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(71) Applicant
Allied Corporation

(Incorporated in the USA - New York)

Columbia Road and Park Avenue, Morris Township, Morris County, New Jersey, United States of America

(72) Inventors
George Anthony Shia
David Nalewajek
Michael Francis Pysczek

(74) Agent and/or Address for Service
Urquhart-Dykes & Lord
91 Wimpole Street, London, W1M 8AH, United Kingdom

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(54) Inhibiting voltage suppression in lithium/fluorinated carbon batteries

(57) Lithium/fluorinated carbon batteries exhibiting much reduced suppression of the initial closed circuit voltage can be produced if the fluorinated carbon has been subjected to treatment with a Group IA metal alkyl (e.g. methyl lithium, ethyl lithium, n-propyl lithium or n-butyl lithium) or a Group IA metal aryl whose aryl groups have at least 10 carbon atoms, (e.g. sodium naphthalide). This treatment removes a proportion (e.g. 5 to 10%) of the surface fluorine.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print incorporates corrections made under Section 117(1) of the Patents Act 1977.

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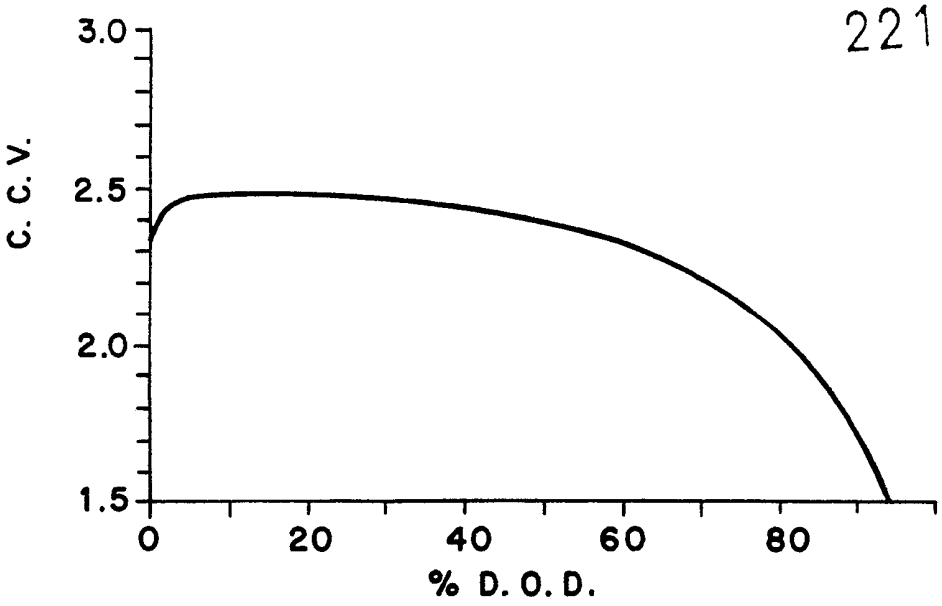

FIG. 1 (Comparative)

