

A correlation between porous structure of the separator and barodynamic characteristics of sealed lead/acid accumulators

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Abstract

The influence of a highly-porous glass web separator on barodynamic characteristics of a model hermetically-sealed lead accumulator was studied. The porous structure of the separator and electrodes were followed by porosimetric methods and the results were used to determinate the electrolyte distribution in the accumulator. The reduction of oxygen in a cell with strongly-pressed separator is practically complete inside the electrode pack.

Introduction

As was shown earlier [1, 2], the barodynamic characteristics, i.e., the changes of pressure in a hermetically-sealed lead accumulator during charging, give useful information about the accumulator, namely about the ionization and generation rates of oxygen and hydrogen. These characteristics depend on the porous structures of the electrodes and separator and quantity of electrolyte. The porous structure of the electrodes in a charged accumulator can be considered as fixed, whereas the pore-size distribution of the separator depends on the pressing pressure.

The influence of the applied pressure of the electrode pack on the barodynamic characteristics of a hermetic lead accumulator, described previously [2], was studied in the present work.

Experimental

Similarly to previous studies [1, 2] dry-charged electrodes were used. The separator was a glass web of the type MSKA (Russia) of 95% porosity and of 1.40 mm thickness in the original state. The accumulator was assembled in the dry state and the pressure applied was either 13 or 65 kPa (cells A and B). The electrolyte (5 M H₂SO₄) was added into the evacuated cell.

The porous structure of the separator was measured on a Carlo Erba Strumentazione mercury porosimeter, the separator being pressed between two metal plates at 13 or 65 kPa.

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Results and discussion

Pore-size distribution curves for the separator pressed at 13 or 65 kPa are shown in Fig. 1, together with similar curves obtained for positive and negative electrodes by the method of contact etalon (comparative) porosimetry [3]. It can be seen that the porosity of the separator is little dependent on pressing, in contrast to the pore-size distribution: at an applied pressure of 13 kPa the distribution is uniform whereas at 65 kPa smaller pores prevail (around $r \approx 1.6 \mu\text{m}$). The pore-size distribution for the positive electrode is somewhat shifted toward smaller radii compared with the negative electrode; this is due to the character of the active materials.

Based on the pore-volume distribution measurements of electrodes and separators it is possible to construct Figs. 2 and 3 as follows: for every pore-size the volume of pores in components (i.e., in the separators and electrodes) was plotted against the sum of these volumes. With regard to the hydrophilicity of electrodes and separators filling of pores with electrolyte proceeds from the smallest to larger pores. From Figs. 2 and 3 it is possible to estimate the quantity of electrolyte in each component of the accumulator V_i as a function of its total content V_Σ (Figs. 2 and 3). The degree of saturation of the electrode pack amounts to 72 and 80% for cells A and B filled with 30 and 25 ml of electrolyte, respectively. Interestingly enough, the separator porosity changes only slightly from 92.4% at 13 kPa to 90.2% at 65 kPa (Fig. 1), whereas its free volume drops from 27 to 17.2 cm^3 , respectively. Accordingly, cell B had a higher degree of saturation although it contained less electrolyte; and this resulted in a higher discharge capacity (by 15% in comparison with cell A).

In Fig. 4 are shown the barodynamic curves measured during charging the cells A and B. Analysis of these curves (the final gas overpressure) shows that the reduction of oxygen is more rapid in cell A than in cell B with the more pressed separator (compare Figs. 4(a) and 4(b)). This is probably related with a larger electrochemically

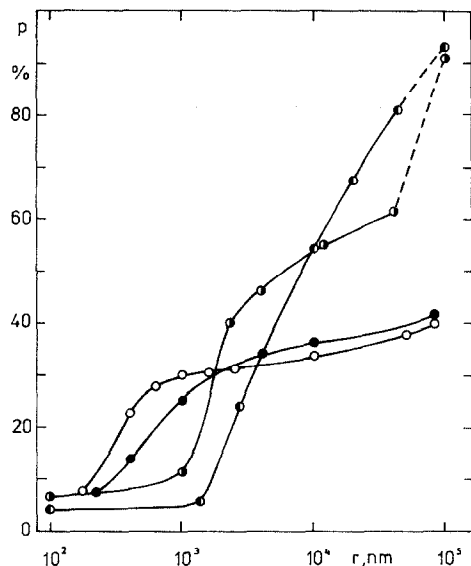


Fig. 1. Pore-size distribution curves for the electrode pack components; (●) negative electrode; (○) positive electrode; (●) separator at 13 kPa; (○) separator at 65 kPa.

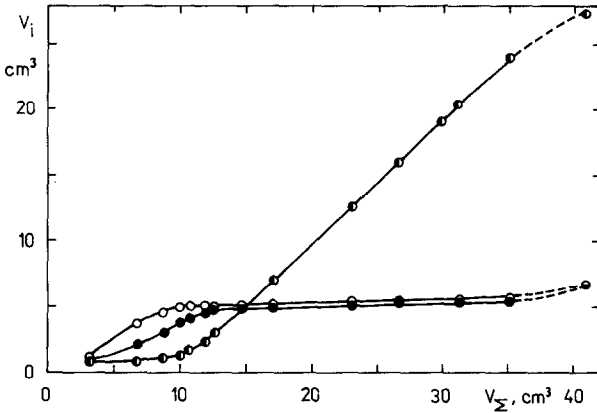


Fig. 2. Electrolyte content in: (●) two negative electrodes, (○) two positive electrodes and (⊙) separator, as function of the total quantity of electrolyte in the cell at $P=13$ kPa.

