

### 2.2. *Refined cell construction*

Some severe drawbacks were recognized in the course of working with the first generation cells. These were equipped with a 40 bar-range manometer which was found to be too insensitive for most measurements. The relatively crude construction did not allow the exchange of either the manometer nor the gas valve (tap). Another problem was the difficult assembly procedure tightening two nuts per bolt using the appropriate spanners and applying almost the same torque.

*Table 1.*

| Experiment | Alloy composition | Pressure/bar |
|---|---|---|
| 1 | Standard/no alloy | 12.9 |
| 2 | $Ti_2NiFe$ | 10.5 |
| 3 | Ti(76)Ni(21) | 10.4 |
| 4 | $Zr_{0.95}Ti_{0.05}Ni$ | 9.5 |
| 5 | TiNi | 8.1 |
| 6 | $Zr_{0.85}Ti_{0.15}Ni_{0.85}Fe_{0.15}$ | 7.9 |
| 7 | $Zr_{0.8}Ti_{0.2}Ni$ | 7.8 |
| 8 | $Ti_2Ni$ | 6.6 |

To allow manometers and valves to be exchanged, the cell construction had to be refined and the manufacturing tolerances significantly improved. The applied O-rings had to provide perfect gas-tightness without the use of additional sealant. The method of cell assembly was simplified by replacing the four steel bolts and all the nuts by a U-shaped steel clamp swivelling around two bolts fixed at the top of the cell. After adjusting the bottom part of the cell which contained the steel can with the active materials, the clamp was brought in vertical position and could then be fixed by turning a single screw into a seat without the use of a tool. A new device (spring + jack) which served to contact the steel can and to act as the positive terminal was installed in this cell version.

In addition to these modifications, the simple gas tap was replaced by a high-precision gas-flow valve which could feed a gas chromatograph with the emitted gaseous reaction products. Thus, the second generation (Figure 4) of pressure test cells was complete.

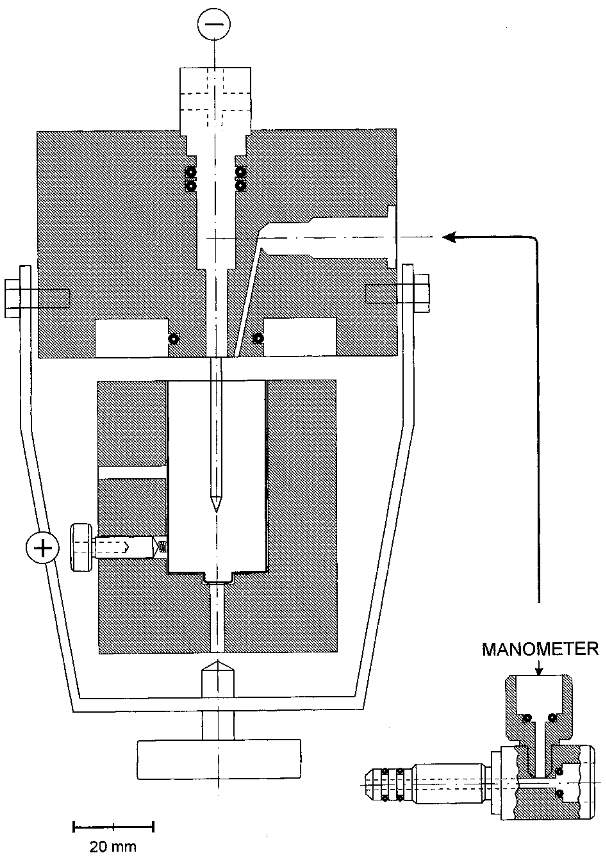

*Fig. 4.* Cross-sectional view of the refined C-size pressure cell.

### 2.2.1. *Corrosion of zinc in contact with other metals*

When the first two pressure cells of the new design were available, corrosion tests of zinc powder for battery anodes were performed in order to study the tolerability of other metals present as either current collector materials or conductive fillers. An initial screening program to find the possible metal candidates was carried out by mixing zinc powder with 5% w/w of the respective powdered metal (alloy) and covering this mixture with a 10 M KOH solution [10]. The pressure caused by the evolving hydrogen (at 45 °C) was monitored by using a manometer with a 250 mbar full-range scale. The most promising mixtures (minimal $H_2$-evolution) were subsequently tested as galvanically deposited layers in direct contact with the other metal: (a) using zinc foil as the substrate and depositing the metal (alloy) on it (Figure 5); (b) using the metal (alloy) as the substrate and depositing zinc on it (Figure 6). Combinations of each type (9 cm$^2$ surface) were exposed to 10 M KOH as before (at 45 °C).

