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(54) Fluorinated carbon fibres.

(57) The invention provides fluorinated carbon fibers having a conductivity at ambient temperature in the range of about 10^{-1} to 10^{-2} S/cm.

EP 0 409 512 A2

CARBON FIBERS

The present invention relates to carbon fibers. More particularly the present invention relates to carbon fibers having reduced conductivity.

Carbon fibers, such as pitch based fibers (Amoco 120) are known and have many uses in industry including for the production of composite materials.

These fibers are characterized by conductivity of 4.5×10^3 S/cm, a Young's modulus of 120×10^6 psi (820 GPa) and an interspacing value of 3.37 Å.

According to the present invention it has now been found that it is possible by simple processing steps to substantially reduce the electrical conductivity of carbon fibers.

The lowering of the conductivity of carbon fibers according to the present invention results in a new product having new and valuable properties and applications including carbon fibers for use in the preparation of cathodes for C/F/Li cells and in the preparation of surfaces capable of changing radar reflection characteristics.

According to the present invention there are now provided fluorinated carbon fibers having a conductivity at ambient temperature in the range of about 10^{-1} to 10^{-2} S/cm.

Preferably the fluorinated carbon fibers of the present invention are produced by the fluorination of carbon fibers with strong fluorinating agents at ambient temperature and in the substantial absence of additives.

Preferred fluorinating agents are BrF_5 and $1F_7$.

Thus the present invention is preferably directed to fluorinated carbon fibers formed by the reaction of carbon fibers with IF_7 or BrF_5, e.g. fluorinated carbon fibers having a composition expressed by the formula

$C_{1.6}FBr_{0.05}$

and fluorinated carbon fibers having a composition expressed by the formula

$C_{1.5}FI_{0.03}$

Graphite fluoride is usually prepared by direct reaction between graphite and elemental fluorine at elevated temperatures. Covalent, nonconducting C-F compounds are obtained which are formulated as $(CF)_n$ and$(C_2F)_n$. Another sort of graphite fluoride compounds are intercalation compounds prepared by reaction of graphite and fluorine in the presence of additives such as HF, LiF, CuF_2 etc. as described e. g. T. Nakajima, I. Kameda, M. Endo and N. Watanabe, Carbon 24, 343, (1986) and I. Palchan, D. Davidov and H. Selig, J. Chem. Soc. Chem. Commun. (1983) 657. These compounds form well organized stage compounds exhibiting high conductivities ("Graphite Fluorides", Studies in Inorganic Chemistry (vol. 8), N. Watanabe, T. Nakajima and H. Touhara, Elsevier 1988).

The enhanced conductivity, caused by charge transfer is strongly influenced by the fluorine concentration. Maximum conductivity is achieved at about stage 2 compound. At higher fluorine concentration the conductivity decreases due to formation of C-F bonds.

Selig, et al. J. Fluor. Chem 12, 397 (1978) demonstrated that halogen fluorides, which are strong fluorinating reagents, react readily without additives such as HF or F_2 (except for IF_5) by fluorination of the graphitic lattice. The reaction of graphite with IF_7 can be described by the following reaction:

$x C + y IF_7 > C_x (IF_5)F_{2y} + (y\text{-}1) IF_5$

However said reaction scheme, which was published more than a decade ago has not been used since then and heretofore it has not been suggested that said reaction would be applicable to fluorinating carbon fibers or that fibers of substantially reduced conductivity could be produced in this manner.

As can be seen, as recently as last year Hamwi et al., Synth. Metal 26, 89 (1988) prepared partially fluorinated graphite at room temperature by using different metallic and nonmetallic fluorides in the presence of fluorine and HF.

As stated, according to the present invention it has now been found that it is possible to produce stable carbon fibers having a conductivity at ambient temperature in the range of about 10^{-1} to 10^{-2} S/cm by reacting the pristine fibers with halogen fluorides at ambient temperatures and without additives.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

Examples 1 and 2

Batches of 50 mg of Amoco, pitch based fibers, P-120 were exposed to I1)200 mmHg of IF_7 and II) 400 mmHg of BrF_5, respectively. Duration time was about 5 days at room temperature. Weight uptake was about 120% which corresponds to a stoichiometry of C_{18}"IF_7" and C_{12}"BrF_5" respectively. The reacted fibers were heated for 4 hours up to 250°C in N_2 atmosphere. A weight loss of about 5-8% was observed.

