

# Nonaqueous UFC suspensions, used as conductive additive in cathodes for lithium batteries

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## Abstract

Three nonaqueous ultrafine carbon suspensions (UFC) were explored as conductive additives in  $\text{LiMn}_2\text{O}_4$  cathodes for Li cell. The specific surface areas, pore volume distributions of the pure materials and of the cathode mixtures were measured. The results were compared with these obtained using TAB2 alone. A considerable decreasing of the specific resistivity and pore volume increasing of the UFC pellets after sintering was established. The electrochemical cycling test showed 5 to 10% higher discharge capacity of the cathodes containing 20% UFC + TAB2 at a ratio from 1:3 to 1:1, than that of the cathodes with only 20% TAB2. It is proposed the better results are due to the two physical chemical properties: pore volume and specific resistivity. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Recently, a new class of conductive additives has been developed and used in electrochemical power sources with aqueous electrolyte [1,2], namely ultra fine carbon (UFC) water suspension [3]. In our previous paper [4], we proved the applicability of UFC water suspension as an additive to the cathode material for Li cells. The use of UFC water suspension as conductive binder through the technology proposed by us has lead to improvement in cathode utilization by 7–10%. A new modification of these materials is UFC nonaqueous suspensions [2,5] intended for use especially as conductive additives to cathode materials for Li cells. In these UFC conductive additives, water has been substituted by an organic solvent, thus preventing any possible adverse effect of water on the active cathode material. The present study is focused on investigating the behaviour of cathodes containing the conductive additive UFC nonaqueous suspension. In preparing the electrode mixture, as in our previous paper [4], teflonized acetylene black (TAB2) [6] was also used as conductive binder. The results obtained were compared with experimental data for cathodes prepared with TAB2 and active material (AM) alone.

## 2. Experimental

The novel UFC nonaqueous conductive additives consist of a carbon–polymer suspension in *N*-methyl pyrrolidone the total amount of dry substance in the suspension being 10%. The carbon material is in the form of short (0.15  $\mu\text{m}$ ), sometimes slightly branched, chains of acetylene black or carbon black. The polymer used comprises particles of polyvinyl pyrrolidone (PVP) with a relatively low molecular mass and small size (about 0.9  $\mu\text{m}$ ), which keep the carbon particles in a suspended state. The following UFC nonaqueous additives were investigated: UFC2/10; UFC3/10 and UFC4/10. The number ratio after the UFC denotes the ratio between polymer and carbon in the dry substance of the suspension. A water suspension of UFC2/10 with the PVP polymer was also investigated. After drying of the suspensions at 110°C, the specific BET surface area of the dry residue was measured using a Strohlein AREA meter. The pore volume and pore distribution were determined by a Micromeritics AutoPore 9200 porosimeter. For the purpose the pure UFC materials were pressed at 10  $\text{t}/\text{cm}^2$  in pellets and then subjected to mercury porometry.  $\text{LiMn}_2\text{O}_4$  spinel [7] was used as AM for preparation of the cathodes. The cathode mixture was prepared by continuous stirring of 80% AM and 20% Conductive Binder (CB). The CB was a mixture of TAB2 and UFC suspension, the ratio between the dry material

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TAB2 and the dry UFC substance in the suspension being 3:1, 1:1 or 1:3, respectively. Cathodic mixtures of 80%AM + 20%UFC (in *N*-methyl pyrrolidone) and of 80%AM + 20%TAB were also prepared by wet mixing, and after that, were dried. Pellets of these cathodic materials pressed at 10 t/cm<sup>2</sup> were subjected to pore volume measurements. Pure UFC materials as well as TAB2 were pressed in pellets and their specific resistance was measured using an automatic RC impedance meter with a fixed frequency of 1000 Hz. The technology of the pellet preparation and the measuring methods are described in detail in our earlier paper [4]. The specific resistance of pellets of pure UFC materials after sintering at 240°C and 340°C for 1 h was also determined. The time of sintering was determined based on the ratio between the weight of the pure UFC pellets and the weight of the UFC materials contained in the cathodes for electrochemical tests, which are sintered for 10 min. The cathodes for the electrochemical tests were prepared by pressing 20 mg/cm<sup>2</sup> of cathode mixture at 10 t/cm<sup>2</sup> onto an Al foil current collector. The electrodes were assembled in laboratory disk cells vs. a Li anode using 1 M LiClO<sub>4</sub> in EC:DMC (1:1) as an electrolyte. The cycling tests were performed galvanostatically at 3 h charge/discharge rate (1/3C) in 3–4.5 V voltage range.