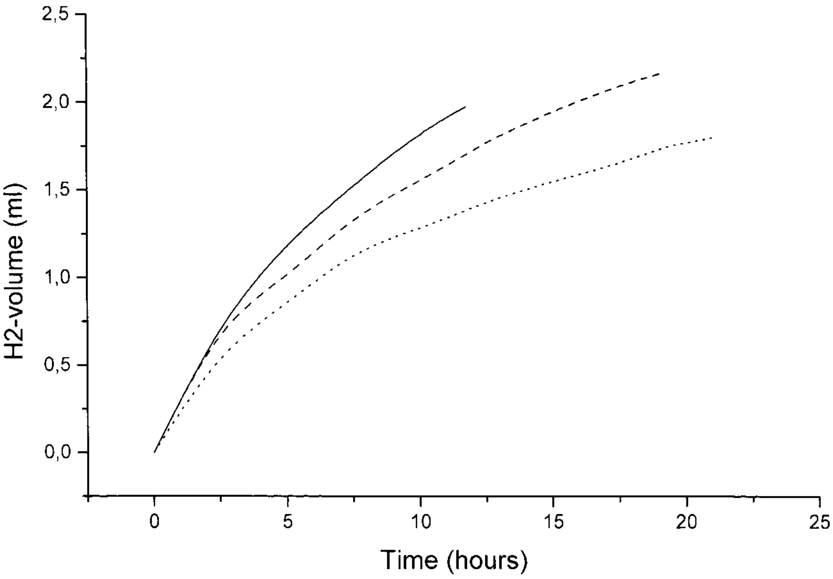

*Fig. 5.* Corrosion of pure zinc foil and zinc foils covered with tin or tin–zinc alloy in 9 M KOH. Key: (– – – –) Zn, (------) Sn–Zn and (——) Sn.

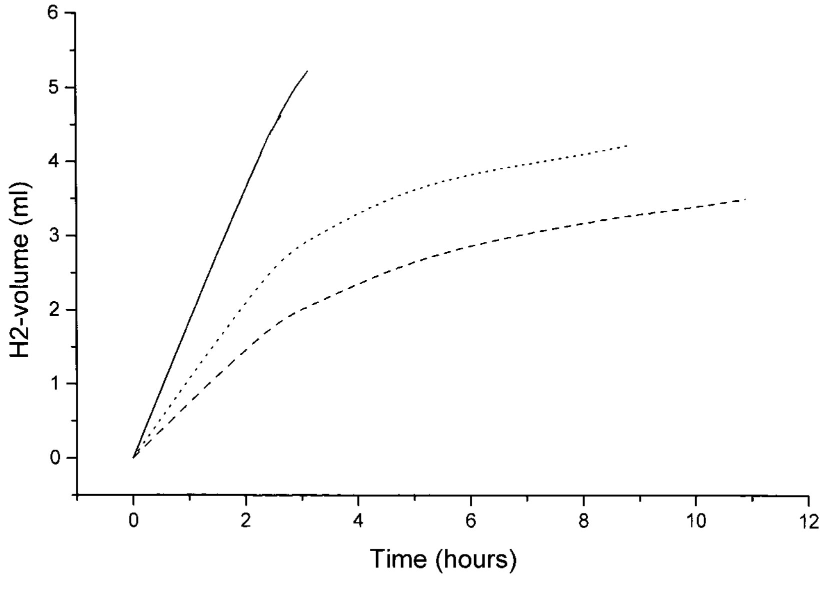

*Fig. 6.* Corrosion of zinc-plated foils of tin and tin alloys in 9 M KOH. Key: (——) Co–Sn, (– – – –) Zn–Sn and (------) Sn.

Since these preliminary corrosion tests did not employ electrochemical reactions, the pressure cells were modified in two ways:

(i) the central brass rod bearing the anode-contact 'nail' was replaced by a shorter one (without 'nail').
(ii) The applied C-size cell containers were equipped with an inner plastic beaker which would be filled with powdered metal samples and KOH, thereby preventing contact with the steel surroundings.

Finally, not only the resistance against chemical attack of KOH, but also the influence of the 'foreign' metals (alloys) on cell parameters, open circuit voltage, short circuit current, cathode reactions, and capacity, was investigated. To obtain this information complete cells were built and encapsulated in the pressure device and cycling experiments were run. The metal (alloy) to be inspected was present as a galvanically deposited layer on the brass foil which served as a large-area current collector [11, 12].

### 2.2.2. *Determination of cell reactions by GC-analysis*

Although in most cases the chemical nature of the gaseous reaction products for a certain battery operation can be assumed, it is not always clear what happens inside a working cell. If the storage capacities of the anodic and cathodic active masses in a battery are of the same size the battery (cell) is regarded to be 'balanced'. In this case anodic and cathodic overcharge reactions will start at the same time. If the active mass on either side (anode or cathode) exceeds that of the other electrode (and this may occur even accidentially!) one overcharge reaction starts earlier. Now, if this happens,a simple pressure measurement and calculation of the evolved gas volume is not sufficient. The composition of the gas (especially the ratio $H_2$ to $O_2$) collected inside the pressure cell has to be measured.

