JOURNAL OF APPLIED ELECTROCHEMISTRY **14** (1984) 117–122

Electrolyte absorption capacity of conducting carbon blacks used in Leclanché type batteries

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Received 23 January 1983
Revised 3 May 1983

An essential property of conducting carbon blacks used in Leclanché type batteries is to absorb electrolyte. This paper shows that the total pore volume is usually accessible to electrolyte. This volume is dependent on the mechanical conditions of preparation of the cathode mixture; it strongly decreases with the pressure applied during compression of the cathode.

1. Introduction

In a Leclanché battery the cathode includes manganese dioxide (MnO_2), conducting carbon black and electrolyte which is often an aqueous solution of zinc chloride ($ZnCl_2$) and ammonium chloride (NH_4Cl).

In a previous paper [1], the chemical behaviour of conducting carbon blacks has been studied during storage and discharge of batteries, using two analytical methods developed by Boehm *et al.* [2] and Caudle *et al.* [3]. It was shown that the reactivity of the carbon is not the controlling step in the processes involved. The surface reactivity does not determine the performance of a conducting black in a depolarizing mixture.

Electrolyte uptake by carbon is considered a major parameter by battery producers. Some routine tests have been developed to evaluate the retention capacity of blacks but most them do not take into account the important effect of mixing pressure or lay stress on electrolyte retention in the carbon.

Caudle *et al.* [4] studied the volume change of MnO_2 and carbon black compacted separately and after mixing. At low pressure the volume of the mixture is equal to the sum of the volumes of components compressed individually (additivity) but there is no longer any additivity above 15 MPa. Sattar Syed and Anwar Hassain [5] studied the change in the properties of acetylene black in mixing mills.

The objective of the present work was to determine the electrolyte uptake by conducting blacks and to correlate the results, either to the compressibility or the porosity of the samples.

2. Experimental details

Conducting carbon blacks and natural MnO_2 were mixed in the appropriate proportion by rotative stirring at 55 r.p.m. The electrolyte was then added and the paste was prepared by simple mixing with a spatula.

The four types of conductive carbon black used are referred to as A, B, C and D. Carbon A, B and D were acetylene blacks whilst sample C was obtained from another hydrocarbon. They have been characterized (Table 1) by their absorption capacity of a water–acetone mixture (volume ratio 9:1).

They are suitable for battery manufacture, although exhibiting different performances. Cathodic mixtures consisted of 50 g of natural

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Table 1. Absorption capactiy of carbon blacks. Capacity of half-batteries

Conductive carbon black	*Absorption capacity* $(cm^3 5 g^{-1})$	*Capacity of half batteries*
A	50	9 h 25 mn
B	30–32	8 h 00 mn
C	30–32	8 h 20 mn
D	15	6 h 30 mn

MnO_2 and 6 g of the conducting black carefully mixed with 22 cm^3 electrolyte (10% $ZnCl_2$, 26% NH_4Cl and 64% H_2O by weight). The mixture was kept for one day at room temperature in a closed vessel before use.

The cathode mixture was introduced to a cylindrical mould of polymethylmethacrylate and compressed at 785 kPa with an Instron dynamometer type 1195H, a possible excess of electrolyte being allowed to exude. The pressure was within the pressure range used industrially for cathode preparation. The pressure build up was gradual and the volume exuded was measured at a given pressure so that the absorbed volume could be calculated by difference. The cathode was withdrawn from the mould after the piston reached an equilibrium position. The samples obtained were 0.55 cm thick and 3 cm in diameter.

Column 3 of Table 1 shows the capacity of the half batteries, characterized by the time required for the cathode to reach a potential of −120 mV with respect to the saturated calomel electrode (this corresponds to about 0.9 V for the whole battery) at a 10 mA cm^{-3} direct current. This type of discharge was used because of its relevance to the exchange rates of protons and electrons, which are strongly dependent on carbon black texture.

In the last part an Instron dynamometer was used to compress the four conductive carbon blacks in a metallic mould whose piston displacement was measured with a Wallace Optical Extensiometer.

3. Results and discussion

In Fig. 1 the amount of electrolyte absorbed by the carbon black/MnO_2 mixture was plotted against the carbon black content for various samples.

