

OXYGEN CYCLE IN SEALED RECHARGEABLE CELLS

J. MRHA*, J. JINDRA and M. MUSILOVÁ

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

Alkaline nickel/cadmium cells

In view of the fact that hydrogen formed in sealed nickel/cadmium cells cannot be oxidized in an economic and reliable manner, it is necessary to prevent its formation at the negative electrode during an advanced state of charging or during overcharging. On the other hand, reduction of oxygen can be carried out economically and reliably at either the cadmium electrode or an auxiliary electrode connected to it. The mechanism of oxygen reduction is either chemical or electrochemical; it is difficult to specify and depends on the nature of the electrode used.

The formation of hydrogen at the negative electrode can be prevented by a suitable choice of capacities of both the positive and negative electrodes (*i.e.*, an excess capacity for the negative) and by careful selection of the materials for the negative electrode. Hence, the term 'sealed' can be used without restriction; pressure valves are occasionally used as a safety precaution in cases of cell mishandling.

The results obtained in this Institute concerning the oxygen cycle in sealed nickel/cadmium cells can be summarized as follows:

(i) reduction of oxygen proceeds mainly on those metal construction parts of the cadmium electrode (steel, nickel) that are in contact with the electroactive material, are covered with a film of the electrolyte, and are easily accessible to oxygen;

(ii) with plastic-bonded cadmium electrodes, the construction materials mentioned in (i) are absent and the rate of oxygen reduction can be increased economically by using additional metallic parts (*e.g.*, nets, perforated foils, etc.);

(iii) the rate of oxygen reduction can be controlled over a wide range by doping the electroactive material with $\text{Ni}(\text{OH})_2$ or Fe_3O_4 , or by adding active carbon, carbon black, and poly(tetrafluoroethylene);

(iv) from the above results, it is concluded that oxygen reduction proceeds via an electrochemical mechanism.

*Author to whom correspondence should be addressed.

Lead/acid cells

From published results, it can be expected that the reduction of oxygen at the lead electrode is, in contrast to that at the cadmium electrode, lowered by certain complicating effects, although the solubility and diffusion coefficient of oxygen are higher in the acid electrolyte. These complications are as follows:

(i) at the negative electrode, hydrogen is formed not only during charging and overcharging but also in the currentless state; hence the partial pressure of oxygen at the surface of this electrode is relatively low;

(ii) the surface of the lead electrode is covered with a layer of composition $x\text{PbO}\cdot y\text{PbSO}_4\cdot z\text{H}_2\text{O}$, which is permeable to the electrolyte ions but not very permeable to oxygen molecules;

(iii) the separator serves as the electrolyte carrier and therefore must (in contrast to sealed nickel/cadmium cells) ensure a sufficient quantity of the acid electrolyte for the electrode processes to occur, and must not hinder the passage of oxygen from the positive electrode to the negative (this condition applies also to the sealed nickel/cadmium cells, although not inevitably).

According to present knowledge, the formation of hydrogen at the lead electrode cannot be prevented, even when impurities that lower the hydrogen overpotential are excluded. If additives are used to catalyse the reduction of oxygen and hinder the evolution of hydrogen, problems arise concerning additive stability. Auxiliary electrodes with catalysts developed for fuel-cell oxygen electrodes will doubtless present problems due to their limited stability, and, moreover, the use of diodes for connecting these electrodes to the negative lead electrodes will cause complications in the manufacturing process.

Thus, at present, it is necessary to provide all sealed lead/acid cells with relief valves that (in contrast to sealed nickel/cadmium cells) operate practically during every charging period. For this reason, the term 'sealed cells' is not accurate. Another necessary provision is controlled voltage during charging.

In the authors' opinion, the problem of achieving an effective reduction of oxygen can be solved by increasing the reaction zone at the surface of the lead electrode. This can be accomplished by the so-called filtration mechanism of the oxygen transport on the one hand, and by using auxiliary hydrophobized lead electrodes on the other hand. The filtration mechanism, which was studied in detail at the Saratov University (USSR), is based on the use of a separator that permits the transport of oxygen through its pores. A glass-microfibre mat proved satisfactory for this purpose. In the work reported here, an attempt is made to correlate the physicochemical parameters of the separator with the electrochemical parameters of laboratory lead/acid cells.

