Published in Progress in Batteries & Battery Materials 15, 81-88, 1996
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ON THE PHYSICO-CHEMICAL PROPERTIES OF CARBON BLACKS IN RELATION TO THE PERFORMANCE OF Zn/MnO$_2$ BATTERIES

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Introduction

Although carbon blacks are not involved in the chemical reaction of Zn/MnO$_2$ (Leclanché) batteries, they play an important role in the actual performance of the system. Properties such as the initial short-circuit intensity I_K, the discharge characteristics, the total energy E and the capactity C strongly depend on the state of the black mixed in the paste of the cell.

The present paper is a contribution from our laboratory, which has been dealing for many years with the characterization of carbons, including carbons blacks (1)(2). The main physico-chemical properties are the surface area, the microporosity-often present in carbon blacks-and the hydrophilic/hydrophobic character of the surface. This information is obtained from gas adsorption and from immersion calorimetry, interpreted within the framework of the standard BET model (non-porous surfaces) and on Dubinin's theory for the filling of micropores (3). We also consider the fractal dimension (4)(5) D of the surface, a measure of its roughness, and the mass-fractal character D_m, which reflects the ramification of the carbon black aggregates (6).

The purpose of our work is to examine the influence of a number of physico-chemical parameters on the performances of Zn/MnO$_2$ batteries prepared under standard conditions.

Experimental

The samples selected for our study are of commercial and domestic origin and are based on acetylene or other hydrocarbons. We also included graphite and a carbon black graphitized at 2700°C, in order to examine the influence of the highly organized structure on the performance of the batteries.The general properties of the solids, including X-ray data (c/2), are given in Table 1. The solids were characterized by

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adsorption and immersion techniques, as described in refs. 1-2. A few samples were also examined by High Resolution Transmission Electron Microscopy and by Scanning Tunnelling Electron Microscopy (STM) (7).

Electrochemical experiments were carried out with home-made batteries prepared in a standard fashion: First, 15 g of synthetic MnO_2 were mixed in a beaker with 3 g of the carbon black to be tested and a solution containing 3 g of NH_4Cl and 3 g of $ZnCl_2$ in 6 g of water was added to it, dropwise. The cathodic paste was then spread out on a glass plate and mixed with a plastic spatula. Finally, it was compacted in the battery with a press, by applying a weight of 17.5 kg, and the carbon rod was introduced in its centre with a plastic guide. The carbon electrode and the Zn cylinders used to manufacture the batteries were supplied by *VARTA GmbH*, Ellwangen, Germany. During the experiments, the batteries were thermostatted at 293 K (20^oC).

Table 1. Main properties of the carbon blacks

Sample	c/2 Å	surface m^2/g	$-h_i$ (H_2O) J/m^2	D	I_K A	I_0 A	a (10^{-3})	n	E_∞ J	C_∞ A·h
AY	3.52	130	0.127	2.11	2.23	0.125	7.50	0.42	11678	13.80
HOE	3.45	52	0.063	2.14	2.14	0.130	1.76	0.54	9957	7.52
LX-100 B	3.45	70	0.055	2.17	1.48	0.127	1.80	0.54	9263	7.13
ACPET	3.41	193	0.061	2.34	1.13	0.119	19.3	0.37	7233	8.87
XE-2	3.48	162	0.133	2.29	1.17	0.126	2.95	0.51	6735	5.66
XYL-30	3.49	145	0.055	2.22	0.97	0.117	3.40	0.50	5793	5.48
XYL-NE	3.50	133	0.044	2.25	0.97	0.114	3.82	0.50	4263	4.14
XC-72	3.43	260	0.036	2.38	1.18	0.124	0.547	0.69	3965	2.43
HUM	3.51	108	0.069	2.33	0.91	0.107	2.15	0.55	3706	3.39
NG2700	3.40	90	0.029	2.12	0.54	0.088	17.3	0.38	1977	3.84
GRAPHITE	3.34	11	~0.030	2.10	0.66	0.085	500	0.14	688	33.6

