

Chemical passivation of lithiated graphitized mesocarbon fibers

K. Zaghib^a, R. Yazami^{a,*}, M. Broussely^b

^a LEPMI-INPG, URA CNRS C5631, BP 75, 38402 Saint-Martin-d'Heres, France

^b SAFT-DGA, BP 1039, 86060 Poitiers, France

Accepted 31 March 1997

Abstract

In order to improve the Faraday yield during the first reduction/oxidation cycle of graphitized mesocarbon fibers (GMCFs) used as the negative electrodes for lithium-ion batteries, chemical lithiation was performed before formation of the electrode. Organic solutions of butyllithium, lithium naphthalenide or molten lithium at 220 °C were used as the lithiation reactives. The effect of chemical lithiation on the morphology and structure of GMCFs was examined by scanning electron microscopy, X-ray diffraction analysis and Raman spectroscopy. The electrochemical study showed the effectiveness of these treatments on the enhancement of the Faraday yield and the reversible capacity of GMCFs. © 1997 Elsevier Science S.A.

Keywords: Carbon fibers; Chemical lithiation; Passivation; Negative electrodes; Lithium; Electrodes

1. Introduction

A lithium-ion battery is typically composed of a lithiated metal oxide as the positive electrode, a carbonaceous material as the negative electrode and an organic lithium conducting electrolyte [1]. Basically at the initial state, the only active electrode that contains ionic lithium is the positive one, and the battery is in the discharged state. The first charge consists of transferring lithium from the positive to the negative electrode through the electrolyte. In order to avoid any irreversible structural changes in the positive electrode and the anodic decomposition of the electrolyte, the charge is a 'potential end' limited operation. On the carbon anode (during charge), freshly deposited lithium reacts with the electrolyte and involves the irreversible consumption of lithium. This reaction, however, makes it possible for the lithium cation to be stored within the carbon microstructure (layers, micropores, etc.) free from any solvent.

The lithium consumed during the first charge cannot be used when the current is reversed. This lost lithium contributes to decrease the faraday yield γ_F of the first cycle and, since the total active lithium is limited in the battery, it also affects the capacity output of the battery.

In this work, we have lithiated graphitized mesocarbon fibers (GMCFs) by chemical treatment before their use as the negative electrode. We found that γ_F was significantly

enhanced as a result of the chemical formation of the passivation film. The reversible specific capacity of the carbon fibers was also increased after the pre-lithiation treatment.

2. Experimental

GMCFs provided by Tonen (FT 700) and Amoco (P120) were first heat-treated at 300 °C in air for 20 min in order to remove the sizing polymer layers and then heat-treated under vacuum for 10 h to remove traces of moisture (sample a). GMCFs were chemically lithiated using three different processes: (i) exposure to 2.5 M *n*-butyllithium solution in hexane for 10 h; (ii) exposure to 1 M lithium naphthalenide solution in tetrahydrofuran (THF) for 10 h, and (iii) exposed to molten lithium. When exposed to molten lithium, GMCFs were sandwiched between two nickel grids and then immersed into the molten metal at 220 °C for 4 h. The nickel grids were periodically shaken in order to homogenize both the reactive medium and the temperature of the melt. At the end of the reaction, excess lithium was removed mechanically from the grids. Only fibers with no observed metallic lithium on the surface were selected and used in this study (sample b). The color of the fibers turned to reddish or dark blue as a consequence of the quantitative lithium intercalation (charge-transfer effect) [2].

One part of the carbon fibers was reacted with an electrolyte containing 1 M LiBF₄ in ethylene carbonate:propylene car-

* Corresponding author.