### 3. Results and discussion

For the sake of clarity and simplicity the following designations will be used further in the text: for the nonaqueous (N) UFC suspensions—2N for UFC2/10; 3N for UFC3/10; 4N for UFC4/10, and 2A for the aqueous UFC suspension. The measured specific surface areas of the dry residue obtained after drying of the suspensions are summarized in Table 1. The specific surface area of TAB2 is also given in the table for comparison. The specific surface area of the dry residue from the suspensions is close to that of TAB2. The observed gradual decrease in specific surface area of the materials 2N, 3N and 4N is probably due to the increasing of the polymer content in the suspension as the polymer particles are larger in size than the carbon chains. Having in mind the size of the suspension's particles it can be assumed that partial agglomeration of these particles proceeds during the drying procedure.

The pore volume and the pore distribution by radius were determined for the pure materials 2A and 4N. The data are given in Table 2 with the data for TAB2 given for comparison. The smaller mean radius of the pores in the

Table 2

Pore volume and median pore radius of UFC2A, UFC4N and TAB2

Material	2A	4N	TAB2
Pore volume	0.3539	0.2023	0.5891
and % (cm <sup>3</sup> /g)	37.55%	24.33%	54.33%
Median pore radius (μm)	0.0121	0.0109	0.0376

UFC materials is probably due to the fact that they contain much shorter carbon chains than those in TAB2 and these chains are more densely packed in the pellets. On the other hand, these shorter chains provide larger contact area with the AM particles in the cathode mixture and thus improve the ohmic contact between the AM and TAB2. Fig. 1 shows comparative data about the pore distribution by radius for pure 2A, pure TAB and a mixture of 80%AM + 10%TAB2 + 10%2A. It can be seen that the porogram of the cathode mixture features no peak for the pure 2A material. The same effect is also observed when the non-aqueous 4N suspension is used in the cathode mixture. This is illustrated in Fig. 2 showing the pore distribution by radius for pure 4N, TAB2 and a mixture of 80%AM + 10%TAB2 + 10%4N. The absence of the peak for pure UFC materials in the porogram of the cathodic mixture is probably due to the uniform distribution of the UFC particles among the other components in the mixture.

The changes in pore volume and pore distribution by radius in pellets of pure 4N and in pellets of the same material after sintering at 240°C and 340°C were followed. It is found that the pore volume increases from non-sintered to sintered materials in the following order: 0.2023 cm<sup>3</sup>/g, 0.3999 cm<sup>3</sup>/g and 0.5995 cm<sup>3</sup>/g, respectively. A corresponding increase in median pore radius is also observed: 0.0109 μm, 0.0240 μm and 0.0261 μm. The observed increase in pore volume and median pore radius after

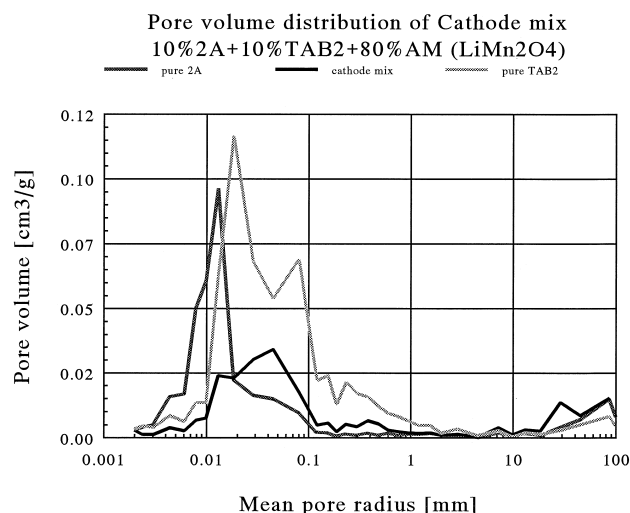


Fig. 1. Pore volume distribution of cathode mixture 10% 2A+10% TAB2+80% LiMn<sub>2</sub>O<sub>4</sub>.