Results and Discussion

As illustrated in Figure 1, in the case of carbon blacks with average and poor battery performances, the short-circuit intensity I_K measured for a given series of batteries appears to be a linear function of the fractal character D of the surface, derived from the adsorption isotherm of different vapours (4)(8) and correlated by Fourier analysis of STM data (7). On the other hand, one observes much higher I_K values for the better samples, such as acetylene blacks AY, HOE and LX-100 B (*Murablack India Ltd.*, based on a light feedstock). This indicates the influence of other structural parameters, for example the mass fractal character D_m, as discussed below. It is important to note that the role of the fractal dimension D of the carbon electrode itself has been described by Le Méhauté *et al.* (9)(10), who showed that it is related to the discharge time τ and the discharge intensity I,

$$I^D \tau = \text{constant} \qquad (1)$$

Therefore, it is not too surprising to find that the fractal dimension of the carbon blacks themselves and of their aggregates may also play an important role in the electrochemical properties of the batteries.

The discharge curves I(t) of the various batteries were determined at 293 K, for an external resistance of 10 Ω, for periods up to 72 hours or beyond. Fig. 2 illustrates the case of the batteries containing carbon blacks HOE and LX-100 B. For the various samples, our experimental results were fitted successfully to the following empirical relation, the time being given in seconds,

$$I(t) = I_0 \exp[-a \cdot t^n] \qquad (2)$$

Since the integral of this function and of its square are known, it is possible to obtain expressions for the total capacity C_∞ and for the energy E_∞ dissipated through an external resistance R,

$$C_\infty = \int_0^\infty I(t)\,dt = [I_0 / n \cdot a^{1/n}] \cdot \Gamma(1/n) \qquad (3)$$

and

$$E_\infty = \int_0^\infty R \cdot I^2(t)\,dt = [R \cdot I_0{}^2 / n \cdot (2a)^{1/n}] \cdot \Gamma(1/n) \qquad (4)$$

where Γ represents the tabulated *'Gamma'* function.

Parameters I_0, a and n of equation (2) are given in Table 1. It appears that for our series of batteries, I_0 is found in the range of 0.110 to 0.130 A, with the exception of graphitized carbon black NG-2700 and graphite, with significantly lower values. In agreement with the work of Bourrat and Oberlin, the comparison of I_0 with I_K and their evolution suggests again that the mass fractal dimension D_m of the carbon black aggregate may play an important role. These authors had shown that the internal resistance of various batteries nearly doubled as D_m increased from 1.46 to 1.80.

The mass fractal character, seen in two dimensions by electron microscopy, is a measure of the ramification of the aggregate. For globular-and therefore spatially limited-structures, as observed for graphite and graphitized carbon blacks, D_m is close to 2. Therefore, it is not surprising that the electric properties of such aggregates are not very good. Preliminary investigations carried out on samples

LX-100 B and XYL-NE, led to values of D_m close to 1.7 and 1.8, respectively. (These values are not very accurate yet, since it is difficult to observe thin aggregates). On the other hand, in the case of good acetylene blacks, of the same class as samples AY and HOE, investigated by Bourrat and Oberlin (6), D_m is close to 1.5. This observation would confirm the influence of the aggregate's ramification on the current I(t) and in particular on I_K. Consequently, it would be advisable to use this type of aggregates in the battery's paste.

As seen in Table 1, parameter n of equations (2-4) is close to 0.5, with the marked exceptions of graphitized carbon black NG-2700 and of graphite itself. Parameter a, on the other hand, shows a much larger variation than n and good battery performances, reflected by high energies E, correspond to low values of a. For samples with poor performances, such as NG-2700 and graphite, parameter a is one order of magnitude larger. (In the case of graphite, it is interesting to note the high values of a and of the total capacity C, but the low energy E, which results from a sharp drop in voltage at the beginning of the discharge). The physical meaning of parameter a is not known yet, but it certainly reflects a number of properties of the carbon blacks.