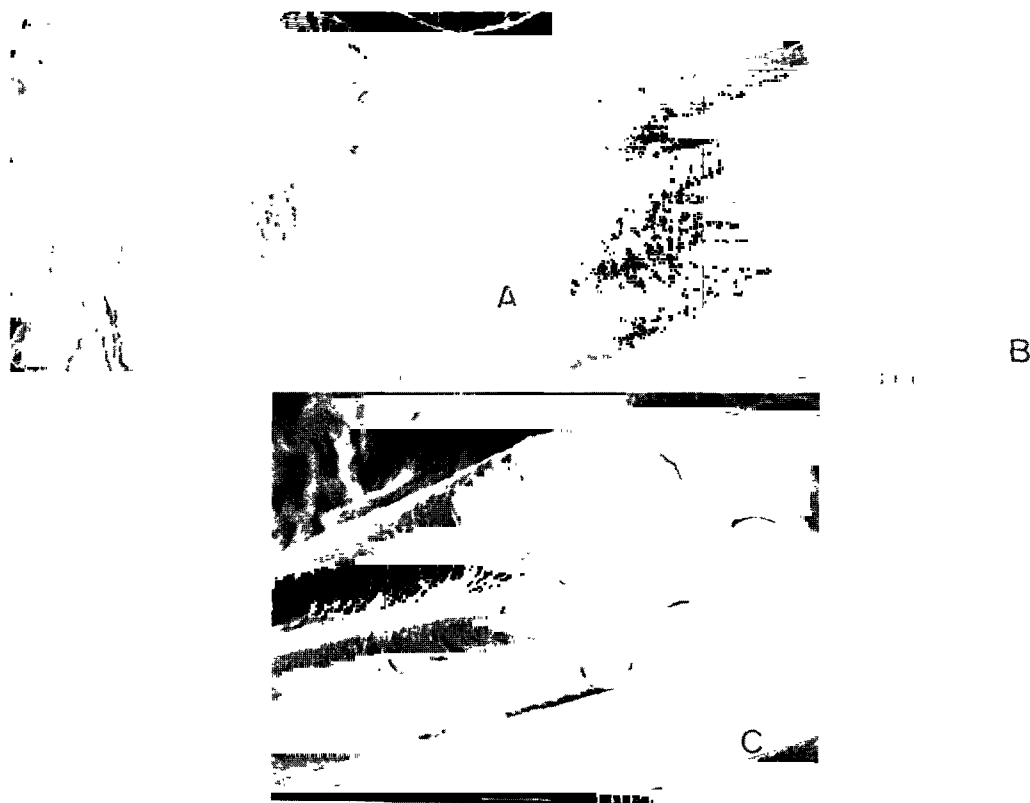


Fig. 1 SEM graphs of GMCFs (Amoco) (a) virgin state, (b) after chemical lithiation with molten lithium, and (c) after reaction of (b) with the electrolyte

bonate:dimethyl carbonate (EC:PC:DME) (1:1:2 v/v%) for 3 to 5 h, washed with DME and then dried in an argon atmosphere and in vacuum (sample c). The second part of the fiber sample was used in a composite electrode that was prepared by mixing 80 wt.% carbon fibers, 10 wt.% polyethylene oxide (binder) and 10 wt.% acetylene black into a THF slurry. After drying the mixture, pellets of 13 mm in diameter were formed by compressing under 1.5 ton/cm². The typical weight and thickness of each pellet was 30 ± 5 mg and 0.4 ± 0.15 mm, respectively.

The electrochemical test cell was a 2430 button type. It was comprised of a metallic lithium (20 mm in diameter), a Celgard 2400 separator and 1 M LiBF₄ into EC:PC:DME (1:1:2) as the electrolyte. The cells were cycled under constant current (*C*/20) between 5 mV and 1.2 V. For prelithiated fibers, the first phase of the cycling was the charge (anodic oxidation) in order to evaluate the amount of active intercalated lithium. For non-lithiated carbon fibers, the first galvanostatic step was the electrochemical reduction.

3. Results and discussion

3.1. Scanning electron microscopy

The evolution of the morphology of the carbon fiber (FT 700) in the initial state, after chemical lithiation with molten lithium and after treatment with the electrolyte is shown in Fig. 1(a)–(c), respectively. The most significant change

occurred between chemical lithiation with molten lithium and then treated with the electrolyte where an external surface film was observed. Such a film results from the chemical decomposition of the electrolyte on the surface of the lithiated carbon fiber. Energy dispersive X-rays (EDX) analysis performed on a selected area of the sample containing mainly film showed the presence of carbon, oxygen, fluorine and boron. A light element such as lithium cannot be observed by EDX. We have assumed that the film contained all elements present in the electrolyte, and because of its lower stability, EC should be the most consumed component. The lithium salt should also be decomposed leading to the formation of LiF and most likely elemental boron. It is worth noting that after the film formation, the GMCFs were physically bonded tightly to each other as a result of the growth of the film.