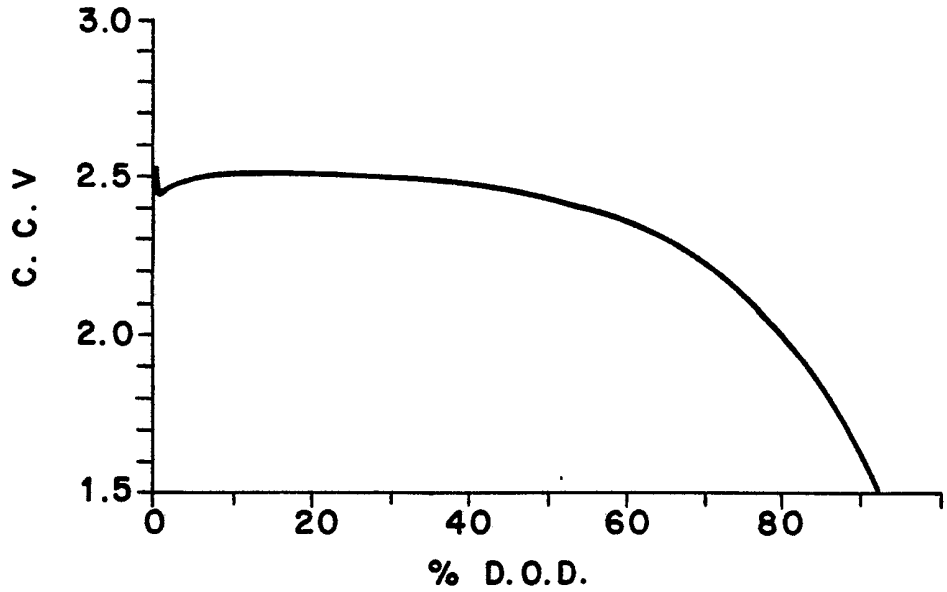

FIG. 2

INHIBITING VOLTAGE SUPPRESSION IN LITHIUM/FLUORINATED CARBON BATTERIES

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This invention relates to an improved lithium/fluorinated carbon (Li/CF_x) battery and to improved forms of fluorinated carbon which are useful in making such batteries.

More particularly, this invention relates to a method for reducing or substantially eliminating the suppression of the closed circuit voltage of a Li/fluorinated carbon battery during the initial part of its discharge by the chemical treatment of the fluorinated carbon with a Group IA metal-alkyl or metal-aryl compound to reduce the fluorine group content of the surface of the fluorinated carbon with the result that there is reduced or no appreciable voltage suppression, while at the same time good battery capacity is retained.

Numerous proposals have been made in the prior art with the aim of improving the initial discharge voltage of lithium/fluorinated carbon batteries. Illustrative of such prior art efforts to eliminate or reduce initial voltage suppression are the following references.

Japanese Kokai No. 76-67921, discloses the chemical treatment of CF_x with triethylamine and ammonia to increase the discharge voltage of the battery. After treatment with the amine, the material must be washed with hydrochloric acid to remove the ammonia and the residual amine, washed with water to remove the acid, and then dried in a vacuum to remove the water. While this multi-step process reportedly reduces the effects of voltage suppression, the number of steps required in the process, and the chance that residual acid or water might be carried into the cell in the treated material (lithium cells are very sensitive to acids and moisture), make this approach less than desirable.

Ultraviolet light has been disclosed in Japanese Kokai No. 83-26457, as a means for partially defluorinating CF_x, reducing the suppression of the initial discharge voltage, and improving storage. The CF_x is soaked or "swelled" in an organic solvent and the slurry is exposed to UV radiation. This process is very time-consuming, as UV radiation is capable of only very slow defluorination of CF_x. The effect of the residual decomposition products in the CF_x sample is not reported.

Another reference that follows along this same line is Japanese Kokai No. 84-86155. UV radiation is used to defluorinate CF_x suspended in a solution of sodium hydroxide and methanol. Subsequent washing with water and drying are required to remove traces of the sodium hydroxide and methanol. This process is also very slow.

Japanese Kokai No. 84-87762 discloses the use of an aqueous solution of HI containing methanol for partially defluorinating CF_x. The CF_x, having a fluorine content of $\geq$ 61.3% (F:C $\geq$ 1) is partly defluorinated to give a material with a fluorine content of $\geq$ 59% (F:C $\geq$ 0.9). Subsequent washing with water to remove HF, formed by the reaction of HI with CF_x, is critical. HF can be very deleterious in a lithium battery.

Irradiation with gamma rays has also been used to defluorinate CF_x and improve its discharge voltage and has been disclosed in Japanese Kokai No. 83-05966. This process requires a nuclear source and would not be convenient or particularly easy to carry out commercially.

An easy, rapid, and safe chemical process to eliminate voltage suppression in the Li/CF_x battery system is clearly lacking. Present practice, as covered in Japanese Kokai No. 82-124865, is partially to discharge the Li/CF_x cell until 10% of its capacity is expended. This procedure is claimed to reduce the effects of voltage suppression, but requires additional equipment and processing time.

Accordingly, while it is known that various chemical treatments of fluorinated carbon have been employed to improve the initial discharge voltage in Li/CF_x cells, a need exists for a simple, rapid, and safe chemical treatment to effectively eliminate voltage suppression.

In accordance with the invention, voltage suppression is reduced or substantially minimized in a lithium/fluorinated carbon battery having a fluorinated carbon cathode, wherein the cathode comprises fluorinated carbon, from whose surface fluorine has been stripped by treatment with a Group IA metal alkyl, or from a Group IA metal aryl whose aryl has at least 10 carbon

atoms. The present invention also provides a method for the treatment of fluorinated carbon which comprises removing fluorine from the surface thereof by exposure to a Group IA metal alkyl or a Group IA metal aryl whose aryl has at least 10 carbon atoms, and also provides fluorinated carbon cathodes produced from fluorinated carbon that has been treated in such a manner.