Experimental

Electrochemical measurements were carried out in a hermetically-sealed organic glass cell (Fig. 1) containing one positive and two negative

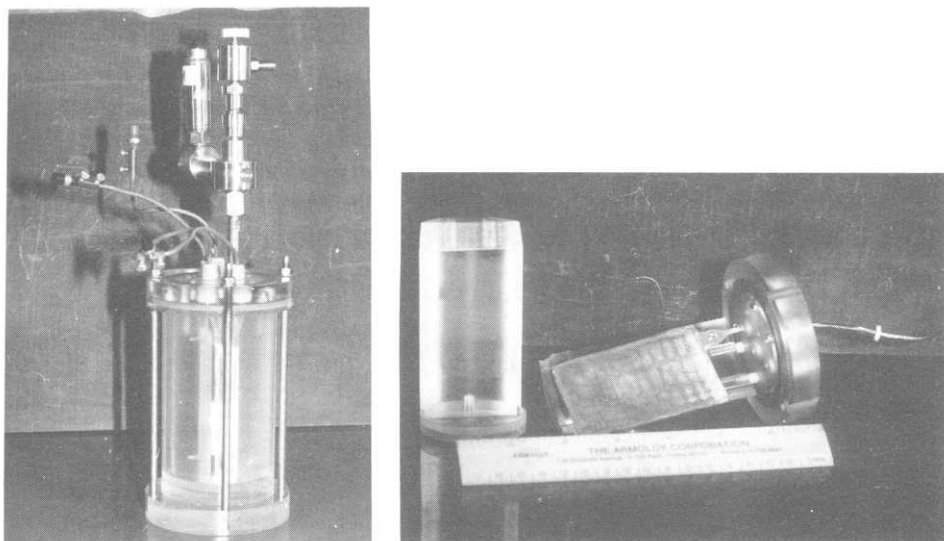


Fig. 1. Test cell and electrode arrangement.

electrodes. The electrodes were prepared by normal procedures as dry-charged pasted electrodes with pure lead grids. The electrode dimensions were $80 \times 50 \times 2$ mm. The nominal capacity of the cell was 3.0 A h. Non-woven glass-microfibre fabric served as both a separator and an electrolyte carrier; its physical parameters are given in Table 1. The back sides of the negative electrodes were covered with the same material. The electrolyte was 4.9 M H_2SO_4 (sp. gr. 1.28 g cm^{-3}).

Results and discussion

The dependence of the internal pressure and potential of the lead electrode on the charge passed during charging of the test cell at four currents is shown in Fig. 2. A correlation between the pressure and potential

TABLE 1

Physical parameters of glass separator

Thickness (as received) (mm)	2.2
Thickness at 100 kPa compression (mm)	1.3
Square density (g m^{-2})	285
Content of binder (%)	2.8
Porosity (%)	92.0
Pore diameter (μm)	1 - 8
Pressure drop at 0.052 m s^{-1} (Pa)	395
Wicking height in 4.9 M H_2SO_4 (mm/15 min)	100
Mass loss in 4.9 M H_2SO_4 (%)	4

