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Porosity of the cathode during the discharge of $SOCl_2$/Li batteries Influence of the porous morphology of the carbons used

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Abstract

During the discharge of $SOCl_2$/Li batteries, the LiCl deposits mainly at the entrance of the widest pores. C/Ni/PTFE cathodes were prepared with 12 varieties of carbon materials. The discharge is strongly depending upon the carbon used. The capacity of the battery is mainly correlated to the pore volume of the cathode. However, for cathodes with a significant pore volume, the capacity is also correlated to the specific surface area.

Keywords: Carbon black; Carbon fibers; Electrodes; Electrochemical properties; Porosity

1. Introduction

In two previous papers, the variation of the porosity of the cathode during the discharge of a $SOCl_2$/Li battery was described for an industrial [1] and for a model [2] cathode.

The comparison of the electrodes by mercury porosimetry before and after discharge points out a significant variation of the porous distribution. The higher the amount of deposited LiCl, the higher this variation. It was noticed [1,2] that the decrease of the pore volume by LiCl deposition does not correspond to the volume of LiCl produced: the pore volume of the electrode simultaneously increases by swelling of the pore network. Such a phenomenon significantly disturbs the description of the location of LiCl in the pore network of the cathode. From the results of partial discharges at low current density, a model of the pore filling by LiCl during the discharge of the battery was given [2]. In this model the storage of LiCl and therefore the energy capacity of the battery is strongly depending upon the volume of pores with diameters higher than 80 nm.

In the present paper, 12 different varieties of carbons are used for the preparation of the cathodes. The performances of the electrodes and the evolution of their porosity during the discharge are determined.

2. Experimental

The discharge is carried out at constant current density and is automatically stopped when the voltage reaches 2 V [1]. The electrochemical cell is made of PTFE which provides a great resistance to corrosion. Three apertures allow the positioning of three electrodes.

1. The working electrode: a flat cylinder of carbon (10 mm diameter) deposited on a platinum electrode.
2. The counter-electrode: a sheet of metallic lithium on a platinum electrode.
3. The electrode of reference: bulk lithium on a platinum electrode.

The electrolyte consists of a solution of lithium tetrachloroaluminate $LiAlCl_4$ in thionyl chloride ($SOCl_2$). A concentration of $LiAlCl_4$ equal to 1.35 mol l^{-1} has been used corresponding to a conductivity of 0.018 Ω^{-1} cm^{-1} at 20°C. The electrolyte is introduced into a cavity at the center of the cell.

Before discharge, the carbon cathode is impregnated by $SOCl_2$ for a few hours. After discharge, the electrode is rinsed up for a few hours in $SOCl_2$ to avoid the crystallization of $LiAlCl_4$. The dimensions and the weight of the electrode are determined before and after discharge.

The porosity of the electrodes is determined by nitrogen adsorption [3,4], thermoporometry [5,6] and mercury porosimetry using a "Quantachrome PoreMaster 33" porosimeter. The total pore volume is also determined from the dimensions of the electrodes measured with a graduated

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sliding caliper gauge assuming, for most of the materials, the densities of the carbons equal to the values given by the producer.

Different varieties of carbons are used for the preparation of the cathodes. The proportions were adjusted in order to obtain an electrode mechanically stable. The cathodic mixture is introduced in a cylindrical mould, 10 mm i.d., used for the preparation of samples for infrared spectroscopy analysis and compressed under a controlled pressure.

The following carbons were used:

- mixture of YS and Y50A acetylene blacks (50/50 wt.%) as a reference;
- activated YS (CO_2 activation at 1000°C for 5 h (65 wt.%));
- Ketjenblack EC 600 JD (AKZO Chemie);
- four conductive furnace blacks: Tokablacks TB #4500 and 5500 (Tokai Carbon) and Black Pearls BP1300 and 2000 (Cabot);
- a coke (DB40) and a graphite (UF440 (Asbury)); and
- two catalytic fibers provided by Applied Science Inc. [7,8]: AN187OX (40 μm length and 0.2 μm diameter) and AN169HT (fibers graphitized at 3200°C).