The reaction between these reagents (e.g., n-butyl lithium) and the fluorinated carbon reduces the fluorine groups on the surface of the material and produces a material suitable for use in a battery which undergoes reduced or almost no suppression of the initial closed circuit voltage.

The invention is further described with reference to the accompanying Drawings, in which:

Fig. 1 shows the closed circuit voltage (CCV) as a function of the depth of discharge (DOD) for a cell made with the untreated material. The voltage suppression (CCV_S) for this cell is 150 mV.

Fig. 2 shows the closed circuit voltage as a function of depth of discharge for a cell made with a material that had been treated in accordance with this invention, viz. 4 cc of n-butyl lithium. The voltage suppression (CCV_S) for this cell is 30 mV.

In accordance with the invention, voltage suppression is reduced or greatly minimized in lithium fluorinated carbon batteries by the chemical treatment of the fluorinated carbon with a Group IA metal alkyl, or with a Group IA metal aryl whose aryl Group has at least 10 carbon atoms. The reaction between such materials and the fluorinated carbon reduces the fluorine on the surface of the material and produces a material suitable for use in a battery which undergoes reduced or almost no suppression of the initial closed circuit voltage, depending upon the extent of the reaction and the corresponding reduction of the surface fluorine. The grade of CF_x is not critical to practice of this invention. Any grade of CF_x which can be used to make a Li/CF_x battery is suitable for use in accordance with the invention.

The Group IA metals in the Group IA metal alkyl or aryl include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and francium (Fr). Lithium is preferred, since in

this case the product formed by chemical treatment in accordance with the invention is LiF, the same product formed when a Li/CF_x battery is discharged. The other Group IA fluorides are, however, not harmful to the battery.

"Alkyl" as used herein means any aliphatic saturated hydrocarbon group including straight-chain, branched chain or cyclic hydrocarbon groups. We know of no technical limitation on the carbon content of the aliphatic saturated hydrocarbon group. For reasons of economics and availability, the preferred carbon content of such groups is from 1 to 4. Illustrative suitable alkyl groups include methyl, isopropyl, n-butyl, neopentyl, n-dodecyl and cyclohexyl.

"Aryl" as used herein means any aromatic hydrocarbon group, which may optionally include aliphatic, saturated, hydrocarbon group side-chains. We know of no technical limitation on the carbon content or number of rings in the aryl group, except that the aryl groups must have at least 10 carbon atoms. Illustrative suitable aryl groups include those derived from naphthalene, anthracene, phenanthrene, pyrene and chrysene. Naphthyl is the preferred aryl group.

Illustrative suitable Group IA metal alkyls Group IA metal aryls are methyl lithium, ethyl lithium, n-butyl lithium, n-propyl sodium, sec.-butyl potassium, n-butyl rubidium, n-butyl cesium, n-hexyl francium, cyclohexyl lithium, potassium naphthalide, sodium naphthalide, lithium naphthalide and cesium anthranide. n-Butyl lithium is the preferred compound because of its ready availability and ease of handling.

The Group IA metal alkyls and Group IA metal aryls compounds are known classes of compounds and particular species are either commercially available or readily prepared by procedures published in the literature.

Voltage suppression is an important problem in the Li/CF_x battery system. The voltage that a Li/CF_x battery will deliver just after the circuit has been closed can be as low as the voltage near the end of battery life. Electronic circuits powered by Li/CF_x batteries are complicated by the need to design around this problem. Even in simpler applications, such as

lighting, a bulb powered by a Li/CF_x battery would appear dim at the beginning of battery life. This observation would tend to confuse inexperienced users to think that the battery is weak or defective. To compensate for this problem, the battery manufacturers have predischarged their Li/CF_x cells, removing as much as 10% of the battery's capacity. This predischarge is an additional manufacturing step which tends to slow down processing and increase costs.

In contrast to the prior art methods, which suffer from being very slow chemical processes, or require that the treated materials be scrupulously cleaned of reactants and by-products because they are deleterious to the battery, or in which the level of fluorine removal is difficult to control because an excess of the reagent must be used to drive the reaction, or which suffer from a combination of all of these problems, the surface fluorine reduction procedure of the present invention produces no by-products which are harmful to the battery if not removed, is rapid, and the level of removal is very easy to control because the Group IA metal alkyls and aryls react rapidly and quantitatively with CF_x.