3.2. X-ray diffraction analysis and Raman spectroscopy

The contribution of intercalated lithium in the GMCFs due to the film formation was investigated by X-ray diffraction analysis (XRD) and Raman spectroscopy. Table 1 gives the graphite interlayer spacing d_{002} and the E_{2g} active mode frequency (ν cm⁻¹) for the samples a, b and c. Both d and ν increased from 3.35 Å and 1680 cm⁻¹ for the virgin fiber to 3.71 Å and 1690 cm⁻¹ in the lithiated state, and then decreased to 3.36 Å and 1685 cm⁻¹ after reaction with the electrolyte. This result shows obviously that not only lithium present on the surface of GMCFs reacts with the electrolyte

Table 1

Evolution of the carbon interlayer average spacing d and the E_{2g} Raman-active mode frequency of GMCFs in the virgin state (a), after chemical lithiation (b) and after reaction with the electrolyte (c)

Sample	Molten lithium			<i>n</i> -Butyllithium			Lithium naphthalenide		
	a	b	c	a	b	c	a	b	c
d (Å)	3.35	3.71	3.36	3.35	3.51	3.36	3.35	3.54	3.36
$\nu_{E_{2g}}$ (cm ⁻¹)	1680	1690	1685	1680	1682	1681	1680	1688	1688

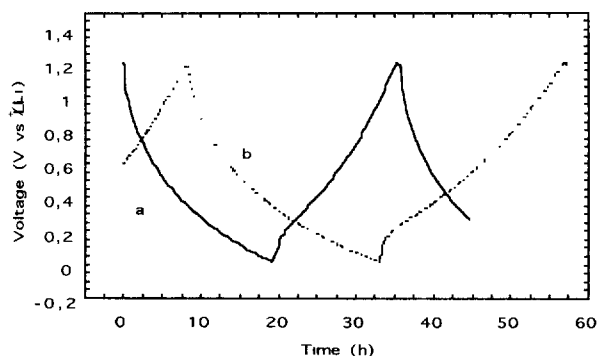


Fig. 2. First galvanostatic (C/20) cycle of lithium/carbon cells (a) non-lithiated GMCf, and (b) chemically lithiated with molten lithium GMCf

but also an emptying of lithium of the carbon layers occurs, and lithium diffuses to the surface and reduces the electrolyte. However, not all of the lithium was involved in this reaction since the initial state of the virgin GMCFs could not be fully recovered as shown by Raman spectrometry, e.g. these results show that no entire recovering of the virgin GMCFs is attained.

Residual lithium may result from a reduction in the reaction kinetics with increasing film thickness or from lithium being 'trapped' in carbon core defects such as the so-called 'Daumas and Herold' domains [3].

Similar results were also obtained with GMCFs lithiated with butyllithium and lithium naphthalenide but higher intercalation stages were obtained with these reactive media, which made it less convenient to observe the microstructural changes especially by XRD when compared with GMCFs lithiated in molten lithium.

3.3. Electrochemical measurements

Fig. 2 shows comparative first cycle data obtained with GMCFs (Amoco P120) in the virgin state (Fig. 2(a)) and

after lithiation with molten lithium (Fig. 2(b)). In the latter case, the electrode was first anodically oxidized from its initial open-circuit voltage (OCV) (0.3 to 0.5 V versus Li⁺/Li) to 1.5 V then reduced to 0.5 V, and finally reoxidized to 1.5 V. This allowed the amount of remaining active lithium in the GMCFs to be determined. Up to 150 mAh/g could be restored during the first oxidation. The second oxidation yielded 430 mAh/g with the corresponding γ_F value close to 95%. In the virgin GMCFs, the restored capacity was only 307 mAh/g with γ_F equal to 87%. The enhancement of both the Faraday yield and the reversible capacity in pre-lithiated carbon fibers is a result of both the chemical growth of the passivation film and the enhanced lithium penetration in the core of the fibers. Lithium can be stored in either the intercalated state (as in LiC₆) or in the fiber surface defects [3].

4. Conclusions

The formation of a film on the surface of chemically lithiated carbon fibers after reaction with EC:PC:DME–LiBF₄ electrolyte was evidenced by SEM, XRD and Raman spectroscopy. Though the chemical nature of the film was not elucidated here, it is very likely that such a film has a complex composition and should behave similar to a film formed electrochemically. However, the latter has a much lower thickness and is formed at a potential much higher than that reported here.

References

- [1] T. Nagawa and K. Tozawa, *Prog. Batteries Solar Cells*, 9 (1990) 209
- [2] D. Guérard and A. Herold, *Carbon*, 13 (1975) 337
- [3] N. Daumas and A. Herold, *C.R. Acad. Sci., C268* (1969) 373.