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Influence of carbon black properties on the behaviour of the cathode of a Leclanché-type battery

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Cathodic mixtures of Leclanché batteries were characterized by their electronic and ionic resistivities and by their volume resistances associated with the electrochemical reaction of MnO_2. The ionic resistivity of the cathodic mixture is much higher than the electronic resistivity for the conductive blacks used. Results allow computation of the thickness of the cathodic mixture in which electrochemical reaction takes place uniformly.

1. Introduction

In a Leclanché battery the cathode includes manganese dioxide (MnO_2), conductive carbon black and electrolyte. It was shown in a recent paper [1] that the reactivity of carbon is not sufficient to be a controlling step in the process involved. The present paper is concerned with the characterization of the electrochemical properties of the cathode.

Electrodes are often represented by an equivalent circuit including a conduction resistance, R_c, (electrolyte and conductors), a polarization resistance, R_p, and a double layer capacity [2–5]. The impedance, Z, of the circuit tends to R_c and $(R_c + R_p)$ for short electric pulses and direct current, respectively. This model, alone, does not allow differentiation between data relevant to carbon black and other constituents (MnO_2, electrolyte).

A more specific model proposed by Euler, 20 years ago [6, 7], appears to be an acceptable way of describing an electrode containing a carbon conductor [8]. In this model, the electron flux propagates through a carbon black chain resistance, R_e; when it reaches a particle of manganese dioxide, MnO_2, part of it participates in the electrochemical reactions and the current breaks up into an electronic and an ionic component. The ionic current passes through an electrolyte channel of resistances R_i. The system can be characterized by three parameters:

ρ_e(Ω cm): electronic resistivity of cathode

ρ_i(Ω cm): ionic resistivity of cathode

r (Ω cm^3): volume resistance associated with electrochemical reaction of MnO_2

The present paper is an attempt to determine the value of these parameters.

The total resistance R_T of the cathode which has geometric surface S, length L [6] and is crossed by a current I, can be represented as:

$$R_T = \frac{\rho_e \rho_i}{(\rho_e + \rho_i)} \frac{L}{S} \times \left[1 + \frac{2 + \left(\frac{\rho_e}{\rho_i} + \frac{\rho_i}{\rho_e} \right) \cosh \alpha L}{\alpha L \sinh \alpha L} \right] \qquad (1)$$

with $\alpha^2 = (\rho_e + \rho_i)(1/r)$.

It is worthy of note that the resistance, r, can be disregarded for a short current pulse. In that case:

$$R_T = \frac{\rho_e \rho_i}{(\rho_e + \rho_i)} \frac{L}{S} \qquad (2)$$

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By analogy with the general model of the electrode [2–5] mentioned above, Expression 2 can be identified with the conduction resistance, R_c, and the second term of Equation 1 with the polarization resistance, R_p

$$R_c = \frac{\rho_e \rho_i}{(\rho_e + \rho_i)} \frac{L}{S} = \rho_c \frac{L}{S} \tag{3}$$

where ρ_c is the conduction resistivity

$$R_p = \frac{\rho_e \rho_i}{(\rho_e + \rho_i)} \frac{L}{S} \times \left[\frac{2 + \left(\frac{\rho_e}{\rho_i} + \frac{\rho_i}{\rho_e} \right) \cosh \alpha L}{\alpha L \sinh \alpha L} \right] \tag{4}$$

The Euler model will be used in the present paper because it is convenient for the presentation of the results. Naturally, this does not imply that this model provides a full description of the properties of a Leclanché-type cathode.

2. Experimental details

Cathodic mixtures made of conductive carbon black, natural MnO_2 and electrolyte were prepared according to a method described elsewhere [1]. The composition of electrolyte (in weight) was: 26% NH_4Cl, 10% $ZnCl_2$ and 64% H_2O.

The conductive carbon blacks used, referred to as A, B, C, D, exhibit different performances [1]. A, B and D are acetylene black; C is a non-acetylene black.

The compositions of the cathodic mixtures used in this part of the study are shown in Table 1.