The pressure cells had were equipped with precisely regulating gas-flow valves in order to allow a controlled supply of gas to the sample loop of the gas chromatograph (GC). Calibration was carried out for $H_2$, $O_2$ and CO (product of carbon oxidation at higher positive potentials). Soon it became clear that gas analysis was a very useful tool to study cell reactions upon charging, overcharging, discharging and at resting periods (Figure 7) [13].

Due to the increasing importance of AA-size cells, an adapter was designed to apply the pressure cells for either C- or AA-sized batteries.

### 2.3. *Final cell construction*

The ultimate pressure cell was exclusively designed for the use of AA-size batteries. The most important changes were: (a) a new cell top bearing two gas valves

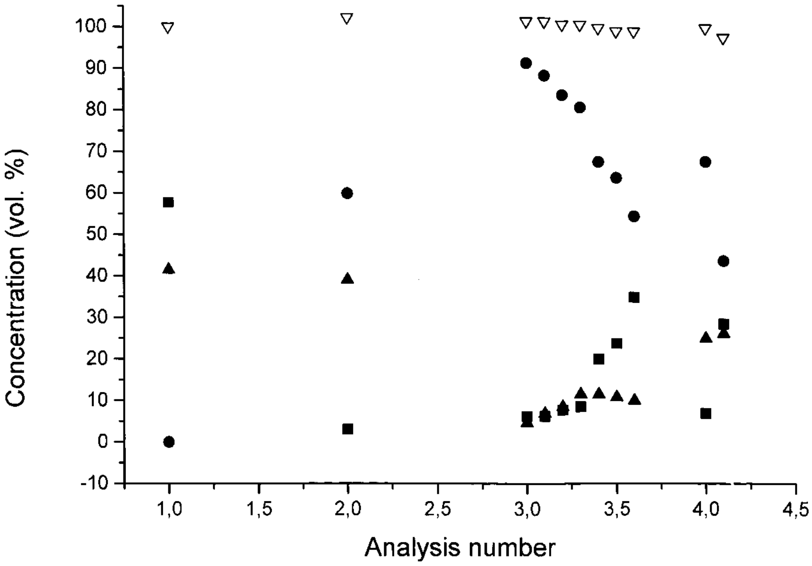

*Fig. 7.* Analyses of the gaseous reaction products at different states of cell operation.
1,0: Gas composition after cell (C-size) storage over 64 h at room temperature;
2,0: Gas composition after overcharging with 75 mA until 1.25 bar internal pressure; composition change reflects oxygen evolution from the cathode;
3,0–3,6: Continued overcharging with 150 to 300 mA upto 9.7 bar; hydrogen evolution starts after complete reduction of reserve ZnO in the anode; seven gas samples taken at intervals of 30 min;
4,0–4,1: Repeated overcharging with 150 mA upto 2.6 bar; two samples (30 min time interval).
Key: (■) hydrogen, (●) oxygen, (▲) nitrogen and (▽) total.

for inert gas replacement of air before the onset of the experiment. This was found to be very useful when the amount of oxygen had to be determined; and (b) the central contact rod for the anode was made from a thin brass tube instead of the usual solid ‘nail’. At the end of this current collector, insulated against the tube by a small polymer ring, a reference electrode disc of the same diameter was attached. The electrical contact to the reference electrode was provided by a thin insulated wire placed inside the hollow current collector which lead to a contact screw in the left gas-valve adapter (Figure 8).

Materials for the reference electrode were zinc and silver. Both were found to be suitable to record anode and cathode potentials separately. The exact starting time of particular anodic and cathodic reactions could be determined by the characteristic deviations in the corresponding electrode potentials [13]. The bottom part of the pressure cell consisted of two separate pieces because this was easier to manufacture. The empty drillhole in the cylindrical part of the pressure cell was intended to accomodate the tip of a temperature sensor (touching the steel can) in order to monitor heat generation or consumption.