It is believed that the surface fluorine reduction or stripping procedure of the invention results in alkyl or aryl groups from the Group IA metal alkyl or metal aryl compounds being substituted on the CF_x for the surface fluorine atoms. This invention, however, is not to be limited to any theory of operation.

In view of the relatively small number of surface fluorine atoms replaced, characterization of the reacted CF_x product is not easy and we have not attempted it. We believe, however, the CF_x product which is obtained by the reaction to be novel and therefore to be a part of the invention. Any amount of surface fluorine reduction of the CF_x will achieve a reduction of voltage suppression in the resulting lithium CF_x battery, and this invention contemplates even small reductions of voltage suppression. If a substantial reduction of voltage suppression is desired, however, a substantial reduction of surface fluorine on the CF_x must be achieved. By substantial we mean a reduction

of at least 5% of the total surface fluorine present. Generally, it is not desirable to reduce more than 10% of the total surface fluorine present since this, depending on circumstances, may result in undue sacrifice of the battery capacity. An inert solvent in which the Group IA metal compound is soluble and in which the CF_x is dispersed should be used for the reaction. Suitable solvents include tetrahydrofuran, alkanes, hexane, and dialkyl ethers, such as dimethyl ether. Other suitable solvents will readily occur to those skilled in the art. The preferred solvents are those in which the Group IA fluoride by-products are soluble. Although not essential, this is preferred in order to facilitate removal of such by-products, if desired.

The reaction temperature should be selected so as to maximize the reaction rate, while achieving uniform results. Generally, acceptable reaction temperatures can be in the range of -78 to (+) 40°C more preferably 0 to (+) 20°C. Generally, the higher the reaction temperature; the higher the reaction rate. Higher temperatures, particularly above 40°C, may produce non-uniform results.

If a temperature is chosen which gives a good reaction rate, reaction times for completion of the reaction are generally from 15 minutes to 1 hour. The progress of the reaction can be monitored by determining the Group IA fluoride by-product produced, or by determining the amount of Group IA metal compound reacted.

One advantage of this invention is that the Group IA metal compounds react rapidly and quantitatively with the CF_x. Their exact concentration can be determined by standard titration methods, thus allowing the operator to add only the stoichiometrically required quantity to the reaction medium. This enables controlled and uniform degrees of stripping (or surface fluorine reduction), as desired.

The invention will be further described by the following specific Examples. ACCUFLOR is a Registered Trade Mark.

EXAMPLE 1

In this example, an alkyl lithium compound in accordance with the invention is used to prepare CF_x with reduced surface fluorine which is, in turn, used to make a cathode for a lithium anode non-aqueous cell. The result is minimal voltage suppression. Four grams of ACCUFLUOR CF_x, grade 1000, were suspended in 20 cc. of tetrahydrofuran (THF). This slurry was cooled to 0 degrees C, and 8 cc. of a 1.55M solution of n-butyl lithium in hexane were added drop-wise over 15 minutes. Mixing was continued for another 15 minutes at 0 degrees C, and another 15 minutes at room temperature. The sample was then washed with acetone and dried. To test the materials for voltage suppression, cathodes were formulated by mixing the CF_x sample with 13% of acetylene black and 4% of PTFE and then blending the forming the material into a sheet as described in U.S. Patent No. 4556618. The cathodes were then tested by incorporating then into lithium anode non-aqueous electrolyte cells and discharging the cells across 1 Kohm resistive loads. Cell voltage was monitored and cell capacity was calculated from the discharge curve. This experiment was repeated using different quantities of n-butyl lithium and the results are shown below in Table A.

TABLE A

cc. of n-butyl lithium/ 4 grams of CF_x	CCV_S	cell voltage, mid-life	cell capacity, mAH/g (CF_x)
8	20	2.39	734
4	30	2.39	797
4	20	2.44	803
2	20	2.39	786
0 (untreated)	150	2.38	798

An 8 cc. aliquot of the n-butyl lithium solution removes about 10% of the fluorine contained in a 4 gram sample of CF_x and concomitantly reduces the capacity of cells made with this

treated material by about 10%. For the experiments using smaller volumes of n-butyl lithium, no loss in capacity could be discerned. These results are for cells discharged on a 1 Kohm load which equates to approximately 2.4 mA/cm^2 of cathode area for the cells used in this experiment. At lower rates of discharge, some minimal (<=5%) loss in capacity might be evident.

All of the cells made with CF_x treated with n-butyl lithium showed practically no voltage suppression and had very flat discharge profiles.

