THE CARBON-LITHIUM NEGATIVE ELECTRODE : AN OUTSTANDING ELECTROCHEMICHAL BEHAVIOUR.

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INTRODUCTION

The successful utilization of carbonaceous material as a host structure for lithium reversible electrochemical storage in the so called "lithium-ion" batteries in liquid electrolytes results from the successive improvement of the operation characteristics of this electrode such as the reversible capacity, the cycle life and the safety [1, 2]. The latter aspect is in relation with the reduction of the dendrite growth of metallic lithium during the cathodic process. To avoid the formation of dendritic lithium, several models have been so far proposed including the formation of intercalated lithium with the staging phenomenum [3, 4] and the preferential deposit of lithium in the micropores [5] or cavities [6] present in disordered carbons.

The formation of dendrites on metallic lithium was also reported in solid polymer electrolytes particularly when high current density (mA/cm^2) or high surface capacity (mAh/cm^2) are required [7]. Therefore the use of carbonaceous materials as a substitute to metallic lithium or to lithium alloys may also be considered in order to enhance the safety of the polymers or gels electrolytes based lithium-ion cells .

EXPERIMENTAL

The carbonaceous materials used in this study are 1) acetylene black (AB) typically entered as electrical conductivity additive in composite electrodes, 2) natural graphite from Madagascar (20 μm in average grain size), 3) coke powder from Carbone Lorraine (France) (HTT à 1100°C) and grinded to c.a. 8 μm, 4) Meso Carbon Micro Breads (MCMB) with two heat treatments : 1000°C (MCMB 6-10) and 2800° (graphitized MCMB 6-28) : grain size ~ 6 μm from Osaka Gas (Japan) . Carbon fibers derived from a petroleum pitch mesophase and heat treated to 2600°C were used for the chemical lithiation and the observation of the passivation film.

For the electrochemical tests, dried carbon powders were dispersed into an acetonitrile solution of polyethylene oxide (PEO), then sprayed on a stainless steel disc of 16 mm in diameter. The mixture was then evacuated at ambient temperature then at 120°C for several hours . The average weight of the obtained composite electrode is c. a. 5 mg and the volume composition is 40 % PEO and 60% carbon (10% NA + 50% carbon) .

For the evaluation of the carbon electrodes,button type (RC 2430) cells were mounted in a dry argon filled box using PEO-LiClO$_4$ film as electrolyte and metallic lithium as the reference and the counter electrode. The cells were operated at 100°C under a C/20 galvanostatic regimes (LiC$_6$ reached in 20 hours) between 1.5 V and 5 mV as potential limits.

RESULTS AND DISCUSSION

- Galvanostatic cycling :

For the Li/PEO/Carbon cells, table 1 summarizes the main characteristics of cycling curves (not presented here) such as γ = coulombic yield of the first cyclei.e. the ratio of the recovered capacity during the discharge (de-intercalation and that transferred to the electrode during the charge (intercalation). It also give the values e$_d$ and e$_c$ = average discharge and charge voltage after the first cycle, Q$_r$ = reversible specific capacity and x the reversible amount of lithium in Li$_x$C$_6$. The γ values are rather lower than those observed with the same carbons in EC:PC:DME-LiBF$_4$ solution [5]. This should be due to poorer interfacial properties between the two solids carbon and polymer.

Table 1

Carbon	γ %	e$_d$ (mV)	e$_c$ (mV)	Q$_r$ (mAh/g)	x in Li$_x$C$_6$
AB	17	262	506	190	0.52
Natural Graphite	30	124	194	280	0.75
Coke	40	306	507	325	0.85
MCMB 6-28	30	168	237	355	0.95
MCMB 6-10	60	267	543	410	1.1

The most striking result given in table 1 is the occurence of a reversible capacity Q$_r$ higher than the theoretical 372 mAh/g (corresponding to the formation of LiC$_6$) obtained with MCMB 6-10 sample that is 410 mAh/g. MCMB 6-10 consists on spherical particles of disordered carbon layers. In liquid electrolytes, Mabuchi et al showed recently that MCMB heat treated at 700°C gives even a higher reversible capacity of 750 mAh/g [6]. They attributed the excess capacity to lithium localisation in the MCMB.

We proposed a new model to deal with excess capacitiy : the multilayers model. We suggest that each a, b face of the carbon crystallite may be covered by several layers of lithium. We have calculated from electrochemical data and crystal parameters that the excess capacity is equal to the capacity due to the formation of three layers of lithium on each a, b face of the carbon crystallite. Since the stability of the carbon-lithium lattice is controlled by the coulombic attraction between the host carbon and the guest lithium resulting from the charge transfer, the most likely type of stacking of the lithium layers should be reached when the first lithium layer occupy the α sites of the hexal structure, the second and third layers occupy the β and γ sites respectively as showed in the figure 1. In such arrangement the possibility of charge transfer with the adjacent carbon hexagons still exists and accordingly, a partial ionic character of the C-Li bonding should be preserved. Should any additional lithium layer be platted above the α, β, γ layers, the character of the Li-Li bonding within this layer would be

metallic due to the screening of the carbon substrate. The appearance of such metallic character would increase the possibility of lithium dendritic growth which is known to hinder the reversibility of the electrode reaction.

