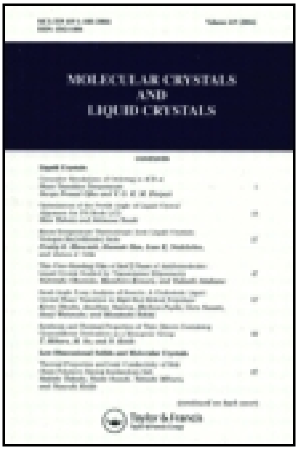

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The Carbon-Lithium Negative Electrode: Effects of the Carbon Origin and of The Electrolyte

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THE CARBON-LITHIUM NEGATIVE ELECTRODE : EFFECTS OF THE CARBON ORIGIN AND OF THE ELECTROLYTE.

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Abstract Carbonaceous materials from different origins are used in order to study the lithium electrochemical intercalation and de-intercalation from a liquid or a solid state electrolyte. The reversible capacity which describes the total relative amount of lithium exchanged with the electrolyte during the charge/discharge operations depends on the crystallinity of the host carbon. A special coal coke allows to reach high capacities in both liquid and solid electrolytes.

INTRODUCTION

The carbon lithium C_6Li_x ($0 \leq x \leq 1$) is now used in mass production as a reversible negative electrode in the so-called "lithium-ion" battery [1]. During the charge/discharge operations, lithium is intercalated and deintercalated into/from the carbon host without any liquid solvent co-intercalation following the scheme :

$$6C + xLi^+ + xe^- \neq C_6Li_x$$

When the stage-1 binary compounds C_6Li is formed at the end of the charge operation, the electrode relative volumic expansion is around 10% (d_{002} varies from 3.35 Å to 3.71 Å). The host lattice experiences small deformation, therefore the number of intercalation/de-intercalation cycles may reach up to 1200 cycles [2]. In addition to the high cyclability which also strongly depends on the nature of the electrolyte, the carbon lithium electrode allows to encrease the safety of the lithium battery (no dendritic growth) and has a low working potentiel in the 0-0.75 V vs. Li^+/Li range.

In this work we have considered the effects of the carbon origin and the nature of the electrolyte on the performance of the C_6Li_x electrode. During the first intercalation/de-intercalation cycle, there appears some "lost lithium" which cannot be recovered during the following cycles. This effect can be described by the faradaic yield ρ_F which is the ratio of de-intercalated to intercalated lithium amounts. We will discuss the possible origins of the "lost lithium". Also we give some results concerning the carbon electrode in contact with the polymer electrolyte .

EXPERIMENTAL

1)Carbonaceous materials

The carbon fibers used in this study derive from three kinds of precursors : an isotropic pitch from Union Carbide/Amoco (UCC-2, UCC-32), a mesophase pitch from Tonen (FT 500 and FT 700) and finally the polyacrylonitrile based fiber from Toray (PAN : T 300). Before use, the fibers were heat treated under air at 350°C during 20 mn to remove the protective (sizing) polymer thin film.

The coal coke was supplied by le Carbone Lorraine. It has a low grain size (4µm) and a quite high specific surface (20 m^2/g). Temperature of carbonization is about 1100°C. After physical activation by CO_2 at 800°C during 8 hours, the specific area increased to $47m^2/g$.

2)Electrochemical study :

2-a) Composite electrode and electrochemical cells :

Prior to their use, the carbon powders were evacuated under vacuum at 300°C for 10 hours. Carbon fibers were then grinded in a mortar to reduce their length to a 0.5 - 1 mm powder. For the tests carried out in liquid electolyte, pallets having 13 mm on diameter have been prepared, by mixing carbon powders (fibers, coke) (55 weight %) with a preparation containing acetylene black (22 weight %), polyethylene oxide (PEO) (11-weight %) and fine powder of polyethylene (12 weight %), dispersed in acetonitrile. After the evaporation of the excess of acetonitrile at room temperature, the mixture is pressed under 2t $/cm^2$. Then the pellets were dried under vacuum at 180°C for 10 hours then put into a RC2430 type button cells. In the case of a polymer electrolyte, the composite electrode was obtained from a suspension in acetonitrile of a mixture containing wt. 60 % of active carbon, 30 % of $P(EO)_8LiClO_4$ and 10 % of acetylene black. The suspension is then spread over an stainless steel disc of 16 mm on diameter. The acetonitrile is evaporated at 60°C in air and then in vacuum at room temperature for few hours. The electrochemical tests have been carried out at room temperature (18-22°C) for liquid electrolyte and at 81°C (±1°C) for polymer electrolyte. Tests have also been carried out with only acetylene black in order to know the relative contribution in the composite electrode specific capacity. This contribution was found less than 5% .

Galvanostatic cycling was used with such current values that the formation of C_6Li in equation (1) occurs theorically in 20 hours (C/20 rate). The potential ranges of (0V-1.2V) for liquide electrolyte and ((-0.015)V- 1.5V) in the polymer electrolyte ($(P(EO)_8LiClO_4)$) were used.