Differences between carbon black grades are apparent for continuous discharges at high current density [9]. For this type of discharge, indeed, the limiting factors are the diffusion of protons and the supply of electrons to MnO_2 [10]. For continuous discharges at low intensity, or discontinuous discharges, the capacity of the cathode is primarily dependent on the proportion of active elements: MnO_2/electrolyte.

Continuous discharge at 10 mA cm^{-3} was performed in the present study, in order to compare the various carbon blacks used.

Table 1 shows also 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 (*ca.* 0.9 V for the total battery), under a direct current of 10 mA cm^{-3}. The samples were cylinders with a cross section of 7 cm^2 and length of 0.55 cm. The weight of a sample varied between 7 and 8.5 g following the composition of the mix. The sample was deposited on a graphite piston which was introduced into a methylmethacrylate cylinder. It was separated from the electrolyte poured into the upper part of the cylinder by a layer of electrolyte gellified with agar-agar. This layer allowed ionic migration and prevented damage to the sample by the electrolyte. The anode was made of zinc perforated in its centre to introduce a reference electrode and a capillary tube.

The values of the parameters ρ_e, ρ_i and r were determined for the different mixtures. Three methods were used, namely, i. a pulse method for measuring the total conduction resistivity, ρ_c ii. a method using direct current in the absence of electrochemical reaction at the cathode for measuring the electronic resistivity, ρ_e and iii. a third technique using direct current (electrochemical reaction occurring) and completed by the pulse method, allowing the measurement of the volume resistance associated with the electrochemical reaction.

Table 1.

Conductive carbon black	*Weight of carbon black (g)*	*Weight of MnO_2 (g)*	*Volume of electrolyte (cc)*	*Capacity*
A	12	100	60	9 h 25 min
B	16	100	60	8 h 00 min
C	12	100	47	8 h 20 min
D	12	100	35	6 h 30 min

2.1. *Pulse method*

When a pulse of intensity I is applied to an electrical circuit, the potential difference is proportional to the total conduction resistance, R_c

$$\eta = R_c I \tag{5}$$

Pulse techniques have been used extensively [2–5]. In the present study a pulse generator of two microseconds was used at a frequency of 500 Hz and with an intensity of 1 mA.

The potential of the cathode, V, measured with respect to the saturated calomel electrode depended on the current intensity.

$$\text{for } I = 0 \quad V(I) = E - E_{\text{ref}} \tag{6}$$

$$\text{for } I \neq 0 \quad V(I) = E - \Delta U - E_{\text{ref}} \tag{7}$$

The fall of potential ΔU in the sample is due to the conduction resistance, R_c, and the contact resistance, C

$$\Delta U = (R_c + C)I \tag{8}$$

whence one infers that:

$$\frac{V(I = 0) - V(I \neq 0)}{I} = \frac{\Delta U}{I} = \rho_c \frac{L}{S} + C \tag{9}$$

Equation 9 points to a linear relation between the $(\Delta U/I)$ ratio and the thickness, L, of the sample. This was experimentally verified in the case of carbon D by the data shown in Fig. 1.

2.2. *Direct current method in the absence of electrochemical reaction*

Mixtures of carbon black, MnO_2 and electrolyte compressed under 785 kPa pressure, were introduced to a methylmethacrylate cylinder between two graphite pistons under a pressure of 140 kPa, and a direct current of 10 mA was applied to the system.

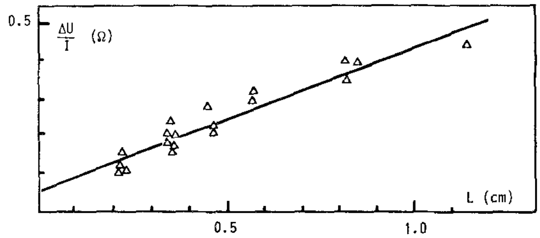


Fig. 1. Ratio of potential difference between cathode and reference electrode to intensity vs sample thickness.

The resistance measured can be represented as:

$$R_e = \frac{\rho_e L}{S} + C' \tag{10}$$

where C' is the contact resistance.

The electronic resistivity, ρ_e, can be determined from the slope of the R_e vs L plot.

