

# An electrochemical cell design with flowing or static electrolyte suitable for use at elevated temperatures and pressures

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**Abstract** The paper describes the design and testing of an electrochemical cell container suitable for working at extremes in temperature and pressure. The cell electrolyte may be changed at any time with ease, the total volume of the system remaining constant, and it is therefore eminently suitable for 'closed' environments. The volume of the electrolyte and the number of electrodes within the cell can be varied readily. PTFE is used mainly as the material of construction.

## 1 Introduction

This short communication describes the design and testing of an electrochemical cell container. Made almost entirely in PTFE, the cell container can accommodate at least three electrodes. Changes of solution within the cell may be accomplished via an electrically operated valve and two electrolyte reservoirs. The whole unit was originally designed for electrochemical studies situated in a pressure vessel which could be taken to 200°C and 3 kbar. However, the design and details of construction should be of use to any worker who is forced to make measurements in a closed environment, and has to change the 'working' solution from time to time. It has the additional advantage that the electrical circuits involved in the measurements need not be interrupted when the solution surrounding an electrode is changed. This relatively simple static/flowing electrolyte type of cell design is the first of its kind to appear in the literature.

## 2 Cell container design

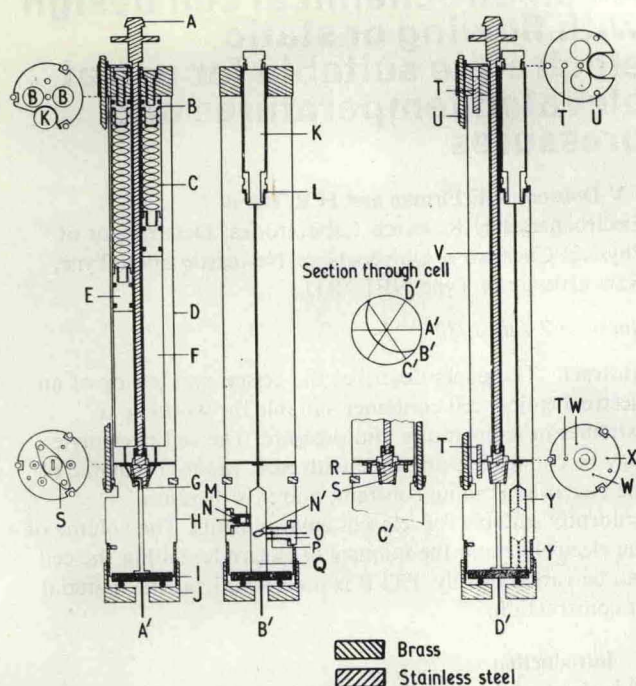
The cell assembly, shown as a sectional diagram in figure 1, is mounted vertically and consists of a solenoid used as a valve-actuator, two PTFE electrolyte reservoirs and a unit containing a valve and the electrochemical cell container also in PTFE. A photograph of the cell with the solenoid and other features not shown in figure 1 is given in figure 2. The components are bolted together by three lengths of brass studding which extend the length of the assembly. Support for the whole assembly, when used for elevated temperature and pressure work, is achieved by screwing a short length of brass studding into the top of the solenoid mounting at one end, and into the head of the pressure vessel at the other. Pressure changes are accommodated using a thin walled PTFE bag K.

### 2.1 The solenoid valve-actuator

The solenoid is coupled to a series of gears which transfer rotary motion to a long shaft V. The shaft passes through a hole in the reservoir unit and is connected to valve R at its lower end. A 90 V DC supply is used to operate the solenoid, whose electrical resistance is 22  $\Omega$  and made from 34 swg coated wire.

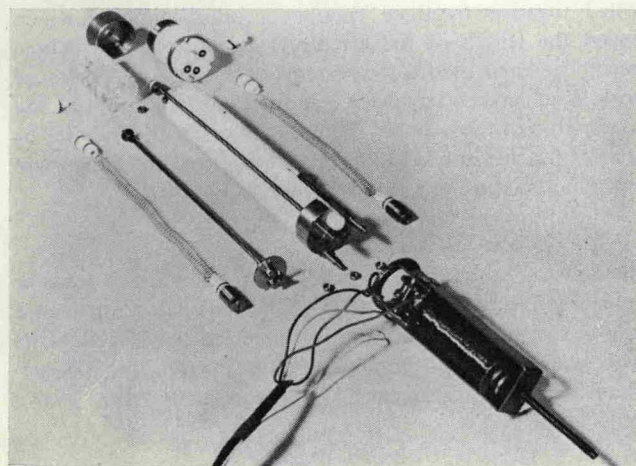
### 2.2 The reservoir unit

The reservoir unit comprises two electrolyte reservoirs F fitted with double-acting PTFE pistons E that have Bridgman



**Figure 1** Sectional diagram of cell container: A, gear; B, PTFE end plug; C, steel spring; D, reservoir unit body; E, PTFE piston; F, electrolyte reservoir; G, PTFE tube inset; H, cell unit body; I, pH electrode; J, brass cap; K, PTFE pressure-sensitive bag; L, viton O ring; M, PTFE F05 sinter; N, N', silver-silver chloride electrode; O, PTFE electrode holder; P, electrode seal; Q, cell compartment; R, valve, EN58J; S, valve liner, EN58J; T, locating pin; U, brass studding; V, drive shaft; W, electrolyte entry port; X, electrolyte exit port; Y, push-in PTFE liner

type seals. In practice, the waste electrolyte is fed to the back of the piston whilst fresh is passed to the cell from the front. This eliminates the need for a separate waste cylinder and thus maintains a total constant volume within the cell container, so necessary for a closed environment. The position of the valve with respect to the cylinders is indicated by electrical means via a small set of insulated contacts mounted on the drive shaft. Although readily replaceable, and not in contact with the fresh electrolytes stored in the reservoirs, the steel springs used to move the pistons are protected against



**Figure 2** The cell container

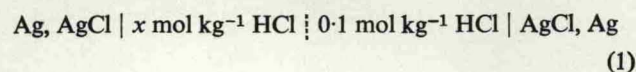
corrosion by the waste solution. These springs were rubbed down with Scotchbrite, an abrasive fibre, and degreased with carbon tetrachloride. A slurry of boron nitride, type A (Carborundum) was applied using a fine brush and allowed to dry. The springs were then heated at 110°C for 4 h. The corrosive effect, if any, of the waste solution on the protected springs does not contaminate the working solution because of the physical arrangement of the cell's construction described above.