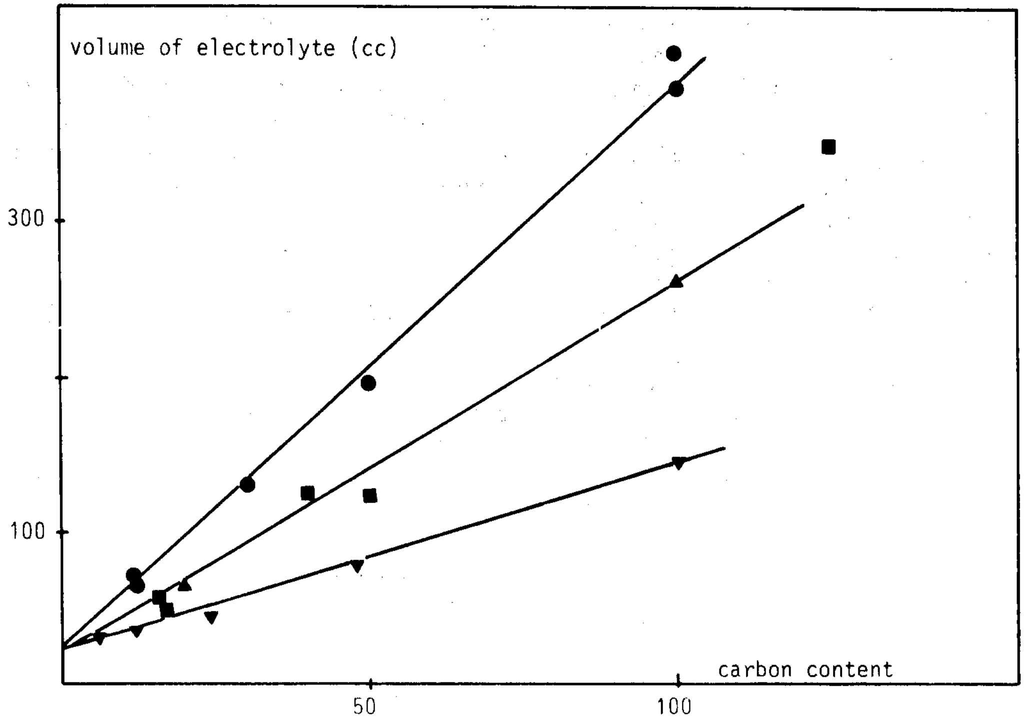

Fig. 1. Volume of electrolyte absorbed by a mixture of carbon black – MnO_2 compressed under a pressure of 785 kPa against carbon black contents (g of black/100 g of MnO_2). Carbon A (●), B (■), C (▲), and D (▼).

The volume of electrolyte absorbed is $20\,\mathrm{cm}^3/100\,\mathrm{g}\ \mathrm{MnO_2}$ when the carbon black content vanishes: this volume corresponds to the absorbing capacity of MnO_2 in the conditions considered. The slopes which are equal to the quantities of electrolyte absorbed per gramme of carbon black can be seen in the second column of Table 2 (experimental uncertainties are about 10%).

The carbon/MnO_2 mixture is wetted by the electrolyte and the absorbed volume is expected to be equal to the porosity of the absorbing material, predominantly interparticle porosity provided the pore size allows the electrolyte to diffuse inside the porous system.

The total volume V_t of a porous material is equal to the sum of the volume of the solid itself ('real' volume V_r) and the porosity (V_p).

If the corresponding density is referred to as ρ the pore volume per gramme is represented by the relation

$$V_p = \frac{1}{\rho_T} - \frac{1}{\rho_r} \tag{1}$$

ρ_T is determined experimentally for MnO_2–carbon black mixtures in the absence of electrolyte; ρ_r is taken equal to 5.0 and 1.95 for MnO_2 and the conducting carbon black, respectively. Results are shown in Table 2.

It is apparent that the volume of electrolyte taken up by each constituent, is equal to the pore volume with the exception of carbon D. In the latter case, volumes prove to be additive even in the presence of electrolyte, and therefore, the results shown in Table 2 reveal that the electrolyte does not enter all the pores of carbon D.

The porous volumes of cathodic mixtures were strongly affected by the pressures applied during preparation of the cathodes. Caudle *et al.* [3] showed that the volume change corresponds to the following phenomena:

(a) compression of the porous network of carbon (in the region of 50% variation for a pressure ranging from 0.7 to 23.7 MPa)

(b) compression of MnO_2 (2 to 5%)

(c) interpenetration of solid constituents (up to 7%) according to the proportion of solids and the carbon type.