RESULTS AND DISCUSSIONS

1)Crystal characterization

X-ray diffraction was perfomed to determine the carbon inter-layers spacing (d_{002}) and the coherence length in the c-direction L_c. Table-1 gives these data for the different carbon fibers. As expected, L_c increases when d_{002} becomes closer to 3.35 Å characteristic of the highly crystallized graphite.

TABLE I Origin and crystal characteristics of the carbon fibers used in this study

Origin	Precursor	Code	d_{002} (Å)	L_c (Å)
Toray	PAN	T 300	3.42	71
Union Carbide	isotropic pitch	UCC-2	3.40	102
Tonen	pitch mesophase	FT 700	3.37	158
Tonen	pitch mesophase	FT 500	3.40	107
Union Carbide	isotropic pitch	UCC-32	3.365	228

2) Galvanostatic cycling

2-a) Liquid electrolyte

Figure 1 shows the first (left column) and 10th (right column) cycles obtained with the different kinds carbonaceous material : actived coke (a), UCC-2 (b), FT 700 (c), UCC32 (d), and T300 (e). Typically, during the first cycle, the discharge curve lasts longer than the charge one which means that more lithium has been transferred to the carbon than removed from it. The faradaic yield ρ_{F1}which is given by the ratio: removed lithium/transferred lithium is roughly comprised between 80 and 90%. This ratio increases after the fisrt cycle and then is stabilized as shown in TABLE II. Other data are given in TABLE II : e_0=initial potential of the cell, $D_{1(10)}$= specific capacity during the first (10th) discharge, $C_{1(10)}$=specific capacity during the first (10th) charge. Starting from a virgin carbon, if the first discharge curve corresponding to the first lithium insertion lasts T_1 (hours), the final theoretical composition of the cathode is $Li_{T1/20}C_6$. The specific capacity is thus $D_1=T_1/20x372$ (mAh/g) (372mAh/g is the theorical capacity of LiC_6). Similar equations can be used for the determination of C_1, D_{10} and C_{10}.

The carbonaceous materials have been classified in a decreasing C_{10} values order. C_{10} constitutes the reversible capacity of the electrode since the C_n (n=cycle number) remain inchanged after the first cycle. The highest reversible capacity of more than 360 mAh/g has been obtained with the activated coke. With carbon fiber, the C_{10} values tend to increase with the graphitization degree. FT 700 fibers, treated at a higher temperature has a reversible capacity, 22% higher than that obtained which FT 500 (301 mAh/g instead of 246 mAh/g). This increase is less important (6.5% or so) for the UCC 2 and UCC 32 fibers, since we obtained 279 mAh/g for the former and 297 mAh/g for the later. We therefore conclude that for carbons fibers the crystallinity is a determinant parameter in the reversible capacity of the electrodes.

The origin of the low faradaic yield during the first cycle is generally attributed to the following effect:

1) formation of a protective film on the surface of the fibers or on the coke grains. This film results from the decomposition of the electrolyte which envolves an irreversible lithium consumption [3,4].

2) Deposit of metallic lithium, especially at low potential close to 0 V vs Li^+/Li.

3) Formation of a residual carbon -lithium compounds from which lithium cannot be removed in the experiment time scale.

TABLE II Electrochemical characteristics of tested carbon materials during the first and the 10th charge/discharge cycles. D_i, C_i=discharge, charge capacity , ρ_{Fi}= faradaic yield= C_i/D_i. The reversible capacity is C_i ($i \geq 2$) remains almost constant after the first cycle.

Type of carbone	D_1 (mAh/g)	C_1 (mAh/g)	ρ_{F1} (%)	D_{10} (mAh/g)	C_{10} (mAh/g)	ρ_{F10} (%)
Pristine coke	391	346	88	342	342	100
Activated coke	413	368	89	368	364	99
FT 700	365	305	83	327	301	92
UCC-32	357	309	86	327	297	91
UCC-2	353	296	81	297	279	94
FT 500	305	253	82	261	246	94
T300	260	197	75	189	175	93

2-b) Polymer electrolyte

Figure-2a and 2-b show respectively the two first and the 64th dicharge/charge cycles obtained with coal coke in polymer electrolyte cells. ρ_{F1} is very low (265/650=40%)