A schematic drawing of the multilayers model is given in figure 2. Note that the formation of molecular multilayers on the carbon a, b surface has been previously reported by several authors [8, 9].

-Impedance measurements during the first electrode reduction (0<x<2 in Li_xC_6).

Figure 3 gives the composition dependence of the double layer and the total impedances. The former decreases monotonously for 0<x<0.75, then tends to stabilize. This enhancement of the interfacial properties with the amount of lithium transferred to the carbon host may result from the increase of the wetting factor between two solids: PEO and carbon. Ideally, PEO should cover the edges of the carbon layers to achieve a full wetting of the diffusion active surface. Due to differences in the surface properties between carbon and PEO, the wetting factor should be lower than the unity. At fixed temperature and internal pressure into the cell, one possible mechanism yielding an improvement of the wetting factor is chemically driven polymer chains motion towards the carbon electrode. A freshly reduced lithium may either be intercalated between the carbon sheets or be adsorbed on their edges. These two forms of lithium are designed Int(Li) and Ads(Li) respectively. Due to strong attraction between the Ads(Li) and the ether group of PEO, the polymer chains should move closer to the carbon layers edges. This may result in the formation of a C-Ads(Li)-O bridging bond which fixes the PEO close to the carbon surface. A schematic drawing of this model (the "zipper" model)is given in figure 4. As a direct consequence of this model, Ads(Li) involved in the C-Ads(Li)-O bonding accounts for the loss of capacity during the first discharge/charge cycle. In the present case, the relative amount of Ads(Li) is c. a. 0.75 Li/C_6 as suggested in figure 3.

CONCLUSION

Carbon-lithium can be used as a reversible negative electrode for "lithium-ion" type batteries operated with polymer electrolyte. A disordered carbon such as MCMB heat treated at 1000°C shows a high specific reversible capacity of 410 mAh/g.

The excess capacity may result from the formation of multilayers of lithium on the a, b faces of the carbon external sheets. The stabilization of such a construction should involve charge transfer between the lithium layers and carbon.

The observed decrease of the interfacial impedance during the first cathodic scanning is tentatively related to the enhancement of the wetting factor between the PEO and the carbon.

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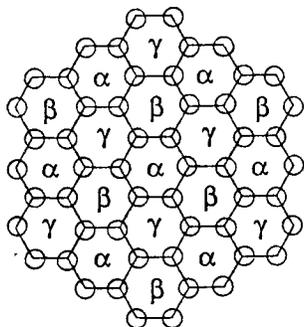9. J. C. Delachaume, M. Coulon and L. Bonnetain Surface Sci. 133(1983)365

figure 1 : planar model showing the α, β, γ sites of the hexal structure.

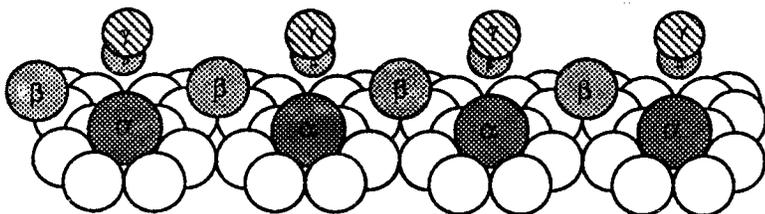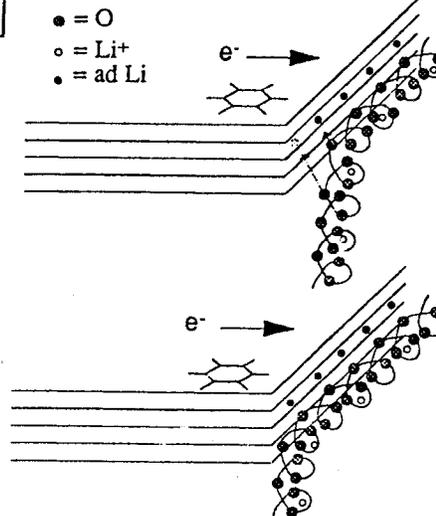Figure 3 : Evolution of resistances as function of insertion degree

figure 4 : Zipper model showing the formation of C-Ads(Li)-O bridges.

Figure 2 : model of lithium multilayers stacking on the graphite a,b face