

INTERCALATION OF LITHIUM IN PITCH BASED CARBON FIBERS CHEMICALLY MODIFIED BY FLUORINE

C. Hung and A. Prisko*

NASA Glenn Research Center, Cleveland Ohio 44135

Cleveland State University, Cleveland, Ohio 44115

Introduction

Carbon materials can be produced from defluorination of graphite fluoride. The structure of these carbon products depends on the defluorination process. For example, the following two very different fiber products were obtained from defluorination of $CF_{0.68}$ fibers:

(1) Rapid heating of the $CF_{0.68}$ fibers to 400°C or higher resulted in fast decomposition, and produced amorphous carbon containing a small amount of fluorine [1].

(2) Heating the $CF_{0.68}$ fibers in a chemically reactive environment to a temperature range of 300-460°C removed the majority of the fluorine in the graphite fluoride without causing much carbon loss. The carbon atoms in this product were essentially two dimensional but contained dislocation and disordering areas. [2].

The defluorinated carbon products and their precursor (P100 carbon fibers) were very different in terms of their ability to intercalate/absorb some metal halides and transition metals [2]. Their difference in terms of electrochemically intercalated/absorbed lithium, however, has not been tested. This information is important in the design of lithium-ion batteries and will be described in this report.

Experimental

For rapid defluorination, $CF_{0.68}$ fibers made from P100 were placed into a nitrogen environment which was preheated to 400-500°C. They were rapidly defluorinated with high carbon loss. For slow defluorination, the $CF_{0.68}$ fibers were placed into $CHBr_3$ environments at room temperature before being heated to 350-450°C in one hour and kept at that temperature for 1.5 hrs. This resulted in defluorination without much carbon loss. Both products were further treated to 1000°C in N_2 to remove the remaining fluorine. The rapidly heated carbon product ("A") was amorphous. The slowly heated product ("B") was "soft" carbon which can be graphitized by further heat treatment.

The electrochemical properties of this carbon were measured in a three-electrode cell containing a counter electrode and a reference electrode of lithium metal, and a working electrode made from a carbon material. The electrolyte used was saturated LiI in a 50/50 mixture of ethylene carbonate and dimethyl carbonate. During tests, the current was controlled, and the voltage measured. For the purpose of visually observing the possible interference of lithium salt, a pyrex glass weighing bottle was used as the cell, and LiI was used as the lithium salt. In this arrangement, whenever and wherever I_2 is formed in the cell during reaction, it can be identified by its color and analyzed. For example, the color of the electrolyte did not change if deintercalation was stopped at 0.7 V, but gradually turned from light yellow to orange after several cycles of cell test if the "cut-off voltage" was 3.0 V.

Trial runs of this cell were made using commercially purchased crystalline graphite powder as working electrodes. The capacity for the first intercalation to 0 V was estimated to be 380 mAh/g, within experimental error of the literature value (390-420 mAh/g) [3].

A few electrochemical tests on the P100 precursor were also conducted for comparison.

Results and Discussions

The products ("B") obtained from slow defluorination of $CF_{0.68}$ fibers in $CHBr_3$ environment consistently had larger reversible and irreversible capacity than their precursor (P100). For example, a carbon sample produced from 450°C $CF_{0.68}$ - $CHBr_3$ reactions had first cycle intercalation and deintercalation capacities of 487 and 280 mAh/g, respectively. This compares to 249 and 223 mAh/g values for P100. Table 1 gives a detailed comparison of

Table 1. Reversible capacity (mAh/g) as a function of voltage for "B" and its precursor P100 ($I=10mA/g$)

V_{wr}	P100			"B"		
	0V	0.3V	3V	0V	0.3V	3V
1 st cycle	0	197	223	0	182	280
2 nd cycle	0	194	220	0	189	274
14 th cycle	0	192	217	0	187	257

reversible (i.e., deintercalation) capacity between these two samples. Their reversible capacities were about the same if the cut-off voltage of the working electrode (V_{wr}) was 0.3 V. The higher total reversible capacity for this carbon material over its precursor is mostly due to its ability to release more lithium after V_{wr} was above 0.3 V.

The above data indicates that the disordering of carbon atoms due to the fluorination-defluorination treatment of a carbon precursor may not affect its ability to electrochemically intercalate and deintercalate with lithium when $0 < V_{wr} < 0.3$ V, but does create new lithium intercalation/absorption sites which are active when $V_{wr} > 0.3$ V. Such creation of lithium sites results in an increase of reversible, or, usable capacity for a lithium-ion battery.