2.3. *Combination of direct current and pulse method*

The previous paragraphs are related to the determination of the conduction resistance by a pulse method and of the electronic resistance by using direct current.

The measurements of the polarization resistance were carried out with the device used in Section 2.1, completed with a galvanostat and a potentiometric recorder for measuring the potential difference between the cathodic mixture and reference electrode as a function of time.

In a first step, the ratio

$$\frac{V(I = 0) - V(I)}{I} = R_c + C \tag{9'}$$

was measured with a pulse and, then, a direct current I' was imposed without modifying the cell.

$$\frac{V(I' = 0) - V(I')}{I'} = R_c + R_p + C \tag{11}$$

The polarization resistance was obtained by subtracting Equation 9′ from Equation 11:

$$\Delta U_p = R_p I' \tag{12}$$

The reproducibility was *ca.* 5%.

It is worthy of note, that when the direct current, I', is applied to the cell containing the cathodic mixture, the potential of the cathode rapidly decreases; indeed, manganese dioxide is reduced and the diffusion of ions is not fast enough to reach a steady state and therefore the polarization, R_p, is a function of time. Extrapolation of curves at $t = 0$ lacks precision, so that R_p was conventionally measured five seconds after closing the circuit. The effect of time on the measured parameters is examined later.

Equation 12 for $t = 5$ s can be written as:

$$\Delta U_p^* = R_p^* I' \tag{12'}$$

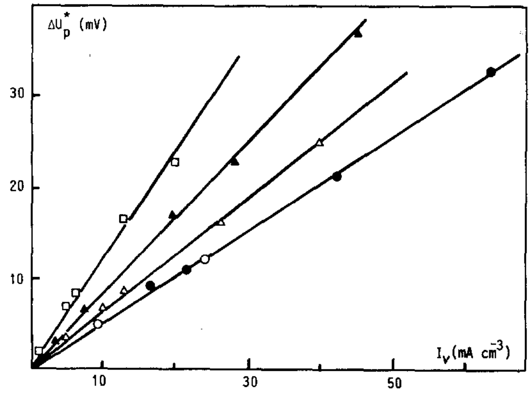


Fig. 2. Bias voltage ΔU_p^* vs current for various thicknesses, L, of samples. L (cm ± 2%): ○ 0.23; ● 0.33; △ 0.55; ▲ 0.76; □ 1.14.

The polarization resistance, R_p (Equation 4), as a function of sample thickness, is independent of the current applied provided parameters ρ_e, ρ_i and r remain constant. Hence the bias voltage ΔU_p for $t = 5$ s is expected to be proportional to the current. Fig. 2 illustrates this point for sample A: the slope $(\Delta U_p^*/I_v)$ is independent of L for low values of this parameter and increases with L for higher values. A critical value L_0 is shown in Fig. 3. The curves obtained are in agreement with the equations developed from the Euler model. For Curve b ($t = 5$ s)

$$\frac{\Delta U_p^*}{I_v}(L \to 0) = \frac{(\rho_e + \rho_i)}{\alpha^2} = r = \text{constant} \tag{13}$$

$$\frac{\Delta U_p^*}{I_v}(L \to \infty) = \frac{(\rho_e^2 + \rho_i^2)}{(\rho_e + \rho_i)^{3/2}}(r)^{1/2} L \tag{14}$$

The value of the plateau corresponds to r, i.e. the volume resistance associated with the electrochemical reaction, and the slope of the line for $L > L_0$ is equal to

$$\frac{\rho_e^2 + \rho_i^2}{(\rho_e + \rho_i)^{3/2}}(r)^{1/2} \tag{15}$$

The electrochemical reaction, occurring initially in a layer of thickness L_0, spreads into the entire cathode; L_0 as well as r and the slope of the straightline for $L > L_0$ are increasing with t_M (Fig. 3). The values of r and L_0 depend on the carbon black used in the cathodic mixture. The parameter L_0 corresponds to the thickness of samples in which the electrochemical reaction takes place uniformly and, from a technical point of view, L_0 should be as large as possible. This parameter depends on the electronic and ionic resistivities ρ_e and ρ_i and also the volume resistance r associated with the electrochemical reaction.