EXAMPLE 2

In this example, it is shown that CF_x treated with alkyl lithium compounds need not be washed to attain suitable battery performance. Ten grams of ACCUFLUOR CF_x, grade 1000, were suspended in hexane. This slurry was cooled to 0 degrees C, and 10 cc of a 1.55M solution of n-butyl lithium in hexane were added drop-wise over the course of 0.5 hours. The treated CF_x was then separated into two approximately equal fractions. One fraction was thoroughly washed with tetrahydrofuran (THF) to remove the LiF reaction by-product and then dried. The other fraction was just dried without washing. The two fractions were formulated into cathodes and tested as described in Example 1. As the following table (Table B) shows, washing the reaction by-products out of the treated material is not necessary.

TABLE B

Sample	CCV_S	cell voltage, mid-life	cell capacity, mAH/g (CF_x)
Washed	30	2.39	743
Unwashed	20	2.37	749

The performance of cells made with the treated CF_x were

in no way affected by the reaction products of the chemical treatment which remained in the unwashed sample.

EXAMPLE 3

In this example, sodium naphthalide is used to treat a sample of CF_x, ACCUFLUOR CF_x, grade 1000. The sodium naphthalide solution was prepared by dissolving 12.8 grams of naphthalene in 100 cc. of tetrahydrofuran (THF). The THF was previously dried over 4Å molecular sieves. Then 2.5 grams of clean sodium metal were added to the solution and the mixture was kept under a dry nitrogen atmosphere and stirred overnight. Sodium naphthalide was formed in situ.

Approximately 17 cc. of the above solution were syringed (over about 5 min.) into a sealed flask containing 10 gram of CF_x in a THF slurry. The slurry was cooled to 0 degrees C. The slurry was vigorously stirred during the addition of the sodium naphthalide and for 10 minutes after the last of the reagent was added. The flask was then opened, the solid material was filtered off and washed with some THF. The treated CF_x was dried and made into cathodes and tested in the same manner as described in Example 1.

The resulting batteries made with this treated CF_x had a CCV_S of about 20 mV and capacities of about 750mAH/g. The untreated CF_x has a CCV_S of about 150 mV.

EXAMPLES 4 to 14

In these examples, various Group IA metal alkyls and aryls are used according to the invention to treat samples of ACCUFLUOR CF_x grade 1000. The treated samples are formulated into cathodes and tested in the manner described in Example 1. The results are the same in that, in all instances, all of the cells tested show practically no voltage suppression and have very flat discharge profiles.

Example	Group IA Metal Compound
4	methyl lithium
5	ethyl lithium
6	n-propyl lithium
7	n-propyl sodium
8	sec-butyl potassium
9	n-butyl rubidium
10	n-butyl cesium
11	n-hexyl francium
12	cyclohexyl lithium
13	lithium naphthalide
14	cesium anthranide

It will be understood that variations in compositions and treating steps may be made within the ranges and procedures disclosed herein.

CLAIMS

1. A lithium/fluorinated carbon battery having a fluorinated carbon cathode, wherein the cathode comprises fluorinated carbon, from whose surface fluorine has been stripped by treatment with a Group IA metal alkyl, or from a Group IA metal aryl whose aryl has at least 10 carbon atoms.

2. A battery as claimed in claim 1 wherein from 5 to 10% of the surface fluorine has been stripped from the fluorinated carbon.

3. A battery as claimed in claim 1 or 2 wherein the Group IA metal alkyl is methyl lithium, ethyl lithium, n-propyl lithium or n-butyl lithium.

4. A battery as claimed in claim 1 or 2 wherein the Group IA metal aryl comprises an aryl group delivered from naphthalene, anthracene or pyrene.

5. A battery as claimed in claim 4 wherein the Group IA metal is lithium, sodium or potassium.

6. A battery as claimed in claim 4 or 5 wherein the Group IA metal aryl is sodium naphthalide.

7. A lithium/fluorinated carbon battery was claimed in claim 1 and substantially as hereinbefore described with reference to any of the Examples.

8. A method for the treatment of fluorinated carbon which comprises removing fluorine from the surface thereof by exposure to a Group IA metal alkyl or a Group IA metal aryl whose aryl has at least 10 carbon atoms.

9. A method as claimed in claim 8 and substantially as hereinbefore described with reference to any of the Examples.

10. A fluorinated carbon cathode produced from fluorinated carbon that has been treated by a method as claimed in claim 8 or 9.

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