

MACROKINETIC STUDY OF THIONYL CHLORIDE REDUCTION ON POROUS CARBON ELECTRODES

V. S. BAGOTZKY, V. E. KAZARINOV, YU. M. VOL'FKOVICH,
L. S. KANEVSKY and L. A. BEKETAYEVA

*A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR,
117071 Moscow (U.S.S.R.)*

During thionyl chloride electroreduction the effective capacity of a porous cathode is, to a large extent, determined by the amount of solid lithium chloride formed in the pore spaces of the electrode in the course of reaction [1 - 4]. The object of this study was to investigate the change in the structure properties of the electrodes during their discharge because these properties influence their performance [5 - 7].

Different types of commercial carbon black: PM 100, PM 100 V, AD 100, activated carbon AG-3, and activated graphitized cloth (Ministry of Electrical Engineering, U.S.S.R.) were used as cathode materials. Their surface areas were, respectively ($\text{m}^2 \text{g}^{-1}$): 130, 150, 800, 900 and 1600. Electrodes were prepared by applying a mixture of carbon material and PTFE (15%) to a nickel grid, followed by pressing, drying a 100°C for several hours, and sintering under load at $310 - 325^\circ\text{C}$ for 5 - 10 min.

The reduction of thionyl chloride was carried out at current densities of $0.5 - 20 \text{ mA cm}^{-2}$ in PTFE cells. Carbon cathodes, wrapped in porous propylene film, were placed between two lithium anodes in the cells. Poly(propylene) is not entirely compatible with thionyl chloride, but in short-time experiments it is of little consequence. A 1 M LiAlCl_4 solution in twice-distilled thionyl chloride, obtained by dissolution of equimolar amounts of anhydrous lithium chloride and aluminium chloride, was used as electrolyte.

Structural measurements (pore size distribution) were obtained by the standard porosimetry method (SPM). The essential principles of this method, the experimental set-up, and the analysis of results, have been described in detail in refs. 8 - 10. In this method, for varying overall amounts of a wetting liquid, ($V_t + V_s$), the amount of this liquid in the test specimen (V_t) is measured and referred to the equilibrium amount of liquid (V_s) in a porous standard specimen

$$V_t = f(V_s) \quad (1)$$

which is in contact with the test specimen and whose pore size distribution

$$V_s = \varphi(r_s) \quad (2)$$

is known. For the filled pores in equilibrium, $r_t = r_s$; thus from eqns. (1) and (2) we can obtain the pore size distribution for the test specimen

$$V_t = f[\varphi(r_t)] \quad (3)$$

The main advantages of SPM over the familiar mercury porosimetry procedure are:

- (i) the absence of high pressures and of deformation of the porous structure of the test specimen;
- (ii) the ability to study structures over a wide spectrum of pore radii (from 10 to $10^6 - 10^7$ Å);
- (iii) the possibility of studying structure changes in a specimen by repeated non-destructive testing (*e.g.*, during discharge).

SPM with decane evaporation was used to study carbon cathodes of the lithium/thionyl chloride system, because decane does not dissolve and wash out lithium chloride deposits from the carbon cathode. The series of porous samples (test specimen and standards) was assembled and dismantled in a box saturated with decane vapour.

After discharge the carbon cathodes were thoroughly washed with twice-distilled thionyl chloride to remove the electrolyte, and dried under vacuum. Each electrode was weighed and its geometric dimensions, porosity, and pore size distribution were determined.

During electroreduction of thionyl chloride, the electrode thickness increases due to the internal pressure of the insoluble products being formed. This increase in thickness is especially pronounced in the case of carbon black electrodes. Thus, after discharge at $i = 1 \text{ mA cm}^{-1}$, the thickness of a carbon black PM 100 electrode increases by 2.7 times the original value, $\delta_{\text{orig}} = 0.25 \text{ mm}$. When large current densities are used the discharge capacity decreases and, simultaneously, so does the relative increase in thickness (Fig. 1). For activated carbon and graphitized cloth electrodes, for which the discharge capacity is much less, the relative increase in thickness is insignificant.

One possible reason for the failure of electrodes to operate after a certain degree of discharge is the formation of insoluble reaction products in the pores. At high current densities the reaction is distinctly non-uniformly distributed across the electrode. Direct tests with three-layer carbon black electrodes polarized on both sides with high current densities showed that the swelling of the external layers is much greater than that of the internal layers. Thus, at high current densities the process is localized, mainly near the external surface of the electrode. This accounts for the decrease in capacity with increasing current density.