Chemical analyses of the treated fibers (after heating) gave the following results: $C_{1.5}FI_{0.03}$ and $C_{1.6}Fbr_{0.05}$. The electrical conductivity of the treated (fluorinated) fibers (after heating) at ambient conditions was in the range of about 10^{-1} to 10^{-2} S/cm.

The fluorination reaction and fluorinated fibers were studied by the following techniques:

1) The weight uptake of the fibers in an IF_7 atmosphere was determined with a magnetic suspension balance Sartorius model 4201. For buoyancy weight corrections and pressure measurements a Baratron MKS gauge was used. A four-point probe connected to the reaction chamber via Teflon insulated nickel feedthroughs enabled simultaneous in -situ measurements of weight and resistance of single fibers.

2) X-Rays diffraction with a powder diffractometer and a Debye-Scherrer camera using CuK radiation.

3) Infrared spectra were recorded on a FTIR Bruker IFS 113V over the range of 400-4000 cm^{-1} by using KBr pellets.

4) ESR measurements as a function of temperature and weight uptake were conducted on an E-line X-band spectrometer. We measured the ESR in-situ during exposure of fibers to BrF_5 of IF_7.

5) Conductivity as a function of temperature was measured with a four-point probe. Single fibers were mounted on an alumina holder by silver conducting paint. A Keithley 220 constant current source was used and voltage was measured with a Keithley 617 electrometer. Low temperatures were achieved and controlled by using an Air Products DISPLEX closed-cycle refrigerator. In order to prevent impurities effects, the pristine fibers were heat treated in chlorine atmosphere. To avoid sample heating effects we used a current of 10^{-7}A.

6) Thermal stability measurements were made on a Stanton Redcroft apparatus (STA 780) in platinum crucibles in a N_2 flow.

The P-120 fibers which had been exposed to BrF_5 or IF_7 for a few days showed weight uptakes of about 120% which correspond to stoichiometries of C_{18}"IF_7" and C_{12}"BrF_5". Exposure for longer periods did not show any change in color, weight uptake, X-ray diffraction and IR spectra suggesting saturation of fluorine content.

Thermogravimetric measurements on the fluorinated fibers in a nitrogen atmosphere up to 250°C showed a gradual small loss of about 5-8% finally reaching a constant weight. The weight loss is probably due to removal of unreacted adsorbed halogen fluorides or volatile reduced products of the fluorination.

Chemical analyses were carried out on fluorinated fibers which had been heated to 250°C in N_2. These gave the following results: $C_{1.6}FBr_{0.05}$ and $C_{1.5}FI_{0.03}$.

In the case of IF_7, after completion of the reaction, the gases remaining in the reactor were transferred by fractional distillation at -23°C. We isolated IF_5 which was identified by IR measurements. When BrF_5 was condensed on the carbon fibers in a KEL-F tube the liquid turned dark indicating reduction to elemental bromine.

In -situ weight uptake of fibers upon exposure to IF_7 shows a gradual increase in weight accompanied by decrease in pressure. The gradual weight increase and pressure decrease continued till about 90% of maximum weight uptake and was followed by a sharp drop in pressure and dramatic increase in weight. Time of reaction was sample dependent but in all cases we observed the same features; namely, a sharp decrease in pressure and a dramatic increase of weight close to the completion of the reaction.

During the course of the reaction samples were removed from the balance at 25%, 50%, 75%, and 85% of the maximum weight uptake. They were analyzed by X-ray diffraction and by IR measurements before and after heating the samples in nitrogen.

The IR spectra did not show the presence of C-F absorption bands. Considering the high sensitivity of FTIR and the very strong absorption bands of the C-F bonds, we assume that little or no fluorination occurred. X-ray diffractions of these samples showed only the graphitic reflections. By using a Debye Scherrer camera there were observed two weak satellites at 2 =24.2 and 28.7 degrees in addition to the normal graphitic (00) reflections.

Heating these samples caused a complete weight loss and the X-ray diffraction shows the patterns of unreacted disordered fibers.

In -situ resistance measurement, using a four-point probe, were done simultaneously with weight uptake, showing an initial drop in resistance followed by a gradual increase and subsequent drastic increase in the resistance. The minimum ratio for R/R_0 is about 0.1 and maximum ratio 105.