Some characteristics of these materials are plotted in Table 1. The BET surface areas of the Ketjenblack and of the BP2000 are probably overestimated; their Dubinin Radushkevitch volumes (V_{DR}) are indeed equal to 0.50 $cm^3\ g^{-1}$ and a capillary condensation is expected in the domain of the BET characterization.

Table 1
Some characteristics of the carbons used for the preparation of the cathodes

	Density (g cm^{-3})	N_2 adsorption	
		S_{BET} ($m^2\ g^{-1}$)	V_{DR} ($cm^3\ g^{-1}$)
Y50A	1.87	70	0.03
YS	1.87	110	0.04
Activated YS	1.87	480	0.19
Ketjenblack EC 600 JD	1.92	1250	0.50
DB40	1.9	58	0.02
UF440	2.2	120	0.05
AN187OX	1.9	27	0.01
AN169HT	1.9	26	0.01
TB #4500	1.83	58	0.03
TB #5500	1.84	207	0.1
BP1300	1.85	560	0.20
BP2000	1.85	1500	0.50

3. Results and discussions

3.1. Preparation of the electrodes

The large spectrum of porous properties of the materials listed in Table 1 is expected to allow the identification of the parameter(s) of the cathodes responsible for their performances during the discharge.

The standard proportions of carbon/nickel/PTFE (55, 20, 25 wt.%) are not appropriate for all the carbon materials. With some materials, the cathode is brittle and the PTFE ratio must be increased which may lead to a significant decrease of the porosity. In that case the compacting pressure is reduced provided the mechanical resistance is still acceptable for the cathodes to be manipulated. It is reminded [2] that an increase of the compacting pressure reduces the pore volume of the electrode without modifying the size distribution of pores which is determined by the type of carbon material and not by its proportion in the electrode.

A very large number of experiments leads to the optimized compositions listed in Table 2 in which the computed porous volumes are deduced from the thickness of the electrode. For most of the selected materials the standard proportions (55% C, 20% Ni and 25% PTFE) lead to electrodes with a significant porosity. For the coke DB40 and the graphite UF440, it was necessary to use 75% C and 5% PTFE by weight to increase the pore volume of the cathode. To reduce the brittleness of the cathode prepared with the catalytic fiber AN187OX, the proportion of PTFE was increased to 40% and the electrode was compacted at 1273 bar in order to

Table 2
Parameters of preparation of the different cathodes

Carbon material	Composition (wt.%)			Applied pressure (bar)	Thickness (mm)	Computed pore volume ($cm^3\ g^{-1}$)
	C	Ni	PTFE			
YS and Y50A	55	20	25	5093	1.30	0.675
YS	55	20	25	5093	1.70	0.991
Activated YS	55	20	25	5093	1.54	0.858
DB40	75	20	5	1273	0.92	0.328
UF440	75	20	5	1273	0.72	0.161
AN187OX	40	20	40	1273	1.32	0.693
AN169HT	55	20	25	5093	1.20	0.579
Ketjenblack EC 600 JD	40	20	40	5093	1.17	0.570
TB #4500	55	20	25	5093	1.10	0.485
TB #5500	55	20	25	5093	1.13	0.511
BP1300	55	20	25	5093	0.86	0.288
BP200	55	20	25	5093	1.66	0.955

keep a significant pore volume. The Ketjenblack has a high porous volume but even diluted with 40% PTFE, the cathode strongly swells when impregnated by the electrolyte. This material could be used mixed to another carbonaceous material as already suggested [9].