The pore volume variation of carbon black was a significant parameter and accordingly the porosity should be defined precisely.

It is important to define what is meant by porosity. The absence of hysteresis in the cycle of nitrogen adsorption and desorption at the liquid nitrogen temperature, shows that there are no intraparticle pores (in the nanometre range). V_ρ, as previously determined, corresponds to large pores, mostly interparticle and interaggregate voids. This porosity and particularly interaggregate voids should be affected to a very large extent by the preparation of the cathodic mixture.

In Fig. 2, the total pore volumes of the samples is plotted against the applied pressure, using Expression 1. The very steep slopes exhibited at pressures commonly used in cathode manufacture demonstrate the necessity of a carefully controlled preparation of the cathodic mixture.

The pore spectra of the four carbon samples were measured by mercury porosimetry, in order to determine whether a given interval of porosity is particularly relevant to electrolyte absorption.

In mercury porosimetry, the Washburn relation [6] provides the pore diameters accessible to mercury at each pressure on the assumption that the solid is not deformed by pressure build up. In the case of particulate solids, this relation cannot be used, unless the pressure of mercury penetration

Table 2. Comparison between volume of absorbed electrolyte and pore volume

Sample	*Volume of electrolyte absorbed* ($cm^3 g^{-1}$)	ρ_T ($g\,cm^{-3}$)	$V_T = \frac{1}{\rho_T}$ ($cm^3 g^{-1}$)	ρ_r ($g\,cm^{-3}$)	$V_r = \frac{1}{\rho_r}$ ($cm^3 g^{-1}$)	V_ρ ($cm^3 g^{-1}$)
MnO_2	0.2	2.45	0.41	5.0	0.20	0.21
Carbon A	3.6	0.25	4.0	1.95	0.50	3.5
Carbon B	2.6	0.32	3.1	1.95	0.50	2.6
Carbon C	2.6	0.32	3.1	1.95	0.50	2.6
Carbon D	1.35	0.48	2.1	1.95	0.50	1.6