Table 1

Specific surface areas of the dry UFC residues and TAB2

Material	2N	3N	4N	2A	TAB2
BET (m <sup>2</sup> /g)	36.9	29.3	20.3	34.5	34.9

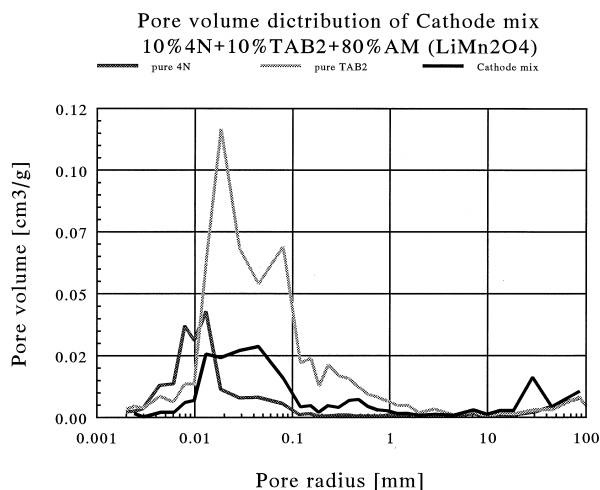


Fig. 2. Pore volume distribution of cathode mixture 10% 4N+10% TAB2+80%  $\text{LiMn}_2\text{O}_4$ .

thermal treatment of the materials is most probably related to decomposition of the PVP at these high temperatures, which is also supported by the smaller weight of the pellets after sintering (see Table 3). The pore volume data for 4N are used further also for calculating the specific resistance of the bulk material. The resistance of pressed pellets of pure UFC conductive additives was measured. The calculated values for the specific resistance of these materials are compared with those for TAB2 in Table 3.

As already mentioned the mass of the UFC pellets decreases after the thermal treatment, which suggests decomposition of the polymer (PVP) at these temperatures. Probably, on polymer decomposition part of it undergoes also carbonization and these two processes lead to a lower specific resistance of the thermally treated materials. Obviously, this effect does not occur with suspension 4N (Table 3). Using the pore volume data for this material, we can calculate the specific resistance of the bulk substance from the formula  $S_{fv} = G_t V_p / l_t$ , where  $G_t$  is the pellet mass,  $V_p$  is the measured pore volume ( $\text{cm}^3/\text{g}$ ),  $l_t$  is the thickness

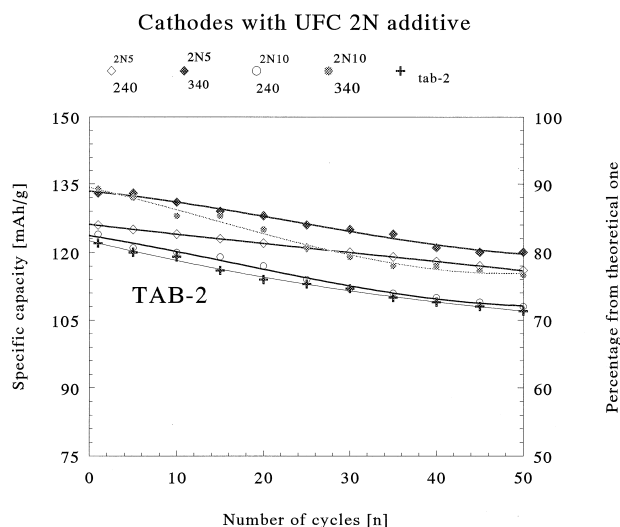


Fig. 3. Specific capacities of  $\text{LiMn}_2\text{O}_4$  cathodes with UFC 2N and TAB2 in various ratios, sintered at 240°C and 340°C.

of the pellet, and  $S_{fv}$  is the area of the free volume for thickness  $l$ . Then, correcting the  $S_{fv}$  area in the formula giving the specific resistance  $\rho = R(S - S_{fv}) / l_t$  we can calculate the specific resistance of the bulk material. The calculated resistivity values are  $\rho = 1.59 \Omega \text{ cm}$  for the non-sintered material,  $\rho = 1.2 \Omega \text{ cm}$  for the material sintered at 240°C and  $\rho = 1.02 \Omega \text{ cm}$  for the material sintered at 340°C. These values also indicate a decrease in specific resistance after thermal treatment. The experimental resistivity data for the materials under test gives us grounds to conclude that they are perfectly suitable for application as cathode materials for Li cells.