The deposition of reaction products in the electrode leads to a decrease in its porosity. We determined the porosity values of the original electrode, β_{orig} , the total porosity of the discharged electrode, β_{tot} (including pores blocked with products and also free pores), and the free porosity of the discharged electrode, β_{free} . The data obtained are listed in Table 1. These data imply that the free porosities of discharged electrodes, though being

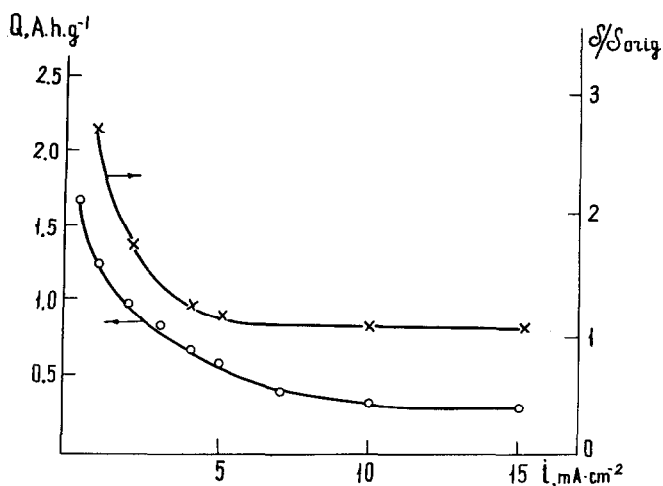


Fig. 1. Dependence of the effective capacity, Q , and the relative change in thickness $\Delta\delta/\delta_{\text{orig}}$ of carbon black PM 100 electrodes, on the discharge current density.

TABLE 1

Porosity of electrodes ($\delta_{\text{orig}} = 0.9 \text{ mm}$) before and after discharge at $i = 1 \text{ mA cm}^{-2}$

	Electrode material	
	Carbon black PM 100	Activated carbon AG-3
Original porosity (β_{orig})	0.73 - 0.76	0.62 - 0.63
Total porosity (β_{tot})	0.85 - 0.89	0.68 - 0.80
Free porosity (β_{free})	0.45 - 0.51	0.60 - 0.61
Relative increase in thickness ($\Delta\delta/\delta_{\text{orig}}$)	1.8 - 2.1	1.2 - 1.3
Capacity, Q (mA h cm^{-2})	30 - 40	5 - 5.5

less than the original porosity, are still fairly large. Thus, the failure of the electrode to operate occurs when relatively little of the overall pore volume is full of reaction products. For activated carbon electrodes the failure to operate occurs with an even higher free pore volume.

To determine the reason for these phenomena we measured the pore size distribution of different electrodes. As an example, Fig. 2 shows the integral pore size distribution curves of a carbon black PM 100 V electrode before discharge (curve 1) and after discharge at $i = 5 \text{ mA cm}^{-2}$ to 13, 30, and 100% of its capacity (curves 2, 3 and 4). The pore radii of the original electrode vary between 300 and 4000 Å for 95% of the pore space. About 5% of the pore volume have radii of less than 300 Å. As the electrode is discharged, the volume of the large pores (radii some tenths of a micron) decreases significantly, and the volume of the small pore increases (though to a much lesser degree). If we plot a difference curve of pore size distribu-

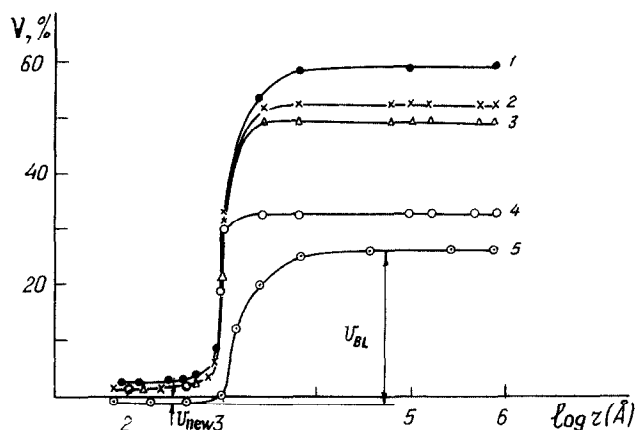


Fig. 2. Integral pore size distribution curves for carbon black PM 100 V electrodes: 1, before discharge; 2, 3, 4, after discharge at $i = 5 \text{ mA cm}^{-2}$ to 13, 30, and 100% of total capacity; 5, difference between the values of curves 1 and 4.

tion (curve 5) between the initial porogram (curve 1) and the porogram for the electrode discharged at 100% (curve 4), we see that the decrease in porosity of the large pores is 28%; the porosity of newly formed fine pores is about 1%. If we assume that these fine pores have been formed only in the lithium chloride deposit, then taking into account the pore volume occupied by this deposit, we find the porosity of the total deposit to be very small (2 - 3%).