### 2.3 The cell compartment and valve

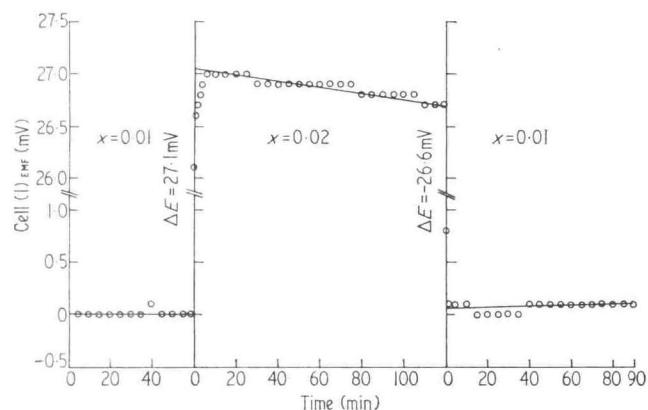
The cell compartment Q is a small cylinder tapered at its upper end and enlarged at the lower end to expose maximum surface area of the disc electrode, a particular type of pH sensitive electrode used in the original work. The arrangement as shown could be modified quite easily to accommodate a smaller or different shape of electrode. In the present case the shape and position of the disc 'working' electrode allows an efficient flow of electrolyte across the surface. The working cell volume can be altered by introducing a PTFE sleeve. The valve material is EN58J stainless steel. This material is moderately acid and alkali resistant. PTFE could not be used because of its plastic nature and distortion when machined. The valve and valve liner were ground-in, using a very fine diamond paste. In use, a very thin smear of Edwards high temperature silicone grease may be used to lubricate the valve, which helps to prevent solution leakage around the valve.

### 3 Testing of cell container

At one stage two silver-silver chloride electrodes were employed in the cell container to measure the efficiency of solution changes within the cell. A measurement of the bias potentials of the silver-silver chloride electrodes gave an indication of the efficiency of washing. To increase the efficiency of washing, push-in PTFE sleeves were used to reduce the overall volume of the cell compartment. The cell volume may be varied from 2 to 1 ml. The reservoir chambers were each of total volume 10 ml. One of the silver-silver chloride electrodes was immersed in a standard solution (0.01 mol kg<sup>-1</sup> HCl) but separated from the main cell chamber by a 5 μm pore PTFE sinter, and was therefore impervious to any change in concentration in the working volume of the cell. The positions of the two silver-silver chloride electrodes relative to one another may be seen in figure 1. To carry out the test of washing efficiency 0.01 mol kg<sup>-1</sup> HCl was introduced into the cell compartment and one of the reservoirs using a PTFE syringe,  $x$  mol kg<sup>-1</sup> HCl was introduced into the other reservoir. The cell container was then placed in an air thermostat (for convenience), controlled in this instance to 20 ± 0.1 °C, and was allowed 2 h to reach thermal equilibrium. Measurements of the EMF of the cell



were made for a period of 1 h using a Wayne-Kerr M141 electrometer linked via a Solartron digital voltmeter and data logging unit to an Addo tape punch,  $x$  in this instance being 0.01. The valve was opened to the reservoir containing 0.02 mol kg<sup>-1</sup> HCl and then returned to the closed position 2 min later. Although solution exchange is complete within 30 s for 10 ml, 2 min were allowed to permit the operator to attend the electrical measuring equipment during the period when the cell EMF is changing rapidly. The EMF of cell (1) when  $x=0.02$  was monitored for a further 2 h before repeating the solution change procedure and re-admitting 0.01 mol kg<sup>-1</sup> HCl from



**Figure 3** Variation of cell (1) EMF with time and changes of electrolyte at 20°C

the other reservoir. The variation of cell (1) EMF with time and solution changes is shown in figure 3. The cell (1) EMFs vary with time in some instances at times greater than 5 min after solution change and this behaviour may be expected if the washing is not efficient. The changes in the EMF of cell (1), obtained by extrapolating EMF-time curves to the instant of transfer and given in figure 3, indicated also that washing was not 100% efficient. If replacement with fresh solution were complete, the EMF change for the example given in figure 3 would be 27.5 mV (0.01–0.02 mol kg<sup>-1</sup> HCl) at 20°C compared with the observed values of 27.1 and –26.5 mV for the first and second solution changes respectively. These experimental values were found using the cell container with the push-in PTFE liners, cell volume 1 ml, and were in error by 1.4 and 3.6% of the expected EMF change. Without the push-in liners, the first and second solution changes gave an error of 6.1 and 8.0% respectively in the EMF change. The introduction of the push-in liners therefore increased the washing efficiency by 5%. Further small refinements should lead to an efficiency of always greater than 99% where non attainment of ideal washing would be insignificant. In any event, the measurement of cell (1) EMF changes ensures that the experimenter could determine the composition of the solution after washing at any point in the experiment if necessary.