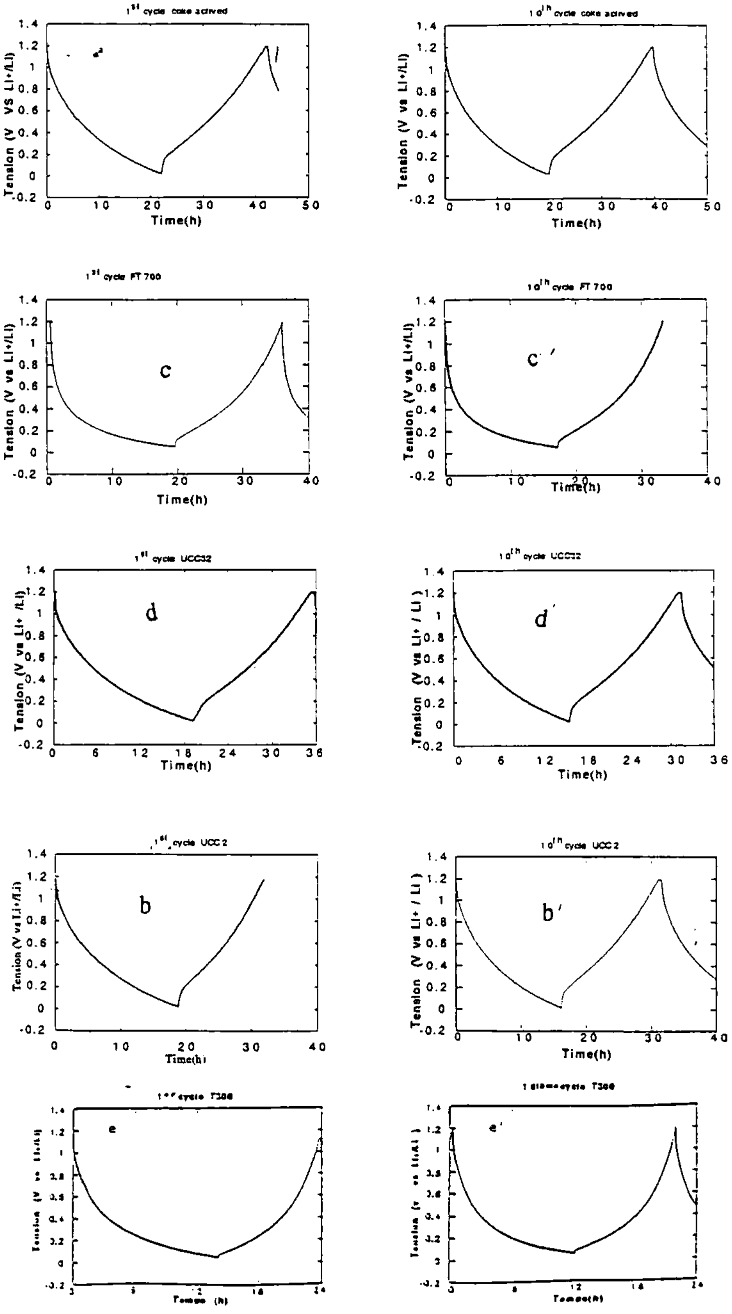

Figure 1 shows the first (left column) and 10th (right column) cycles obtained with the different kinds carbonaceous material : actived coke (a), UCC-2 (b), FT 700 (c), UCC32 (d), and T300 (e).

then it stabilizes close to unity for the next cycles. The attained reversible capacity is 270 mAh/g which corresponds to $Li_{0.73}C_6$. When the low potential limit is decreased to (-15 mV) vs Li^+/Li, a capacity as high as 325 mAh/g ($Li_{0.873}C_6$) was achieved. Further decrease of the potential limit results in the irreversible destruction of the cell probably due to dendritic growth at the coke surface and/or to reduction of PEO. To our knowledge, 325 mAh/g is the highest published reversible capacity for a carbon lithium electrode reached with solid state electrolyte[5]. The differences in the reversible capacity in liquide electrolyte and solid state polymer could come from a better wetting of the carbon grains with liquid electrolyte.

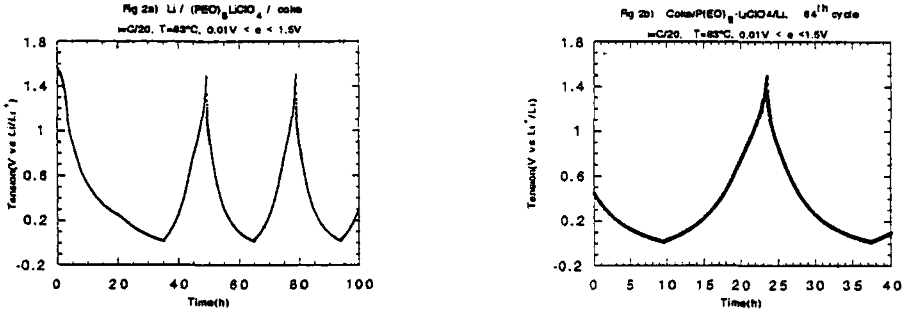

Figure-2: Discharge/ charge curves obtained with coal coke in $P(EO)_8$-LiClO4 electrolyte (a: 1st and 2nd cycles, b: 64th cycle).

CONCLUSION

The reversibility of the lithium insertion in differents carbon material was studied in liquid and solid state electrolytes. The best performances can be reached with the carbon coke in terms of reversible capacity : 370 mAh/g in a liquid medium and 325 mAh/g in a solid medium. For the carbon fibers, this capacity increases with the graphitization degree to reach about 300 mAh/g for the FT 700 and UC32 fibers. The low efficiency of the first cycle can result from the formation of a passivation film, but also from a less efficient wetting of carbon by the electrolyte and from the occurence of residual lithium in the carbon host lattice.

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