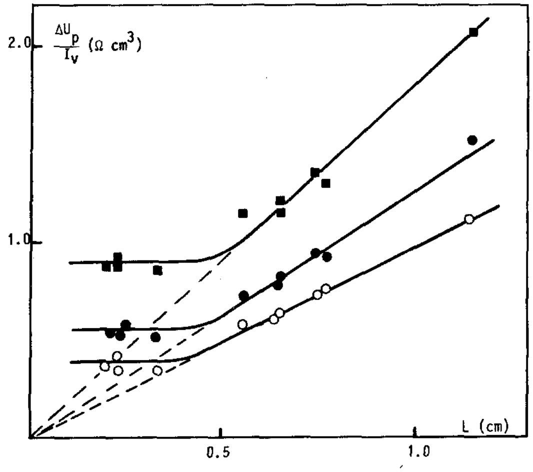


Fig. 3. Values of $\Delta U_p/I_v$ vs sample thickness L from measurements carried out at various times t_M after closing the circuit curve: ○ $t_M = 3$ s; ● $t_M = 5$ s; ■ $t_M = 10$ s.

Table 2 summarizes experimental conditions (Column 1) as well as experimental relations (Column 2). These relations compared with those corresponding to the theoretical model (Column 3) give correlations (Column 4) between parameters ρ_e, ρ and r and experimental values ΔU, I and L.

3. Experimental results

3.1. *Determination of the conduction resistivity*

The values of ρ_c (and those corresponding to electronic resistivity, ρ_e) are shown in Table 3.

The reproducibility for ρ_c and ρ_e is *ca.* 15% and 5%, respectively.

3.2. *Determination of the electronic resistivity*

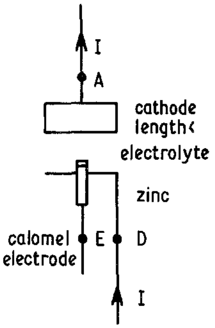
The electronic resistivity of cathodic mixtures as determined by means of the method described in Section 2.2. (Table 3) is plotted against the carbon black content (volume and weight percentages) in Fig. 4.

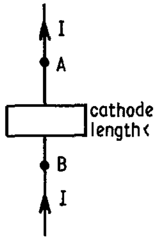
It is apparent from Table 3 that the total and electronic resistivities of the mixtures are

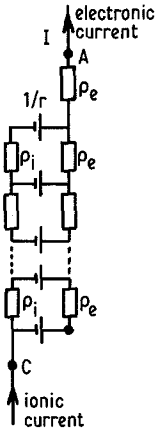
Table 2.

Experimental methods	*Experimental relations*	*Theoretical relations*	*Correlations*
2.1. Pulse method I_A^D imposed ΔU_A^E measured	$\Delta U_A^E = (R_c + C)I_A^D$	$\Delta U_A^C = R_c I$ $R_c = \rho_c \times \frac{L}{S} = \frac{\rho_e \rho_i}{\rho_e + \rho_i} \times \frac{L}{S}$	$\frac{\Delta U_A^E}{I_A^D} = \rho_c \frac{L}{S} + C$
2.2. Direct current in the absence of electrochemical reaction I_A^B imposed ΔU_A^B measured	$\Delta U_A^B = (R_c + C')I_A^B$	$R_e = \rho_e \times \frac{L}{S}$	$\Delta U_A^B = \rho_e \frac{L}{S} + C'$
2.3. Direct current (electrochemical reaction occurring) I_A^D imposed ΔU_A^E measured	$\Delta U_A^E = (R_c + R_p^*)I_A^D$	$R_T = R_c + R_p$	
2.1. then 2.3.	$(\Delta U_A^E) - (\Delta U_A^E) = R_p^* I$ direct pulse $\Delta U_p^* = R_p^* I$	$R_p LS(L \to 0) = r$ $R_p LS(L \to \infty) = \rho L^2$	$R_p LS(L \to 0) = r^*$ $R_p LS(L \to \infty) = \rho L^{*2}$

Experimental systems		*Theoretical cathode model*
2.1. 2.3.	2.2.	







extremely close, except for Sample C where the agreement is not very good. This means that for the carbon blacks studied, the ionic resistance of the cathodic mixture is large as compared to the electronic resistivity.