In -situ ESR experiments with magnetic field perpendicular to the fibers axes showed a gradual resonance broadening by factors of 2 and 1.2 upon exposure to BrF_5 and IF_7, respectively. During exposure the resonance of the pristine fibers at g = 2.018 was also gradually shifted. The final g-value of both sorts of fluorinated fibers is g = 2.002. Within the accuracy of the measurements, for both fluorinated fibers, the integrated intensity of the resonance remains constant. The fibers exposed to BrF_5 showed a single resonance for all concentrations and the fibers exposed to IF_7, above 50% showed the progressive appearance of a narrower resonance at the same g-value. Up to concentrations of the order of 80% the intensity of the resonance was temperature independent (Pauli-like), characteristic of mobile spins. The fully fluorinated fibers showed a Curie-like temperature dependence of the resonance intensity, characteristic of localized spins.

X-ray diffractions of both fully fluorinated fibers showed in the range of $6^0<2\theta>65^0$ two diffractions at 2 = 15^0 and 42.3^0. These two diffractions are associated with the (00ℓ) out-of-plane reflection and the in-plane (100) basal plane reflection, respectively. The (00ℓ) reflection corresponds to a d-value of 5.8-5.9 A. This value is similar to the interlayer spacing of high temperature fluorinated graphite. The presence of the in-plane diffraction indicates that planarity was preserved. The absence of higher harmonics of in- and out-of-plane reflections and the fact that the in-plane reflection is more intense than that of the pristine fibers indicates that the system is disordered with short correlation length.

The conductivity of both fluorinated fibers at room temperature is in the range of 10^{-1}-10^{-2} S/cm. The diameter of the fibers increased from 10 to 18 upon fluorination. This conductivity is about 4-5 orders of magnitude lower than that of the pristine P-120 fibers but much higher than that of fluorinated graphite ($<10^{-12}$ S/cm). As was suggested by Hamwi, et al, ibid, this can be attributed to partial "ionicity" of the C-F bonds.

Temperature dependence of the conductivity of pristine P-120 fibers (no changes were observed before or after the chlorine treatment) and the fully fluorinated fibers, suggests two thermally activated processes for conductivity. In the high temperature region (T>100K) the activated process seems to be the same for pristine and fluorinated fibers with activation energies being comparable (E = 100-200K). However in the low temperature region (T<100K) the fluorinated fibers show higher activation energies (E = 10K) than that of the pristine fibers (E = 1K). This suggests that the fluorination process contributes to an increase of the potential barrier of the low temperature activated process without influence on the high temperature one.

Although the functional behaviour of the resistivity versus temperature is very similar for the pristine fibers and the fluorinated fibers, the former exhibits a five order of magnitude lower resistivity. This may suggest that the concentration of the charge carriers is dramatically reduced in the fluorinated fibers. The change from Pauli to Curie-like behaviour with no significant change in the total number of spins support the assumption of reduction in the number of charge carriers due to fluorination. The fluorinated fibers were evaluated electrochemically in a Li battery by VARTA GmbH. As cathode material they showed a constant discharge of 3.1V.

The results obtained suggest the following mechanism for the reaction between P-120 fibers upon exposure to IF_7: At the beginning of the reaction the weight uptake of IF_7 is caused by absorption in the graphite fibers (IR spectra give no evidence of fluorination in the bulk). The partially reacted samples give only the (002) and (004) diffraction peaks of the pristine fibers (together with another two weak satellites). This indicates that the halogen fluorides penetrate into the fibers probably by an absorption process and not via mechanism of intercalation. The in -situ resistance showing an initial decrease in resistance may be due to surface effects of halogen fluoride adsorption. The in -situ ESR measurements showing a constant resonance intensity and a shift of the resonance can be attributed to disorder effects caused by the halogen fluoride absorption. This is consistent with the temperature independent ESR intensity observed up to weight uptake of 85%. Since upon completion of the reaction the fibers are clearly fluorinated, it is concluded that two steps are involved. First, an absorption (probably chemisorption) of the halogen fluoride causing increasing disorder of the fibers and probably slight fluorination of the surface. The second step is fluorination of the bulk. Finally, it is important to note and emphasize that by exposure of P-120 fibers to halogen fluorides according to the present invention it is now possible to obtain stable moderately low conducting fibers.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

Claims

1. Fluorinated carbon fibers having a conductivity at ambient temperature in the range of about 10^{-1} to 10^{-2} S/cm.

2. Fluorinated carbon fibers according to claim 1 formed by the reaction of carbon fibers with IF_7 or BrF_5.

3. Fluorinated carbon fibers having a composition expressed by the formula
$C_{1.6}FBr_{0.05}$

4. Fluorinated carbon fibers having a composition expressed by the formula
$C_{1.5}FI_{0.03}$