Whether these newly created lithium sites are absorption sites or intercalation sites is not known. However, they are more likely to be absorption sites because most lithium deintercalation takes place when $0 < V_{wr} < 0.3$ V [4].

For the carbon materials ("A") obtained from rapid defluorination of the $CF_{0.68}$ fibers, the electrochemical data were very different from its precursor. Data on the first lithium insertion is shown in Figure 1. Data on the irreversible and reversible capacity of this carbon material is summarized in Table 2. These data were highlighted as

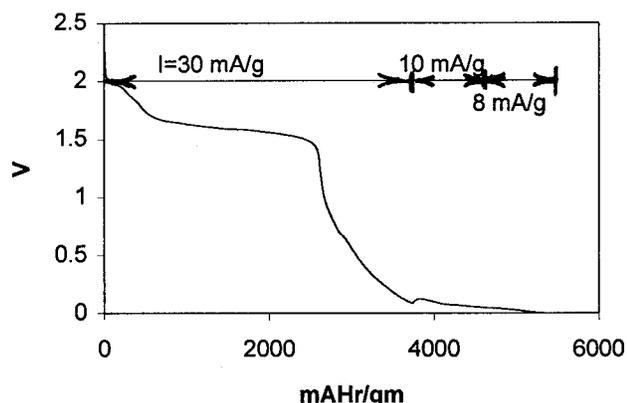


Figure 1. 1st cycle of lithium insertion for the chemically modified carbon product "A".

follows: (1) During the first lithium insertion described in Figure 1, there was a very large capacity (2000mAh/g) when V_{wr} was in the 1.75 to 1.40V range. There was also a very large total capacity of 5400 mAh/g. These large capacities were found mostly irreversible or nonrechargeable. (2) After 3 cycles between 0 and 0.7V, the reversible capacity was stabilized at 400 mAh/g for the next 8 cycles. (3) In the cases of very high current density (2000 mA/g), the reversible capacity remained to be 400 mAh/g. At that current density, the lithium deintercalation was completed in less than 12 minutes. (4) The cut-off voltage was set at $V_{wr}=0.7V$ except for the final deintercalation, where it was set at 3.0V. At this final V_{wr} value, the reversible capacity was found to be 862 mAh/g.

Conclusions

Treating a carbon material with the process of fluorination and then slow defluorination in halocarbon environments resulted in disordering of carbon atoms but little carbon loss. The products had larger reversible and irreversible capacity to electrochemically intercalate lithium than their precursor, probably due to the creation of new lithium sites which were active when $V_{wr} > 0.3$ V.

Treating a carbon material with the process of fluorination and then rapid defluorination in N_2 greatly changed the precursor's electrochemical reactions to lithium. The product had a very large irreversible capacity at 1.5 V (2000 mAh/g). Its reversible capacity can be large (400 mAh/g if the cut-off V_{wr} was 0.7 V), and its deintercalation rate can be high (400 mAh/g can be delivered in 12 minutes).

References

1. Hung C., *Mat. Res. Soc. Symp. Proc.*, 1994, **349**, 19
2. Hung C., *U.S. Patent 5662683*, 1997
3. Ohzuku T., Iwakoshi Y., and Sawai K., *J. Electrochem. Soc.*, 1993, **140** (9), 2490.
4. Endo M., Takahashi T., Rahim I., Takamuka A. and Nakamura J., in *Extended Abstracts 22nd Biennial Conference on Carbon*, San Diego, CA, 1995, P.806.

Table 2. Capacities at a cut-off voltage of 0.7V for the chemically modified carbon product "A"

Cycle number		1	2	3	4	5	6	7	8	9	10	11
Current Density (mA/g)	I ^a	30-8	20-11	20	15-26	30	25	83	25	20	20	20
	D	10	14-42	16	90	180	380	380	16	500	2000	20
Capacity (mAh/g)	I ^a	5400	594	482	472	435	445	405	436	439	427	423
	D	329	357	360	395	386	400	390	369	400	386	386 ^b

a: I and D stand for the half cycles of intercalation and deintercalation, respectively. b: In this last half cycle, the voltage was allowed to go past the cut-off value (0.7V) until it reached 3.0V. When $V_{wr}=3.0V$, the capacity was 862 mAh/g.