Table 3.

Conductive carbon blacks	*A*	*B*	*C*	*D*
ρ_c (Ω cm)	1.3	1.6	2.7	2.7
ρ_e (Ω cm)	1.3	1.4	2.2	2.8

3.3. *Ionic resitivity of the cathodic mixture*

The exact value of the ionic resitivity ρ_i cannot be computed from the values of ρ_e and ρ_c (*cf.* Section 3.2), but some information on the behaviour of the cathodic mixture can be derived from the parameters r and L_0 (volume resistance associated with electrochemical reaction and thickness of sample in which the electrochemical reaction takes place uniformly, respectively).

Fig. 5 allows determination of the values of L_0 and r for the cathodic mixture prepared from the

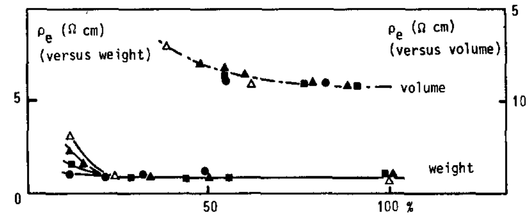


Fig. 4. Electronic resistivity of cathodic mixture vs carbon black content. —— percent weight; – – – - percent volume. Samples: A ●; B ■; C ▲; D △.

four carbon samples. The values obtained are shown in Table 4.

3.4. *Relation between the parameters* L_0 *and* r

For the critical thickness L_0, the value of $\Delta U_p^*/I_v$ corresponding in Fig. 3 to the intercept of the two linear parts of the curves satisfies simultaneously Expressions 13 and 14 and, therefore, L_0 can be written as:

$$L_0 = (r)^{1/2}\frac{(\rho_e+\rho_i)^{3/2}}{\rho_e^2+\rho_i^2} \tag{16}$$

We have seen that, for the four carbon blacks studied, the electronic resistivity is much smaller than the ionic resistivity, so that Equation 16 can be approximated by

$$L_0 = \left(\frac{r}{\rho_i}\right)^{1/2} \tag{17}$$

If ρ_0 denotes the resistivity of the electrolyte, the ionic resistivity, ρ_i, of the cathodic mixture can be written [6] as:

$$\rho_i = \rho_0\tau^2\frac{V_T}{V_e} \tag{18}$$

in which

$$\tau = \frac{\text{real travel distance of ions}}{\text{thickness of sample of cathodic mixture}}$$

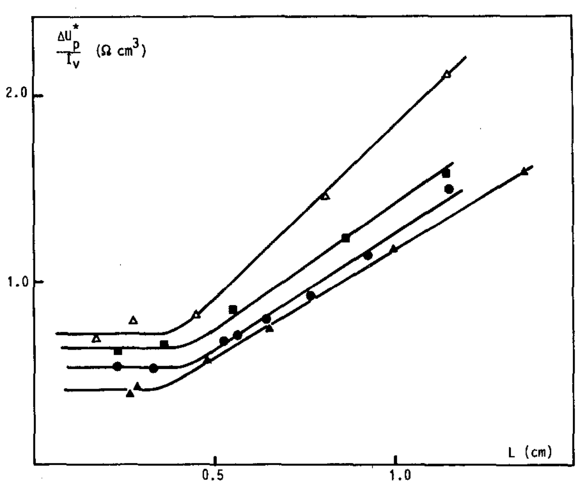


Fig. 5. Values of $\Delta U_p^*/I_v$ vs sample thickness for various samples ($t_M = 5$ s). Samples: A ●; B ■; C ▲; D △.

V_T = total volume of cathodic mixture

V_e = volume of electrolyte

Parameter τ, correlated to the porosity of the mixture, is called the tortuosity.

Combining Equation 17 and 18, leads to the relation

$$L_0 = \left(\frac{r}{\beta\rho_0}\right)^{1/2} \tag{19}$$

where β is a constant for a given mixture of carbon black and MnO_2.