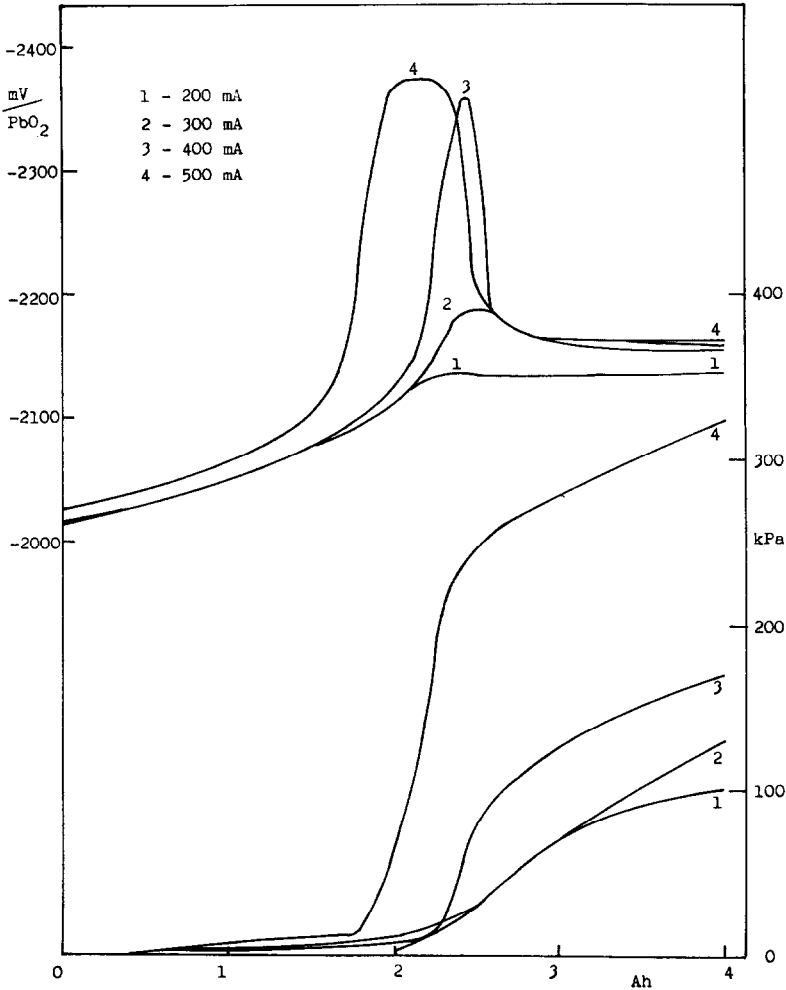


Fig. 2. Cell pressure and lead electrode potential during galvanostatic charging.

dependences is apparent. The pressure dependence can be divided into three regions. The first region exhibits only a moderate pressure increase. As soon as gas evolution commences at the negative, or at both the negative and positive electrodes, a steep rise in pressure is observed in the second region. This is, however, considerably moderated in the third region as a consequence of the start of the oxygen cycle.

The potential dependence of the lead electrode correlates with the above behaviour in that there is only a slight increase to negative values in the first region, a more-or-less pronounced maximum in the second region, and a constant value in the third region. The observed potential drop

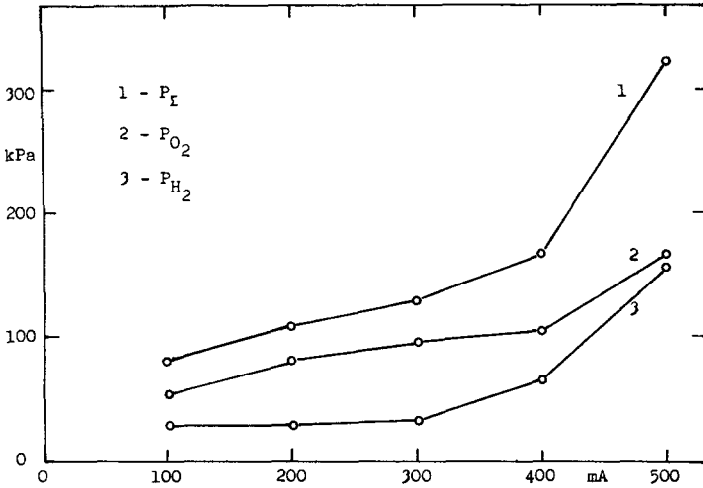


Fig. 3. Dependence of pressure on charging current.

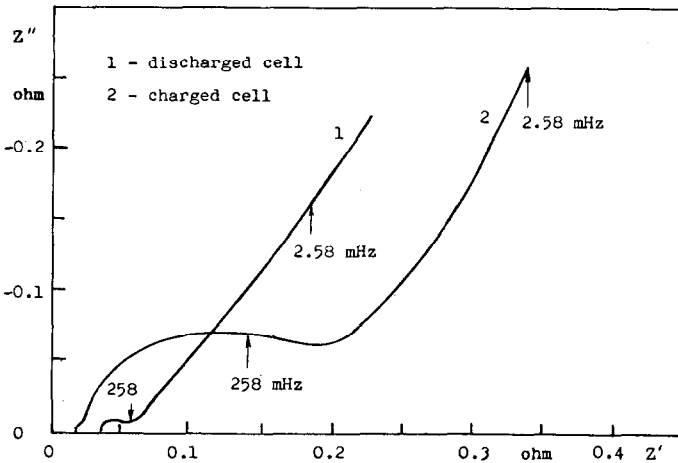


Fig. 4. Impedance characteristics of test cell.

suggests that oxygen depolarizes the lead electrode, *i.e.*, functioning of the oxygen cycle.

Figure 3 displays the dependence of the total pressure, P_{Σ} , the partial pressure of hydrogen, P_{H_2} (determined from the stationary pressure after nearly complete reduction of oxygen at the lead electrode on open circuit), and the partial pressure of oxygen, P_{O_2} (determined by difference), on the charging current after supplying a charge of 4 A h to the test cell. It can be seen that the three dependences are linear up to a charging current of 0.4 A; at 0.5 A, the depolarization with oxygen is less efficient.

Impedance characteristics of the test cell were measured with a Solartron 1250 frequency analyzer in both the (fully) charged and (fully) discharged states (Fig. 4). The results are similar to those published by Keddam *et al.* [1]. Further measurements are in progress.

Reference

- 1 M. Keddam, Z. Stoykov and H. Takenouti, *J. Appl. Electrochem.*, 7 (1977) 539.