3.2. Pore distributions of the cathodes

The cathodes were characterized by mercury porosimetry (Figs. 1–4) and nitrogen adsorption. The electrodes selected for the discharge were also characterized by thermoporo-

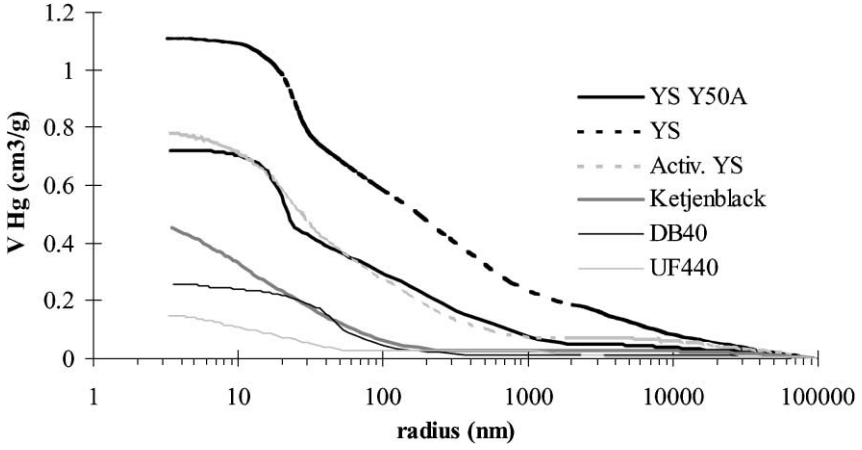

Fig. 1. Mercury porosimetry: cumulated volumes of cathodes.

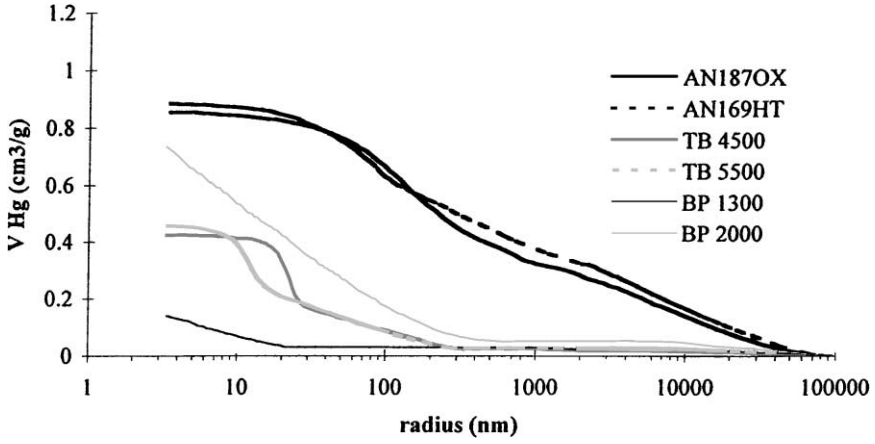

Fig. 2. Mercury porosimetry: cumulated volumes of cathodes.

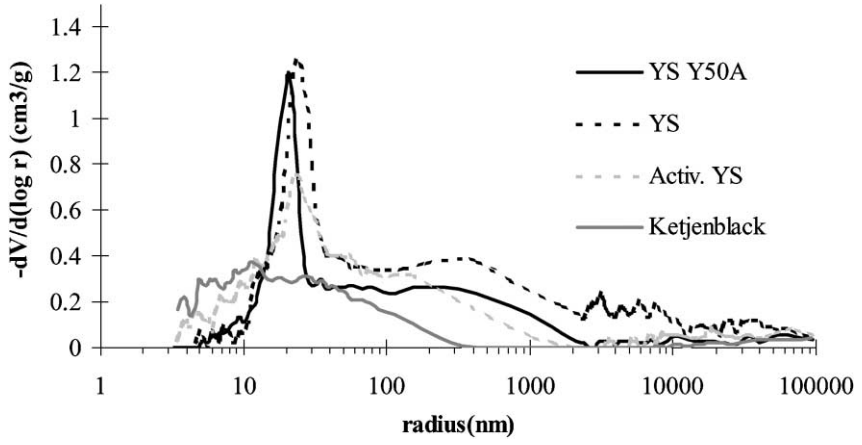

Fig. 3. Mercury porosimetry: pore distributions of cathodes.