L_0 was determined for cathodic mixtures in which the ionic resistivity of electrolytes ranged from 4.4. to 31.0 Ω cm, the pH being kept constant and equal to 4.6 by adding a few drops of hydrochloric acid before the electrolyte was added to the cathodic mixture. Expression 18 is verified when ρ_0 is less than 10 Ω cm (Fig. 6).

For a cathodic mixture, small values of ρ_i are beneficial as they result in large values of L_0.

Table 4.

Conduction carbon black	*Carbon weight for 100 g MnO_2 (g)*	*Volume of electrolyte (cc)*	*Capacity* (h)*	*Capacity (Cg^{-1}) MnO_2*	L_0 *(cm)*	r *(Ω cm³)*
A	12	60	9 h 25 min	300	0.44	0.55
B	16	60	8 h	260	0.45	0.65
C	12	47	8 h 20 min	235	0.35	0.42
D	12	35	6 h 30 min	155	0.39	0.72

* Cathode 0.55 cm thick; time required to reach a potential of −120 mV with respect to saturated calomel electrode for a direct current of 10 mA cm^{-3}.

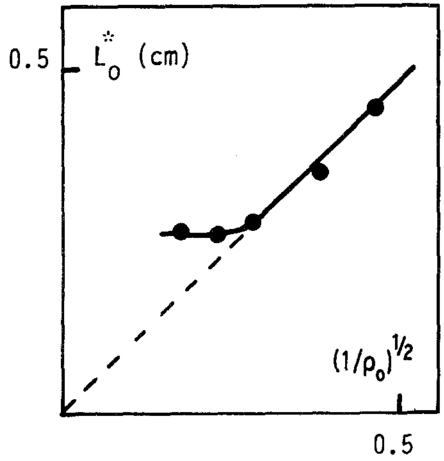


Fig. 6. Critical thickness of sample L_0 vs square root of reciprocal of ionic resistivity of electrolyte.

Parameters L_0 and r for the various cathodic mixtures are related by Expression 17. By plotting the values of L_0 against $(r^*)^{1/2}$, the ionic resistivities of cathodic mixtures can be compared (Fig. 7). The ionic resistivity (reciprocal of square of slope) are identical for the conductive carbon blacks used.

3.5. *Variation of volume resistance,* r_i *with composition of cathodic mixture*

For low values of bias voltage, the first term of the series expansion of the Tafel equation leads to:

$$\Delta U_p = \frac{RT}{nF}\frac{1}{i_0}\frac{I}{s_z} \qquad (20)$$

where *R*, *T*, *n* and *F* are the usual symbols and

i_0 = exchange current density

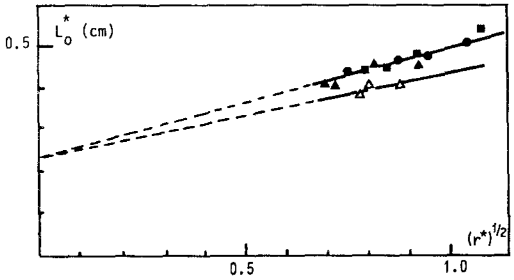


Fig. 7. Critical thickness of sample L_0 vs square root of volume resistance associated with the electrochemical reaction $(r)^{1/2}$ for different compositions of cathodic mixture.

I = total current

s_z = surface of electrode where electrochemical reaction occurs

For $L < L_0$, i.e. when the reaction proceeds uniformly through the whole volume,

$$S_r = s_r^0 SL \qquad (21)$$

By making use of Equations 20, 21 and the limit of Equation 13 when L approaches zero, it can be written as:

$$\frac{1}{r} = \frac{nF}{RT} i_0 s_r^0 \qquad (22)$$

The reactive surface s_r^0 is a function of both contact surfaces MnO_2–carbon black and MnO_2–electrolyte, which determine respectively the migration of electrons and ions, required for the cathodic reaction $MnO_2 + e^- + H \rightarrow MnOOH$.