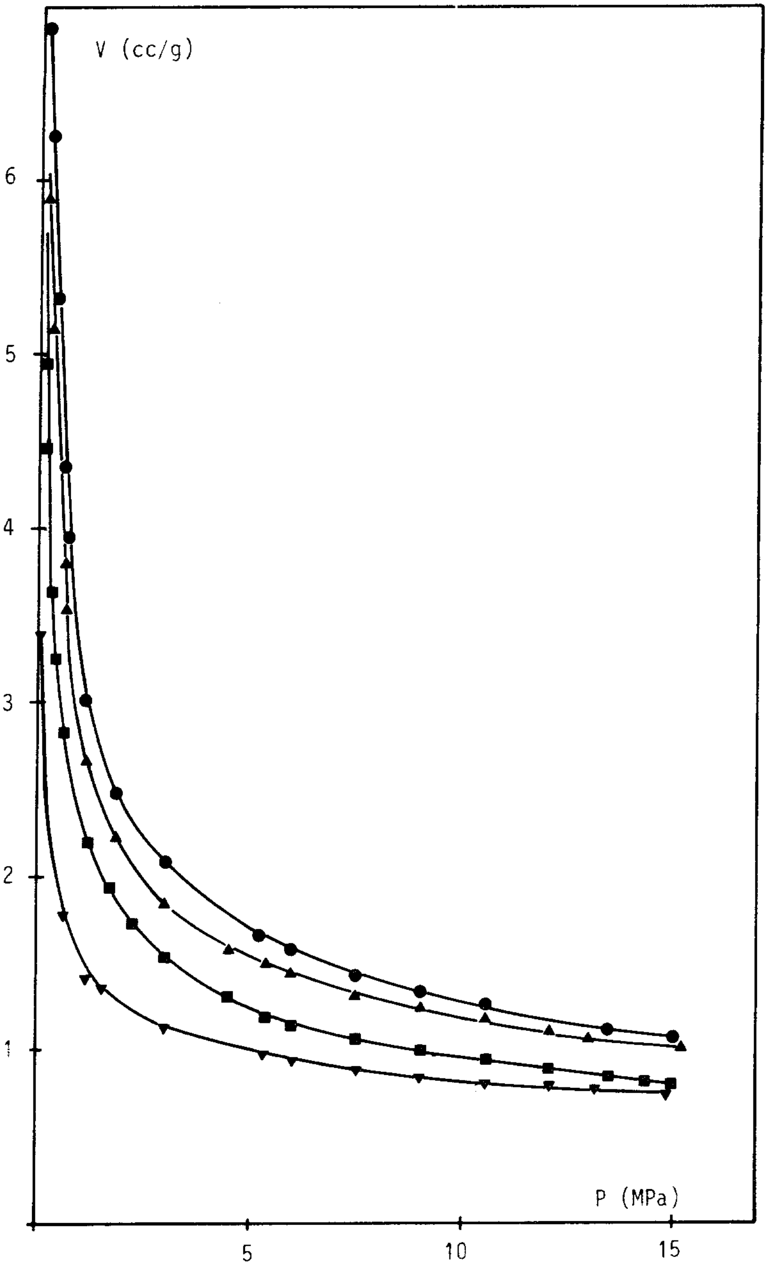

Fig. 2. Pore volumes of samples against applied pressures; Carbon A (●), B (■), C (▲), and D (▼).

is lower than the deformation pressure of the solid. In that case, mercury which penetrated into a given population of pores establishes an isostatic pressure preventing the destruction of the structure of aggregates. In Figs. 3 (carbon A and B) and 4 (carbon C and D), the pore volumes of the four samples is plotted against the pressure applied (i) with an Instron dynamomenter (ii) in a Carlo Erba mercury porosimeter.

The two techniques yield steeply falling curves for each sample which means that mercury deforms the structure before penetrating voids. The pore volume remaining at a given pressure in the mercury porosimetry is slightly lower than the equivalent value obtained by mechanical compression. This result can be interpreted as a small penetration of mercury into the porous system. The main phenomenon, however, remains the compression of aggregates. Accordingly, the pore spectrum cannot be determined but, a mercury