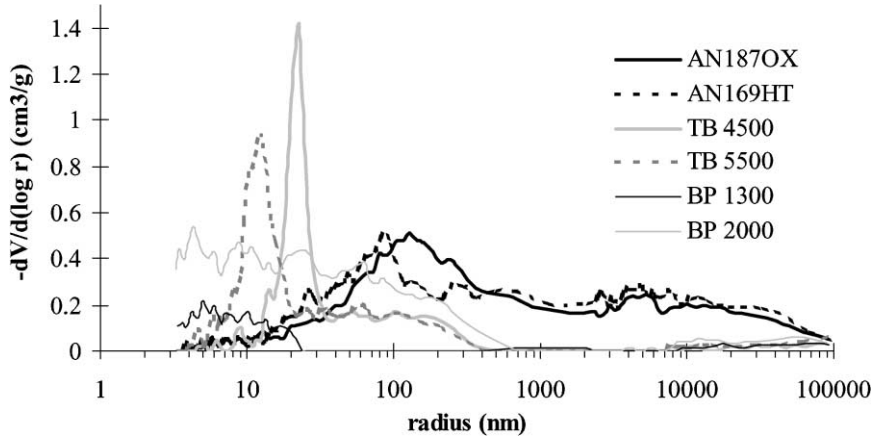

Fig. 4. Mercury porosimetry: pore distributions of cathodes.

metry with the undecane (Figs. 5 and 6). The results obtained with the different techniques are plotted in Table 3.

The values obtained with the three techniques are naturally different as the accessible pores are different. For example, the surface areas obtained by nitrogen adsorption and by mercury porosimetry agree for non or weakly microporous materials but, for microporous materials, most of the surface corresponds to the micropores which are not accessible to mercury; in practice, a good correlation is obtained for electrodes whose specific surface areas are lower than 100 $m^2\ g^{-1}$. In the same way, there is in general no agreement between the pore volumes determined by porosimetry with undecane and mercury porosimetry as the first method corresponds to pores between 10 and 200 nm, while the second one covers a much wider domain of porosity. In the case of the two Tokablacks, the agreement is good as the porosity lies in the 10–200 nm domain (Fig. 1).

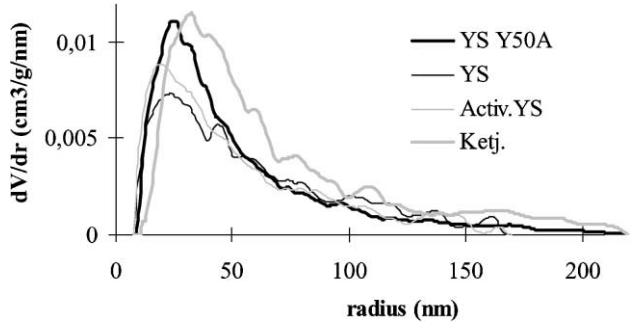

Fig. 5. Thermoporometry with undecane: pore distributions of cathodes.

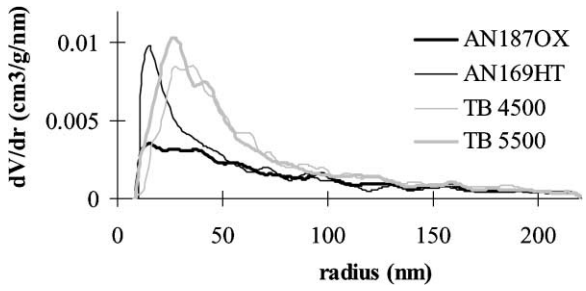

Fig. 6. Thermoporometry with undecane: pore distributions of cathodes.