An overall examination of our data shows that beside the fractal character, neither parameter c/2, nor the total surface area alone seem to be decisive criteria for the performance of the battery, which probably result from a combination of factors. However, graphite and the graphitized carbon black NG-2700 have a low energy of interaction with water (the specific enthalpy of immersion h_i is around -0.030 J/m^2) and the comparison with the better carbons of Table 1 suggests that an extremely hydrophobic character may have an adverse effect on the electro-chemical properties of the battery.

At the present stage, it appears that the best battery performances arise from a good ramification of the carbon black aggregates (i.e. D_m values below 1.7), a c/2 value around 0.345 nm and a relatively hydrophilic surface area ($-h_i > 0.06$ J/m^2). The external surface area itself, as opposed to the internal surface area, found in micropores, should also be sufficiently large, to ensure a contact between the carbon and the fluid around it. Moreover, as indicated by experiments with physically activated carbon blacks, it appears the creation of microporosity reduces the performances of the material in a battery. This may result from the disorder induced in the structure by the treatment.

As illustrated by Table 2, there also exists an interesting correlation between the well-known AS number of various carbon blacks and the specific enthalpy of immersion into water, $h_i(H_2O)$. This is not too surprising in view of the fact that the AS number is normally associated with the performance of the battery and it may provide an explanation for this empirical quantity. It is likely, that the fractal dimension D_m is also reflected in AS. On the other hand, it appears that the specific surface area of the solid and the AS number are not as well correlated.

Table 2. The correlation between the AS number and the specific enthalpy of immersion into H_2O. LX-100 B is an improved sample, produced in March 1995.

Sample	DE	LX-A	LX-100 B(I)	LX-100 B(II)	HOE	AY	XE-2
AS	21	23	28	35	35	50	53
$-h_i(H_2O)$	0.022	0.038	0.055	0.064	0.063	0.126	0.133
S (BET) m^2/g	74	100	70	103	52	130	162

Finally, sample LX-100 B has been used in a battery subjected to light intermittent flashlight (LIF) trough an external resistance of 5 Ω, for periods of 5 minutes with a recovery time of 10 minutes. As illustrated by Fig. 3 and 4, the performances are close to those of a typical commercial acetylene black. This shows again, that it is possible to obtain carbon blacks with properties close to those of acetylene blacks.

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Fig.1. Influence of the surface fractal dimension D on the short-circuit intensity I_K