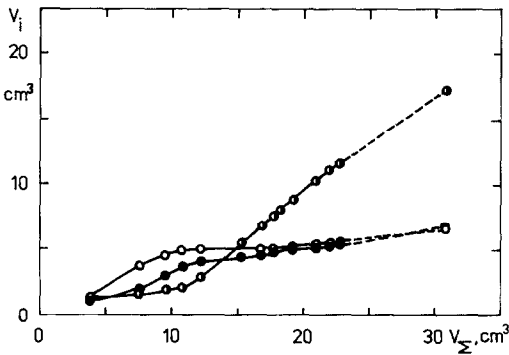


Fig. 3. Electrolyte content in: (●) two negative electrodes, (○) two positive electrodes and (⊙) separator, as function of the total quantity of electrolyte in the cell at $P=65$ kPa.

active surface area of the negative electrodes in cell A. The oxygen evolved during charging on the positive electrode can simultaneously escape also into the gas space of the cell and then be reduced on negative electrodes. This is favoured with a more efficient oxygen transport through the separator due to a lower electrolyte content (in vol.%) wherein. On the contrary, with the more strongly pressed separator (cell B) containing smaller pores, the pressure increase is due to a small portion of the gas escaping from the electrode pack without being reduced.

The oxygen accumulation rate in the gas phase, I_g , during overcharging with a current I (when $I=I^{O_2}$) is given as:

$$I_g = I^{O_2} - I_{O_2} \quad (1)$$

where I^{O_2} and I_{O_2} denote the rates of formation and ionization of O_2 , respectively. From this it follows that:

$$\frac{I_g}{I_{O_2}} = \frac{I^{O_2}}{I_{O_2}} - 1 = \frac{I}{I_{O_2}} - 1 \quad (2)$$

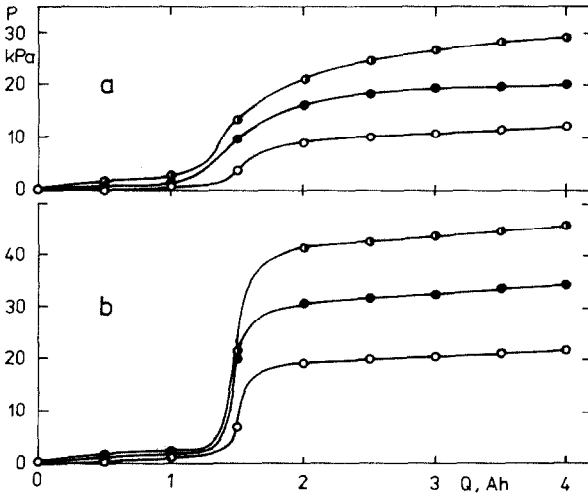


Fig. 4. Barodynamic curves for (a) cells A and (b) cells B at various charging currents; (○) 300 mA; (●) 500 mA; (◐) 700 mA.

It was shown earlier [2] that values of I_{O_2} and I^{H_2} (hydrogen generation current at the negative electrode) can be determined from the barodynamic characteristics as:

$$I_{O_2} = I - \frac{4}{3\alpha_0} \frac{dP}{d\tau} \quad (3)$$

$$I^{H_2} = \frac{4}{3\alpha_0} \frac{dP}{d\tau} \quad (4)$$

where P denotes pressure in the accumulator, $\alpha_0 = RT/FV_g$ is the cell constant and V_g is the volume of gas in the accumulator. Thus, by combining eqn. (2) with eqn. (3) we obtain:

$$\frac{I_g}{I_{O_2}} = \left(\frac{3}{4} \alpha_0 I \frac{d\tau}{dP} - 1 \right)^{-1} \quad (5)$$

for the ratio of oxygen accumulation to oxygen ionization. This ratio was found to be equal 0.014 (or 1.4%) for cell B during charging with a current $I = 0.7$ A, hence the ionization of oxygen inside the electrode pack was practically complete.

With cell A (lower compression) the penetration of oxygen occluded between the separator and electrode into the gas space is easier than with cell B; the diffusion of oxygen from the gas space through the separator to the pores of the negative electrode is also more efficient than with cell B.

Conclusions

(i) The quantity of electrolyte in a sealed lead/acid accumulator depends on the pore-size distribution of the components of the electrode pack, taking into account the compression of the separator.

(ii) If the separator is strongly compressed then oxygen is reduced practically complete inside the electrode pack.

List of symbols

I	charging current (A)
I^{O_2}	rate of oxygen ionization (A s^{-1})
I_{O_2}	rate of oxygen ionization (A s^{-1})
I_{g}	rate of oxygen accumulation (A s^{-1})
I^{H_2}	rate of hydrogen generation (A s^{-1})
P	pressure
τ	time of charging (s)
α_0	cell constant
R	gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
T	temperature (K)
F	Faraday constant, $96484.56 \text{ C mol}^{-1}$
V_{g}	gas volume (m^3)

References

- 1 B. I. Tsenter, R. V. Mustafin, J. Mrha, J. Jindra and M. Musilová, *Zh. Prikl. Khim.*, **63** (1990) 692.
- 2 J. Mrha, J. Jindra, M. Musilová, B. I. Tsenter, I. A. Aguf and R. V. Mustafin, *J. Power Sources*, **32** (1990) 303.
- 3 Yu. M. Volf'kovich and E. I. Shkolnikov, *Elektrokhimiya*, **15** (1979) 8; **16** (1980) 1620.