Table 3
Influence of the carbon materials on the porous characteristics of the cathodes

Carbon material	N_2 adsorption		Thermoporometry ($cm^3\ g^{-1}$)	Mercury porosimetry		Thickness expansion (%)
	S_{BET} ($m^2\ g^{-1}$)	V_{DR} ($cm^3\ g^{-1}$)		V_p ($cm^3\ g^{-1}$)	S_p ($m^2\ g^{-1}$)	
YS and Y50A	38	0.01	0.51	0.735	43	21
YS	44	0.01	0.45	1.123	48	18
Activated YS	150	0.05	0.47	0.781	58	28
DB40	26	0.01	–	0.256	17	2
UF440	16	–	–	0.146	20	2
AN187OX	17	–	0.30	0.857	16	31
AN169HT	13	–	0.38	0.886	18	121
Ketjenblack EC 600 JD	350	0.13	0.69	0.454	67	184
TB #4500	24	0.01	0.50	0.425	32	4
TB #5500	58	0.03	0.54	0.456	56	3
BP1300	159	0.06	–	0.142	32	4
BP2000	540	0.22	–	0.748	105	21

In can be noticed that the total pore volumes computed from the dimensions fit the results of mercury porosimetry. It means that, on the one hand, in spite of the presence of the PTFE, most of the porosity is accessible to mercury and, on the other hand, the porosity of the electrodes is not modified by the high pressures used in mercury porosimetry (up to 2275 bar).

Three cathodes exhibit a fairly low pore volume, namely, those containing DB40, UF440 and BP1300. Such electrodes are not expected to be appropriate for an industrial utilization.

The two electrodes containing the Tokablacks have very close volumes and their distributions cover a narrow domain of pore diameters; ca. half the volume lies between 10 and 30 nm (Fig. 3).

Several cathodes have a total pore volume between 0.7 and 0.8 $cm^3\ g^{-1}$ but the pore distributions are different. As an example, the pores of the cathodes with catalytic fibers are distributed in almost the entire domain covered by mercury porosimetry while those containing the BP2000 exhibit practically no porosity above 300 nm.

Finally, it is noteworthy that the two cathodes containing the YS acetylene blacks have a peak of pore distribution at 20/30 nm while those containing the activated YS which has approximately the same pore volume below 50 nm (the narrow micropores are not accessible to mercury) exhibits no maximum of the pore distribution. Such an observation can also be make for the other electrodes presenting some microporosity (Ketjenblack and BP2000).

3.3. Discharge of the different cathodes

The discharge was carried out at 20°C with a cut-off at 2 V. For the electrode containing the graphite, the discharge is not possible as the initial voltage is lower than 2 V. In the case of the Ketjenblack, in spite of the optimization of the electrode, the discharge of the cathode was not possible because of its very high expansion in the cell.

3.4. Discharge at 5 mA cm^{-2}

The electrochemical behavior of the electrodes is strongly depending upon the carbon material which is used (Tables 4 and 5; Fig. 7). The time of discharge before cut-off is correlated to the pore volume of the electrode. Klinedinst [10] showed that the electrochemical performances are correlated to the pore volume obtained by absorption of dibutylphtalate. It can be noticed that the electrodes with a small initial pore volume (DB40 and BP1300) have a lower initial voltage and capacity.

When the pore volume is high enough (ca. 0.6 $cm^3\ g^{-1}$ and above), the total porosity does not allow to predict the electrochemical behavior of the cathode. For example, the two electrodes containing the two Tokablacks have close porous properties and give very close performances, but the comparison of these two electrodes to those containing the mixture YS and Y50A show that the performances are very close though the total pore volume of this mixture is much higher. All these electrodes have fairly low surface areas so

Table 4
Electrochemical performances of the batteries

	Time of discharge (s)	Mass LiCl (mg)	Tension of plateau (V)
YS and Y50A	37680	41.6	3.33
DB 40	6420	7.1	3.28
AN169HT	94140	103.9	3.41
TB #4500	31800	35.1	3.37
TB #5500	30360	33.5	3.40
BP1300	3360	3.7	3.10
BP2000	51540	56.9	3.30