The reactive surface is zero for cathodic mixtures containing 0 and 100% of carbon black and hence it is bound to pass through a maximum for an intermediate value. As a matter of fact, $(1/r)$ displays a maximum on the assumption that

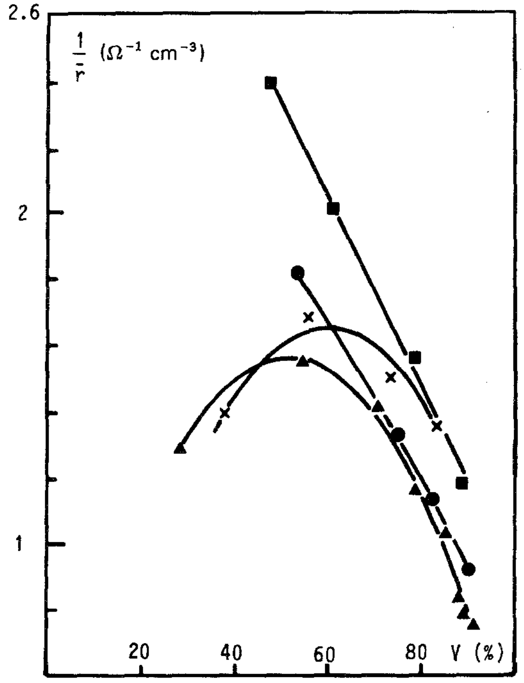


Fig. 8. Reciprocal of volume resistance associated with the electrochemical reaction of MnO_2 vs volume percentage of carbon black in the cathode. Carbons A ●; B ▲; C ■; D X.

Table 5.

Carbon volume (%)	*MnO_2 (g)*	L_0 *(cm)*	*Volume of electrolyte per gram MnO_2 ($cm^3 g^{-1}$)*	*Total capacity (C)*	*Capacity per gram MnO_2 ($C g^{-1}$)*
27.5	6.85	-	0.35	995	145
55.0	4.25	0.45	0.60	1100	260
79.0	1.95	0.48	1.45	965	495
88.5	1.09	0.50	2.70	780	715

the exchange current density is constant (Fig. 8). For carbon A and C the maximum is not located inside the domain of the carbon black content studied (40–90%). It may be noted that for carbon B the maximum corresponds to a carbon content (55% in volume) very close to the value of Leclanché-type batteries.

Table 5 shows, in the case of Sample B, the total capacity of the battery (as previously characterized) and the capacity per gram of MnO_2 as a function of the carbon content.

The larger the amount of carbon black in the mixture the higher the yield of electrochemical conversion of MnO_2.

At the same time, however, the quantity of MnO_2 available decreases: the total capacity of the batteries passes through a maximum around 55% carbon black, in agreement with the variation of $(1/r)$. Accordingly, the capacity per gram of MnO_2 increases with the carbon content of the cathodic mixture.

The cathode capacity, in coulombs per gram of MnO_2, is expected to be also dependent on the carbon black grade used. Carbons B and C are compared in Table 6.

For identical volume percentages of carbons, the volumes of electrolyte are equal. The difference in capacity for carbons B and C results neither from the quantity of electrolyte nor from the thickness L_0, but might be correlated to S_r^0, the reactive surface per gram of MnO_2. The reactive surface would depend on the morphology of the carbon used.

4. Conclusion

Cathodic mixtures are characterized by their electronic and ionic resistivities and also by the resistance associated with the electrochemical reaction. Values of ρ_e and ρ_i are quite similar for the four carbon grades used. The r values depend on concentration and type of carbon black; they are correlated to the active surface of the MnO_2/carbon/electrolyte systems.

The capacity of batteries passes through a maximum for a given composition, depending on the carbon used. The position of the maximum depends on the amount of electrolyte taken up by the carbon black and the extent of the MnO_2/carbon interface.

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Table 6.

Carbon weight per 100 g MnO_2	*Volume* percentage of carbon*	*Volume of electrolyte per g of MnO_2 (cm^3)*	L_0 *(cm)*		*Capacity ($C g^{-1}$ MnO_2)*	
			Carbon B	*Carbon C*	*Carbon B*	*Carbon C*
16	55	0.6	0.45	0.40	260	310
50	79	1.45	0.48	0.45	490	590
100	89	2.7	0.5	0.45	715	805

* Volume percentage with respect to total volume of the sample.

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