The cathode mixture pressed onto an Al current collector is not hard enough to allow cathode impregnation with electrolyte under vacuum. Therefore, first we subjected the cathodes to sintering at 240°C or 340°C. In our previous paper on UFC aqueous suspensions with PVA [4], we found that 240°C is the optimum sintering temperature for

Table 3

Weight, thickness and specific resistivity of the pellets, pressed from UFC2N, UFC4N, UFC2A and TAB2, before and after sintering

Type of material	Measured parameters	Nonsintered	Sintered at 240°C	Sintered at 340°C
2N	$G$ (mg)	200	200	170
	$d$ (mm)	172	194	195
	$\rho$ ( $\Omega \text{ cm}$ )	1.75	2.35	1.4
4N	$G$ (mg)	200	180	150
	$d$ (mm)	152	170	173
	$\rho$ ( $\Omega \text{ cm}$ )	2.1	1.95	1.94
2A	$G$ (mg)	200	200	170
	$d$ (mm)	172	195	197
	$\rho$ ( $\Omega \text{ cm}$ )	1.43	2.03	1.35
TAB2	$G$ (mg)	200	200	198
	$d$ (mm)	182	190	200
	$\rho$ ( $\Omega \text{ cm}$ )	1.0	0.96	0.9

these cathodes, whereas the optimum temperature of sintering of cathodes with TAB2 is 340°C. Fig. 3 shows the changes in specific capacity of the AM of cathodes sintered at 240°C and 340°C as a function of the number of cycles at 3 h charge–discharge rate. The data are for cathodes with addition of 2N suspension in two ratios: 5%2N + 15%TAB2 + 80%AM and 10%2N + 10%TAB2 + 80%AM. These data are compared to the results obtained for cathodes prepared with 20%TAB2 + 80%AM and sintered at 340°C. It can be seen from the data in the same figure that the cathodes sintered at 340°C exhibit the highest AM utilization which is about 10% higher than that for cathodes with TAB2 only. This indicates that the optimum temperature of sintering for these suspensions containing PVP is 340°C, i.e., the same as for electrodes with TAB2. Another observed tendency is that the cathodes with 5%2N and 10%2N have initially the same utilization, but after the first several cycles the AM of the cathodes with 5%2N preserve a higher specific capacity than those with 10%2N. Cathodes with 20%2N + 80%AM were also investigated. The results are also given in Fig. 3. The specific capacity of the AM of these electrodes is higher by about 5–6% than that of the cathodes with TAB2.

It is interesting to compare the behaviour of cathodes prepared with aqueous 2A suspension containing the same polymer PVP. The cycling test results for cathodes prepared with different quantities of the 2A suspension are presented in Fig. 4. The active materials of the cathodes with 5%2A and with 10%2A have almost the same specific capacity which, at the beginning of cycling, is a bit lower than that of cathodes with 2N (Fig. 3), and becomes equal to that of 2N containing cathodes after 50 cycles. During the initial cycles, the specific capacity of cathodes prepared with 20%2A is almost equal to that of electrodes containing 20%TAB2 and increases with cycling to be-

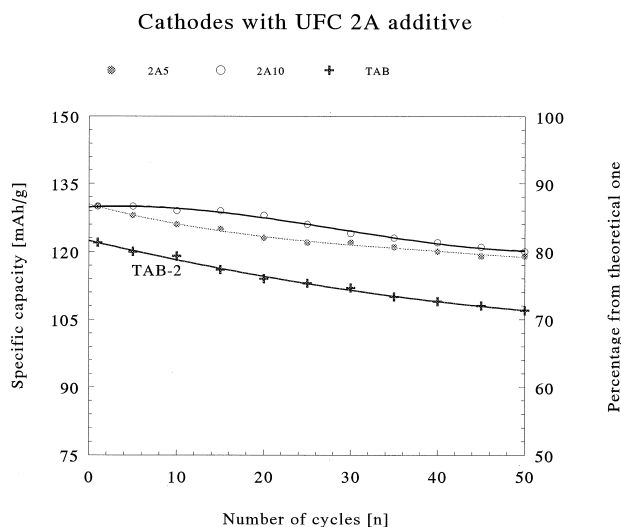


Fig. 4. Specific capacities of  $\text{LiMn}_2\text{O}_4$  cathodes with UFC 2A and TAB2 in various ratios, sintered at 340°C.