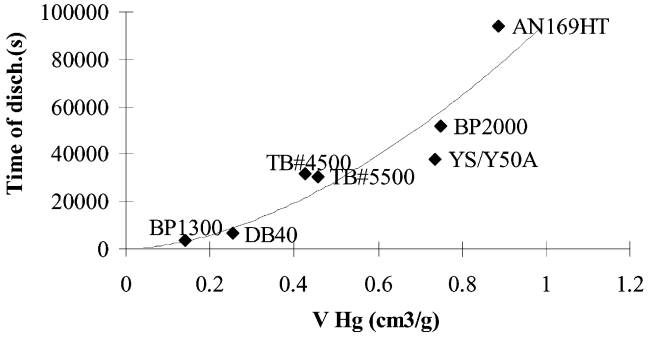

Fig. 7. Electrochemical performances of batteries vs. total pore volumes determined by mercury porosimetry (discharge at 20°C under 5 mA cm^{-2}).

Table 5
Morphology of the cathodes

	Thickness (mm)		Mercury porosimetry			
	Before	After	Pore volume ($cm^3\ g^{-1}$)		Specific surface area ($m^2\ g^{-1}$)	
			Before	After	Before	After
YS and Y50A	1.29	1.70	0.735	0.751	43	43
DB 40	0.92	1.06	0.256	0.262	–	–
AN169HT	1.2	3	0.886	0.809	18	25
TB #4500	1.10	1.44	0.425	0.462	33	39
TB #5500	1.13	1.58	0.456	0.486	56	54
BP1300	0.86	0.90	0.142	0.124	32	47
BP2000	1.66	3.1	0.748	0.949	105	142

that the behavior cannot be attributed to the surface area. In these three electrodes half of the volume corresponds to the mesopores and narrow macropores. Their pore volumes determined by mercury porosimetry are close to 0.5 $cm^3\ g^{-1}$. This result agrees the work of Bagotzky et al. [11]. It is clear that the total pore volume is not the only parameter; the size distribution is also important.

The two electrodes containing the BP2000 and the fiber AN169HT have very high capacities though their initial volumes are comparable to the electrode YS and Y50A. In the case of the BP2000 cathode, the high specific surface area may promote the interfacial exchange of electrons and therefore a better use of the available porosity. Conversely, the specific surface area of electrodes made of fibers is low and cannot be responsible for the performances of the cathode. The high performances of catalytic fibers have already been mentioned [12], but for the moment these fibers are too expensive for an industrial application.

At this stage of the investigation it appears that the pore volume and the specific surface area are two important parameters but the results with the fibers demonstrate that they are not the only ones.

The variation of the porous distribution after discharge (Figs. 8 and 9) shows the disappearance of the largest pores to the benefit of smaller pores while the total volume remains practically constant. As shown before [1,2], this redistribution of the pore volume can be explained by the preferential growth of the LiCl deposit at the entrance of the widest pores (ca. above 100 nm) without clogging; the unfilled volume appears as pores with narrower diameters. The total volume is not much affected, because the volume of the deposit is compensated by the swelling of the electrode [2].

3.5. Discharge at 20 mA cm^{-2}

It was shown above that the capacity of the battery determined by the time of the discharge at constant current density is depending upon the pore volume and on the specific surface area of the cathode. The different carbons used had different origins so that an unidentified parameter might bias this conclusion. A few experiments have been carried out with three acetylene blacks with the same origin: mixture YS and Y50A, YS and activated YS (Table 6). The pore volume of the three cathodes determined