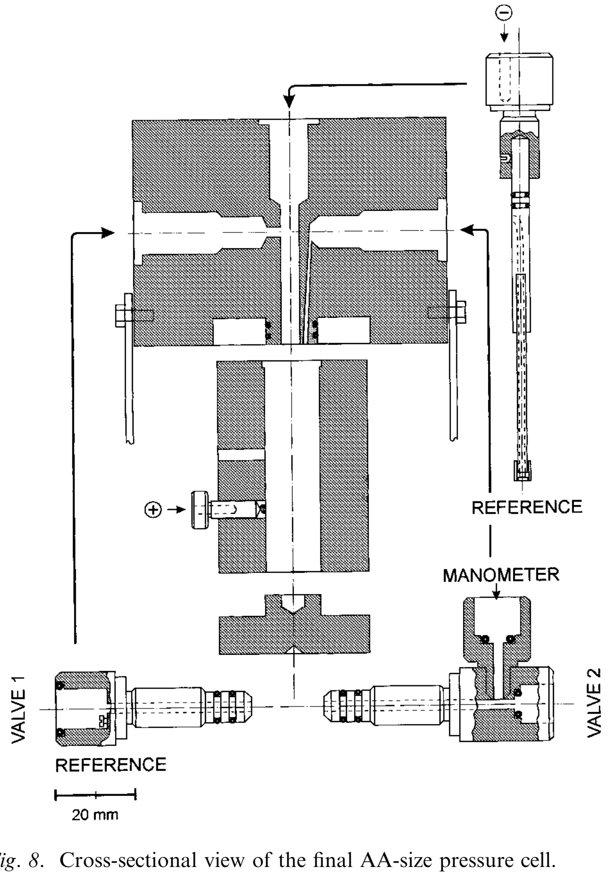

*Fig. 8.* Cross-sectional view of the final AA-size pressure cell.

### 2.3.1. *Measurements in complete cells upon storage, discharge, charge, overcharge and overdischarge (in series with two ‘good’ cells)*

The improved pressure cells (third generation) were found to be useful tools to study all types of battery reactions including corrosion studies of the active materials or other battery components in the chosen electrolyte. Some of the measurements described in the previous Sections were repeated to obtain additional information by recording anode and cathode potentials versus the new reference electrodes. One case of irregular battery operation was added to the programme: the AA battery enclosed in the pressure cell was partly discharged and connected in series with two other (fully charged) AA batteries. The whole pack was discharged using a constant load resistor until the partly discharged cell was reversed. Pressure build-up and the composition of the evolved gas was studied under these circumstances [13].

Initial problems with short circuiting between the reference electrode disc and the anode contact rod were solved by wrapping the lowest part of the current collector–reference electrode unit with a few layers of separator laminate. The measured potential differences were stable in the case of zinc and showed some fluctuations in the case of silver, both serving as reference electrode materials. Although zinc was accepted to be a corroding electrode with an almost constant potential, silver was covered with either silver chloride or silver oxide in order to keep the potential within narrow margins. Unfortunately, these layers were more or less soluble in the electrolyte and seemed to disappear when the experiment was run over prolonged periods.

Despite these complications, an improved correlation between the start of gas evolution and a certain electrode reaction was possible by means of the new reference electrodes. Information concerning gas pressure, gas composition, cell voltage and single electrode potentials were useful to study battery reactions under all possible operating conditions. A complete collection of data can be found in [13].

## 3. Results and discussion

The step-by-step improved construction of pressure-tight test cells made it possible to investigate battery reactions under ‘real’ application conditions in a convenient manner.

Figures 2, 3, and 5–7 show some of the results obtained in different applications of the described pressure test cells. These improvements were found not only to deliver more information about the tested battery system (in the meantime the cells were used to study gas evolution in cylindrical nickel/zinc-batteries [14]) but also to make the manipulations more convenient. The first group of changes included the insertion of the reference electrode, the installation of a means to analyse gases, and the possibility to use a temperature sensor. In addition, the ease of pressure cell assembly was improved. This was realized by replacing the four threaded bolts with a single clamp and screw. Moreover, the new high-precision fittings enabled the exchange of manometers and valves without any gas tightness-problems. This increased the number of applications by varying the pressure ranges. Furthermore, this feature allowed easy replacement of faulty or unsuitable components (e.g., valves). In a few experiments the cells were exposed to over 35 bar internal pressure and showed no failure due to this high pressure. Actually, the only dangerous event which may cause cell destruction is the contact of the cell with solvents of low evaporation temperature or high vapour pressure at room temperature. It is nearly impossible to temper complicated PMMA-parts so perfectly that they remain absolutely free of internal stress. Rapid cooling (as done by the cited organic solvents) initiates the formation of cracks starting at sensitive edges or corners. In future work, the pressure cells could be further improved by replacing the manometers by mechanical/electronic pressure sensors with digital data recording.

## 4. Conclusions

Apart from a few additional refinements (e.g., electronic pressure sensors for recording the pressure against time function), the described pressure cells (third generation) may be used for the study of many different types of battery reactions as well as for the examination of the corrosion of (metallic) materials in the respective battery electrolytes.

The upper pressure limit was dictated by the manometers employed (40 bar full-range); 35 bar could be reached in these tests without any problem. Test temperatures ranged from room temperature to 45 °C, limited by the construction of the controlled temperature chamber. Higher temperatures, up to 90 °C, may also be used, this being the absolute maximum in the low pressure region. However, any contact with low-boiling point organic solvents and strong acids must be prevented. If such media have to be studied, another material for the cell housing has to be chosen.

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