It should be noted that lithium chloride is first deposited in the large pores. In the course of discharge its deposition extends to progressively finer pores. Data in Figs. 2 and 3 indicate that this pore filling order does

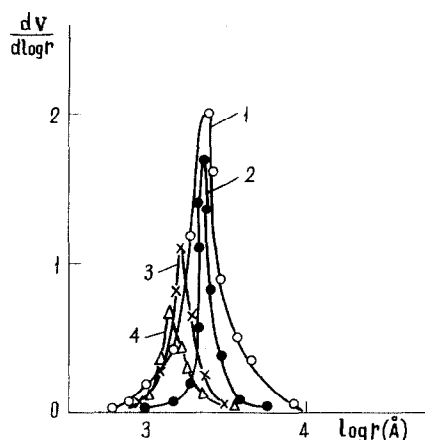


Fig. 3. Differential pore size distribution curves for carbon black PM 100 V electrodes: 1, before discharge; 2, 3, 4, after complete discharge at current densities of 10, 3 and 1 mA cm^{-2} , respectively.

not depend on the current density. The formation of a solid deposit in the large pores seems to be thermodynamically more advantageous than does that of a finely-dispersed deposit with a large specific surface.

We compared the electrical characteristics — the discharge voltage, U , and the discharge capacity, Q , measured at $i = 1 \text{ mA cm}^{-2}$ — with the porous structure parameters of the electrode which were classified by the relative pore volumes: micropore, V_{mi} (less than 20 \AA); mesopores, V_{me} (from 20 to 10^3 \AA); macropores, V_{ma} (greater than 10^3 \AA). The carbon materials used had a different structure (Fig. 4) and specific surface (from 80 to $1600 \text{ m}^2 \text{ g}^{-1}$).

As can be seen from the data of Table 2, the discharge voltage of cells with carbon black and activated carbon cathodes was 3.4 V ; for graphitized

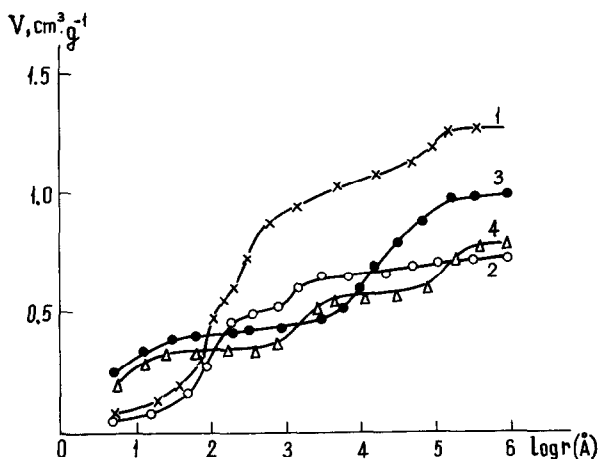


Fig. 4. Integral pore size distribution curves for electrodes of different carbon materials: 1, carbon black PM 100; 2, carbon black AD 100; 3, activated graphitized cloth; 4, activated carbon AG-3.

TABLE 2

Original structure and electrical parameters (at $i = 1 \text{ mA cm}^{-2}$) of electrodes from different carbon materials

	Electrode material			
	Carbon black PM 100	Carbon black AD 100	Activated carbon AG-3	Graphitized cloth
Porosity (β_{orig})	0.67 - 0.78	0.69	0.62	0.80
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)				
total	1.24 - 1.32	0.61 - 0.66	0.78	1.03
micropores	0.09	0.03	0.27	0.29
mesopores	0.83 - 0.85	0.53 - 0.55	0.09	0.04
macropores	0.32 - 0.38	0.04 - 0.10	0.42	0.70
Capacity, Q (mA h cm^{-2})	42.5	33	5.5	14
Voltage (V)	3.45	3.45	3.40	3.30

cloth it was 3.3 V. Thus, the discharge voltage values for different carbon materials are similar in spite of considerable differences in the specific surfaces of these materials. This suggests that the role of micropores in current generation is small.

It follows from the data in Table 2 that there is a marked correlation between the volume of the mesopores and the electrode capacity. Activated carbon and graphitized cloth electrodes have a small mesopore volume ($0.04 - 0.12 \text{ cm}^3 \text{ g}^{-1}$) and a very low capacity, 3 - 6 times less than that of different kinds of carbon black electrodes which had relatively large volumes of mesopores. This fact is of interest in that carbon black electrodes have much smaller specific surfaces and micropore volumes than graphitized cloth electrodes.