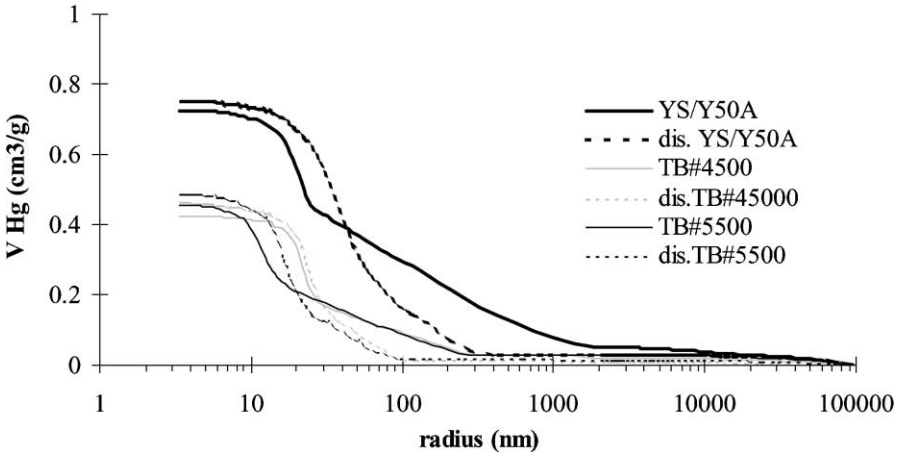

Fig. 8. Mercury porosimetry: cumulated volumes of cathodes after discharge.

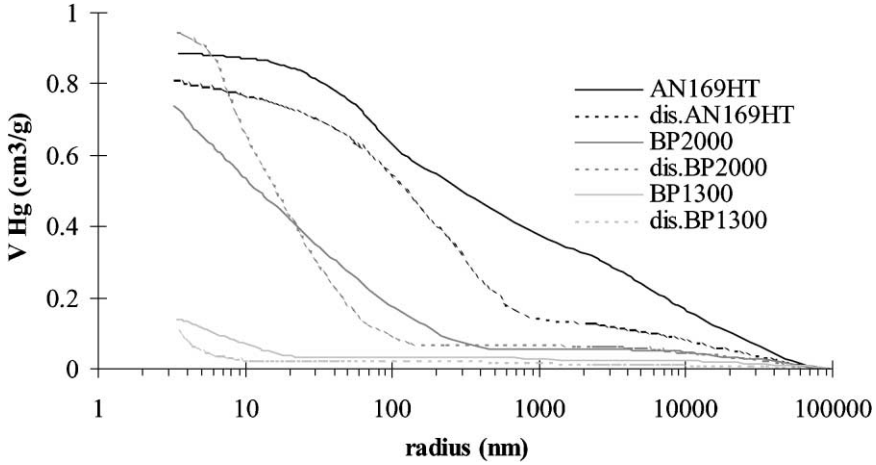

Fig. 9. Mercury porosimetry: cumulated volumes of cathodes after discharge.

Table 6
Comparison of cathodes containing acetylene blacks

	Thickness (mm)	S_{BET} ($m^2\ g^{-1}$)	V_{Hg} ($cm^3\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)		Time of discharge (s)	Tension of plateau (V)	LiCl volume ($cm^3\ g^{-1}$)	$\Delta e/e$ (%)
				Before	After				
YS and Y50A	1.30	38	0.735	0.51	0.48	3121	3.0	0.066	32
YS	1.72	44	1.123	0.45	0.42	3966	3.1	0.085	26
Activated YS	1.54	150	0.781	0.47	0.43	4832	3.3	0.103	42

by thermoporometry are very close within experimental uncertainties (Figs. 10 and 11) (S.D. of this technique is 0.07 $cm^3\ g^{-1}$ in the conditions of the present work). The cathode containing the YS sample has a higher volume accessible to mercury and those with the activated YS acetylene black has of course a higher specific surface area.

The higher electrochemical performances are obtained with the activated YS which shows the contribution of the micropores in the electrochemical phenomena. The presence of micropores improves the current distribution in the electrode which induces a higher initial voltage. The voltage of the plateau of the discharge curve is higher leading to a later cut-off at 2 V.