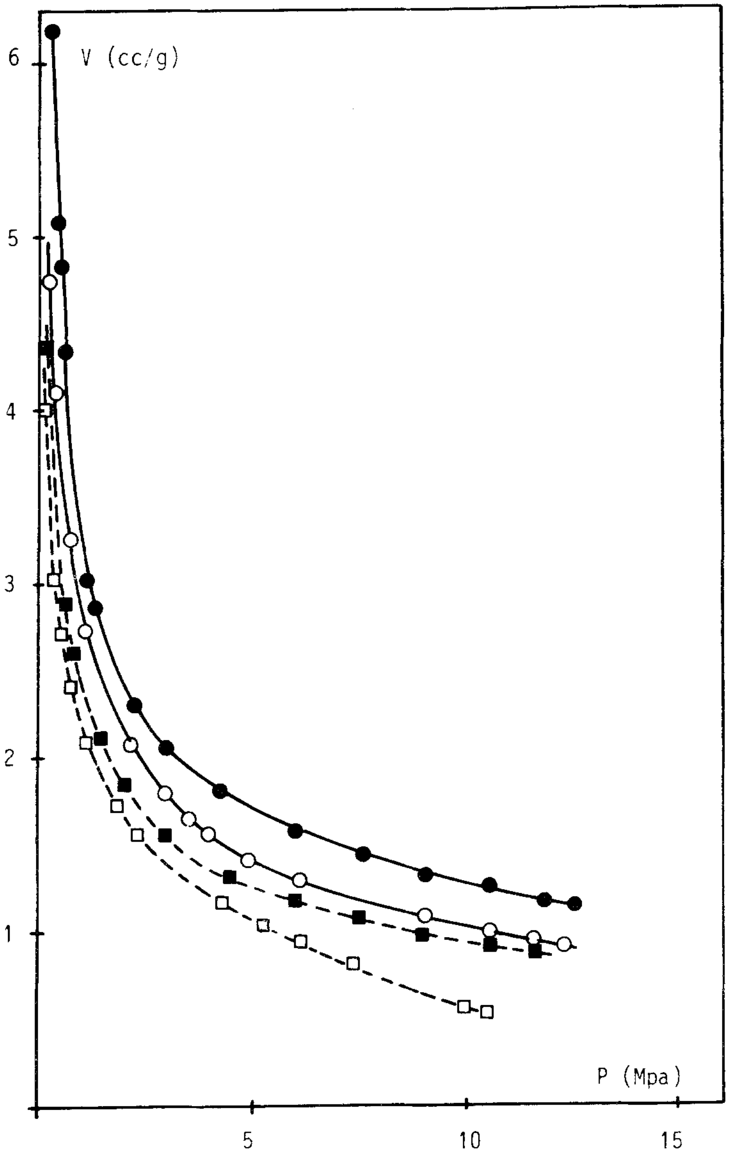

Fig. 3. Pore volumes of samples against applied pressures. Dynamometric measures Carbon A (●) and B (■). Mercury porosimetry Carbon A (○) and B (□).

porosimeter can be used to give a good approximation of how the morphology of aggregates varies with the pressure applied; this is of interest for carbon and battery manufacturers.

4. Conclusion

In cathodic mixtures, interparticulate and inter-aggregate voids in the conducting carbon black are filled with electrolyte. This volume is strongly dependent not only on the initial morphology of the black but also on its modification during the preparation of the cathodic mixture. It is affected by the pressure for preparation of the cathode mixture to a very large extent.

Acknowledgement

This work was supported by the 'Produits Chimiques Ugine Kuhlmann'.

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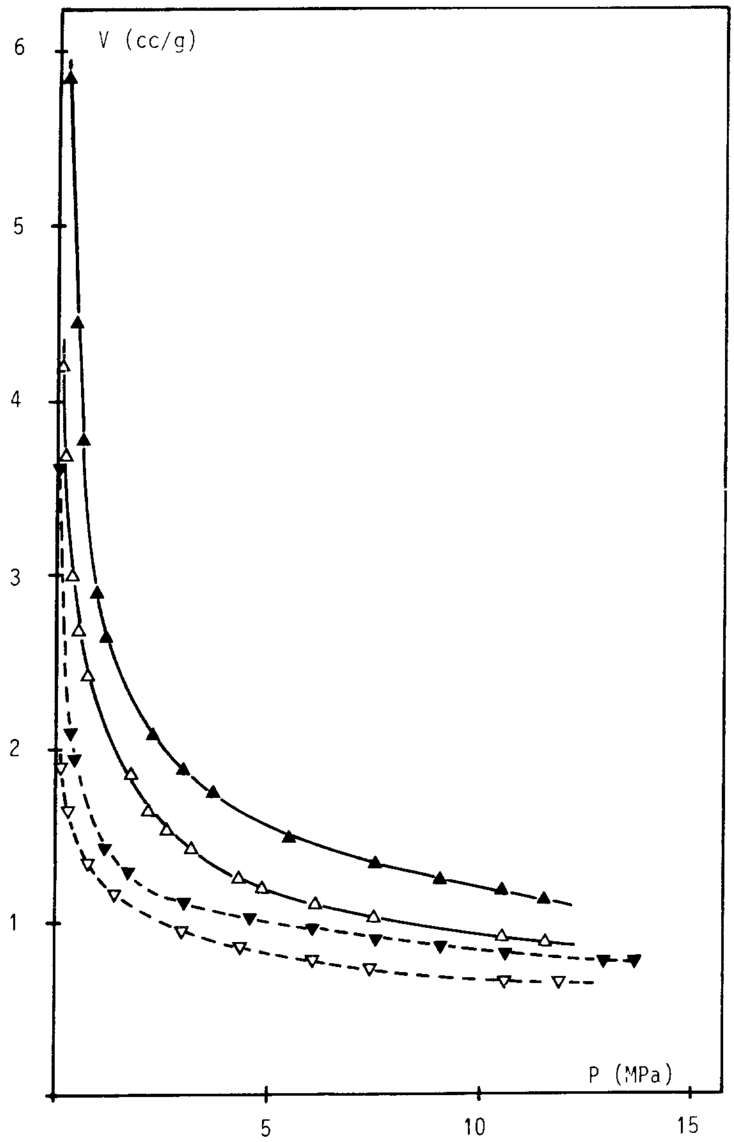

Fig. 4. Pore volume of samples against applied pressure. Dynamometric measures. Carbon C (▲) and D (▼). Mercury porosimetry Carbon C (△) and D (▽).

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