This result indicates that current generation occurs mostly in medium size pores. The small contribution of micropores to this process is probably associated with their specific surface properties. Macropores cease to participate in the reaction quite quickly due to the deposition and accumulation therein of solid products.

Insoluble reaction products, which first of all block the macropores, do not, in practice, decrease the working surface of the electrode, and this is an aid to keeping the voltage constant over prolonged discharge times. Hence, this order of the blocking of pores is beneficial to cell operation.

The accumulation of reaction products in the pores results in pressure on the pore walls and in electrode stretching (swelling), *i.e.*, an increase in the thickness and the total pore volume. Termination of discharge — a sharp drop in cell voltage — can result from both hindered mass transfer in the pores due to some decrease in the real free porosity, and from deterioration of the mechanical, and hence electrical contact between carbon particles (*e.g.*, incorporation of nonconducting reaction product interlayers between the particles), which leads to a sharp increase in ohmic polarization during discharge. Direct measurements of ohmic polarization (by oscillographic recording of the voltage drop when current is switched off) showed that within 7 h of the beginning of discharge, the ohmic resistance of activated carbon electrodes increases dramatically (from $40 \Omega \text{ cm}^{-2}$ at the beginning of discharge to $200 \Omega \text{ cm}^{-2}$), whereas for carbon black electrodes the resistance does not increase significantly, even at the end of discharge (it increased from 20 to $40 \Omega \text{ cm}^{-2}$).

Thus the first of the suggested reasons for limited electrode capacity (deterioration of the mass transfer conditions) plays a major role for the elastic carbon black electrodes, and the second reason (decrease of electronic conductivity) is controlling for the much less elastic activated carbon electrodes.

The elasticity of carbon black electrodes is, to a considerable extent, probably due to the branching structure of the carbon black particles. Individual branches are capable of contracting and expanding, and maintaining electrical contact with neighbouring particles. In the general case, the elasticity of the electrode structure is affected both by the shape

of the particles and by their surface properties, as well as by the properties of the binder.

Thus the considerably lower elasticity of the activated carbon electrodes, as compared with that of the carbon black electrodes, is the second reason (apart from the small volume of the mesopores) for their lesser capacity. Presumably, for graphitized cloth electrodes, which are more elastic than activated carbon electrodes, the main reason for the low capacity is the very small volume of mesopores.

It follows from the foregoing that the electrochemical properties of cathodes involved in thionyl chloride reduction are affected by their porous structure, catalytic activity, the surface properties of the particles, and the mechanical properties of the electrode as a whole.

References

- 1 J. A. Auburn, K. W. French, Sh. I. Lieberman, V. K. Shah and A. Heller, *J. Electrochem. Soc.*, 120 (1973) 1613.
- 2 W. K. Behl, J. A. Christopoulos, M. Ramirez and S. Gilman, *J. Electrochem. Soc.*, 120 (1973) 1619.
- 3 A. N. Dey, *Electrochim. Acta*, 21 (1976) 377.
- 4 L. A. Beketayeva, Yu. M. Vol'fkovich, Yu. M. Povarov and V. S. Bagotzky, *Sov. Electrochem.*, 13 (1977) 1563.
- 5 K. A. Klinedinst, *J. Electrochem. Soc.*, 132 (1985) 2044.
- 6 P. W. Krehl and D. A. Danner, in *Proc. 21st Intersoc. Energy Convers. Eng. Conf., San Diego, CA., Aug. 25 - 29, 1986*, Vol. 3, Washington, D.C., 1986, p. 1581.
- 7 V. Danel, J. P. Seccroix and A. Petit, in *Proc. Symp. Lithium Batteries, Washington, DC, Oct. 9 - 14, 1983*, The Electrochemical Society, Pennington, NJ, 1984, p. 136.
- 8 Yu. M. Vol'fkovich, V. S. Bagotzky, V. E. Sosyonkin and E. J. Shkol'nikov, *Sov. Electrochem.*, 16 (1980) 1325.
- 9 L. A. Beketayeva, Yu. M. Povarov and Yu. M. Vol'fkovich, *Sov. Electrochem.*, 16 (1980) 737.
- 10 V. E. Karzarinov, Yu. M. Vol'fkovich, M. Ya. Katz *et al.*, *Microprocessor Devices and Systems*, 2 (1987) 84 (in Russian).