The cathodes prepared with YS and with YS and Y50A have similar specific surface areas and pore volumes determined by thermoporometry. Their pore volumes determined by mercury porosimetry are significantly different. The higher time of discharge obtained with YS can be attributed to the higher volume.

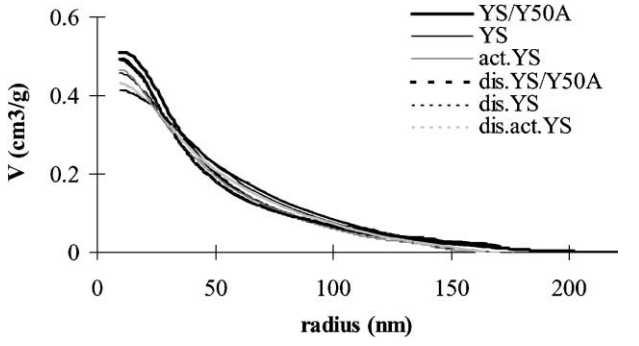

Fig. 10. Thermoporometry with undecane: cumulated volumes before and after discharge.

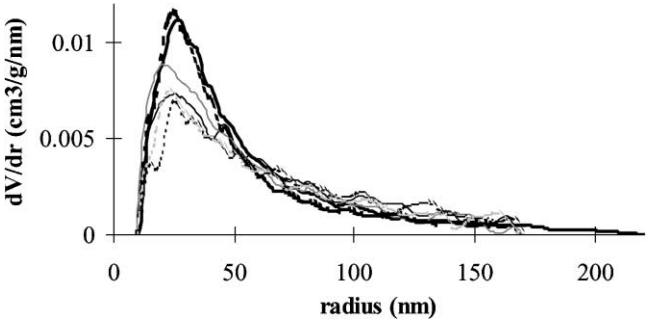

Fig. 11. Thermoporometry with undecane: pore volume distribution before and after discharge (same legend as Fig. 10).

These results confirm the influence of the pore volume and of the specific surface area on the performances of the $SOCl_2$/Li batteries. It is useful to determine the evolution of the pore distributions after the discharge.

By thermoporometry with undecane, the variations of volume observed are lower than the volume of the LiCl produced in agreement with results obtained with cathodes containing YS and Y50A discharged under different current densities [2]. Whatever the amount of LiCl deposited (it is significantly higher with activated YS), the evolution of the pore distribution is similar. This means that the filling of the pores with diameter between 10 and 200 nm is the same for the three types of carbon materials. This observation shows that, on the one hand, only a part of the LiCl deposits in the pore network accessible by thermoporometry and, on the other hand, the 10–200 nm pore population contributes as the other populations to the LiCl storage. The previous comments do not take into consideration the swelling of the electrodes which significantly varies with the type of carbon used as confirmed by the variation of the thickness of the cathodes during the discharge (Table 6). Such a swelling may induce the disappearance of wide pores (their diameters becoming higher than 200 nm) and/or the appearance of pores whose diameters were initially too narrow to be measured by thermoporometry (narrower than 10 nm). If the shift of the pore distributions due to swelling is significant, the comparison by thermoporometry of the pore distribution before and after discharge may become misleading.

4. Conclusions

The discharge of C/Ni/PTFE cathodes is strongly depending upon the carbon material used. The capacity of the battery is mainly correlated to the pore volume of the cathode. It was shown that the electrochemical performances are also depending upon the surface area of the cathode. Actually, the presence of a large surface area is not enough to reach high electrochemical performances, but for a given pore volume the performances are improved by a large surface area. The study of the pore distribution shows that the filling of pores by LiCl occurs at the entrance of the pores as demonstrated before [1,2]. This type of filling without clogging of the pores occurs preferentially in the widest pores which induces a disappearing of the widest

pores and a shift of the pore populations towards narrower pores.

Acknowledgements

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