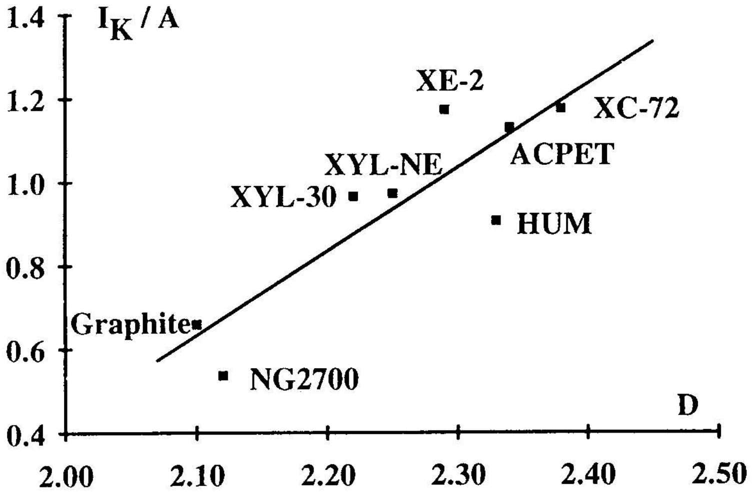


Fig.2. Discharge curves of selected samples

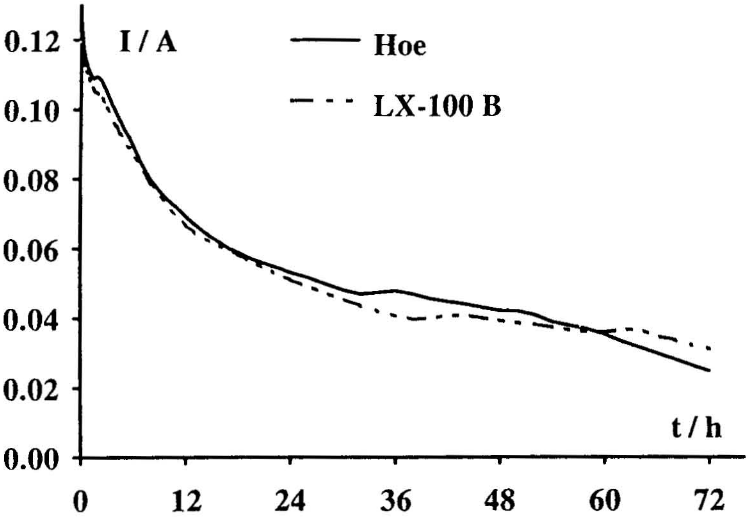
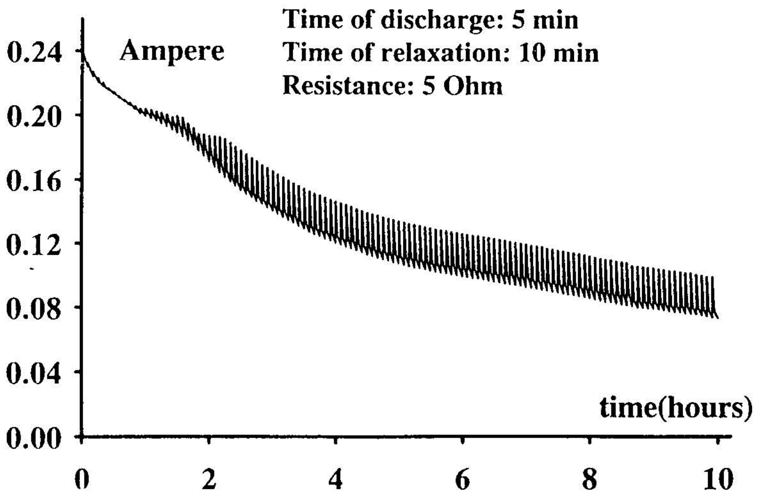
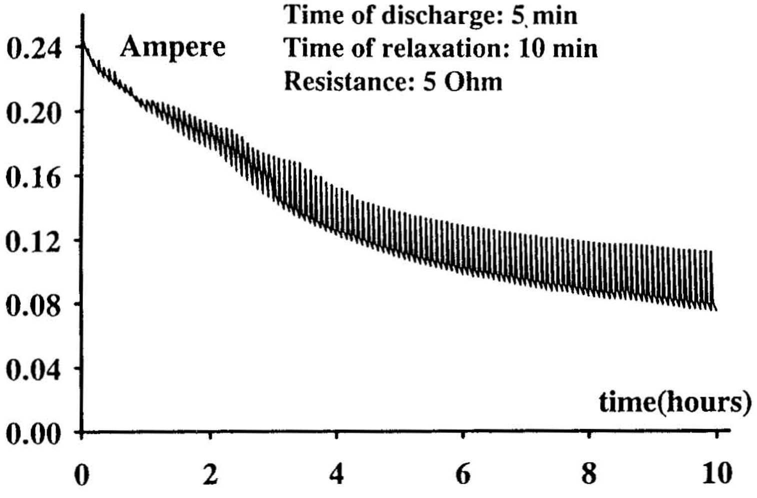


Fig.3. Light intermittent flashlight; acetylene carbon black



Time of discharge: 5 min
Time of relaxation: 10 min
Resistance: 5 Ohm

Fig.4. Light intermittent flashlight; grade: LX-100 B



Time of discharge: 5 min
Time of relaxation: 10 min
Resistance: 5 Ohm