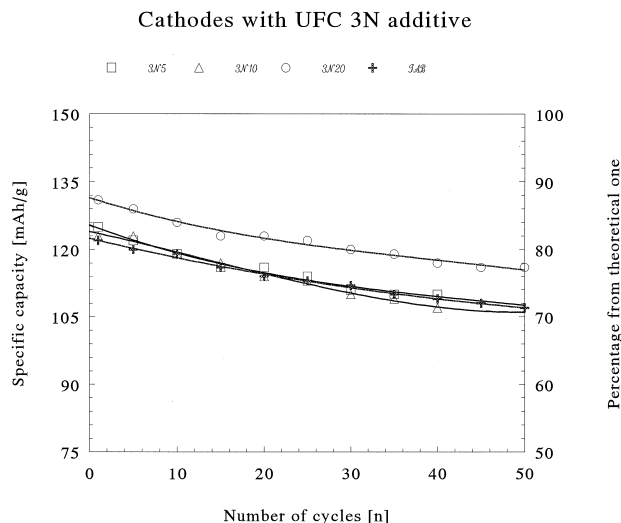


Fig. 5. Specific capacities of  $\text{LiMn}_2\text{O}_4$  cathodes with UFC 3N and TAB2 in various ratios, sintered at 340°C.

come after 50 cycles slightly higher than that of cathodes with TAB2.

The cathodes prepared with 3N suspension differ in electrochemical behaviour from all other types of cathodes. Fig. 5 illustrates the cycling test results for cathodes prepared with 5%3N + 15%TAB2 + 80%AM, and 10%3N + 10%TAB2 + 80%AM and 20%3N + 80%AM cycled at 3-h rate. The AM utilization for the cathodes containing 5%3N and 10%3N is the same as that for the cathodes with 20%TAB2, whereas the electrodes with 20%3N exhibit about 8% higher AM utilization.

The test results from cycling at 3 h rate of discharge of cathodes with various amounts of the 4N UFC suspension are presented in Fig. 6. The AM utilization of the cathodes with 5%4N with 10%4N is higher by about 5–6% than that of cathodes prepared with TAB2 conductive binder

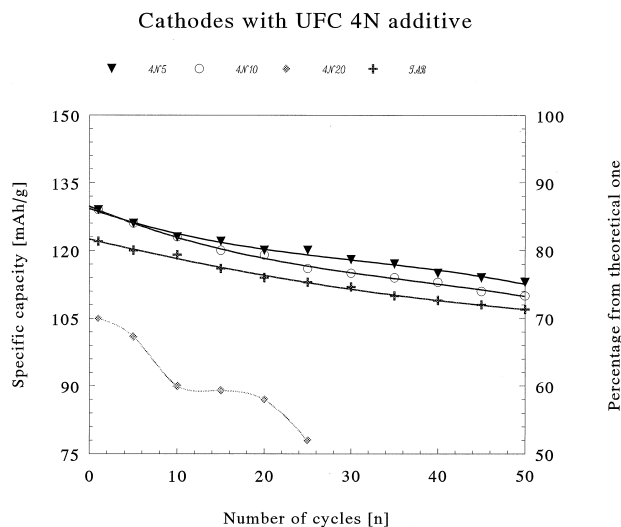


Fig. 6. Specific capacities of  $\text{LiMn}_2\text{O}_4$  cathodes with UFC 4N and TAB2 in various ratios, sintered at 340°C.

alone. The cathodes containing 20%4N have shown a poor utilization of the AM on cycling, a behaviour for which we find it difficult to give a logical explanation.

#### 4. Conclusions

From the obtained results it can be concluded that cathodes with an addition of 5% and 10% UFC non-aqueous suspensions have the best electrochemical performance except for those containing the 3N suspension. The better electrochemical behaviour of the cathodes with UFC is due to the two factors: decreasing of the specific resistivity and increasing of the pore volume of the cathodes. Finally, it can be supposed that these new UFC conductive additives are applicable in Li and Li-ion batteries and could lead to an improvement of up to 10% in the AM

utilization of the cathodes as compared to the cathodes prepared with TAB2 only as conductive binder.

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