

The power factor of carbon fibers

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The chemical composition and thermoelectric properties of carbon fiber bundles (CF) have been studied. It is shown that the change in the sign of thermopower after modification of CF can be explained by the formation of additional bonds of oxygen-containing complexes on the branched surface of CF. The temperature dependences of thermal (S) and resistivity (ρ) of n - and p -type carbon fibers were measured. In the temperature range from 300 to 600 K in both types of CF, an increase in thermal EMF is observed with an increase in temperature and a decrease in resistivity in the initial and modified CF, which leads to a rapid increase in the thermoelectric factor (S^2/ρ) of fiber power in the specified temperature range. The combination of high mechanical and thermal stability of the fibers with temperature-increasing thermoelectric efficiency opens up the possibility of using such materials for thermoelectric converters at extremely high temperatures.

Keywords: thermal EMF, resistivity, power factor, carbon fiber, spectral analysis.

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1. Introduction

Search for new low-cost and efficient materials for thermoelectric energy conversion is a crucial materials science objective. Carbon is one of the most widely used, low-cost and commercially available materials in various modifications. Carbon fibers (CF) are widely used in various applications and are increasingly more often used in equipment [1,2]. They are defined as a chemically pure substance, have a fiber diameter from 6 to 10 μm and high resistance to weather effects and chemicals, high modulus of elasticity and strength together with low density and coefficient of friction. Moreover, carbon fibers have almost zero linear expansion coefficient that makes them indispensable for some applications.

This study addresses the problem of CF applicability for thermoelectric energy conversion.

2. Objects of the study

Tenax® HTS 5331 graphitized CF bundles were used as the objects of the study. Preparation of such CF involves three stages: pyrolysis, carbonization and graphitization. Graphitization is defined as a high-temperature treatment at 1500–3000 °C when carbon content in graphitized CF exceeds 99 wt.%. CF samples consisted of bundles of parallel non-twisted fibers up to 30 mm in length. Carbon fibers feature high porosity with internal surface area from 50 to 400 m^2/g .

A previous investigation of the CF resistance dependence on pulse currents [3] has established that Tenax® HTS 5331 graphitized CF in initial state have n -type conductance and negative thermal emf in the room temperature region. When the initial CF is exposed to pulse current, CF is modified and acquires p -type conductance. Many n -type carbon nanotubes (CNT) change sign of thermal emf after several hours or days due to interaction with air oxygen [4,5]. Our initial CF samples are stable in air and do not change the type of conductance voluntarily. To perform chemical analysis of both types of CF and identify the reasons behind the thermal emf sign reversal after modification of initial CF, X-ray photoelectron emission spectra were examined.

Chemical analysis of the CF was performed on PHI-5500 (Physical Electronics, USA) Auger and photoelectron spectrometer. The X-ray photoelectron spectra were measured using $\text{AlK}\alpha$ X-ray radiation, both non-monochromatized (for survey spectra measurement) and monochromatized (for measurement of photoelectron peaks C1s, O1s with high energy resolution and for quantitative analysis).

Spectra in Figure 1, *a* and *b* include carbon-specific (C1s and C KVV) and oxygen-specific (O1s and O KLL) sequence of peaks.

For non-monochromatized radiation, the occurring satellite peaks were removed. Different form of secondary electron background in the survey spectra for n - and p -type conductance samples may be associated with the difference in morphology of their surface.

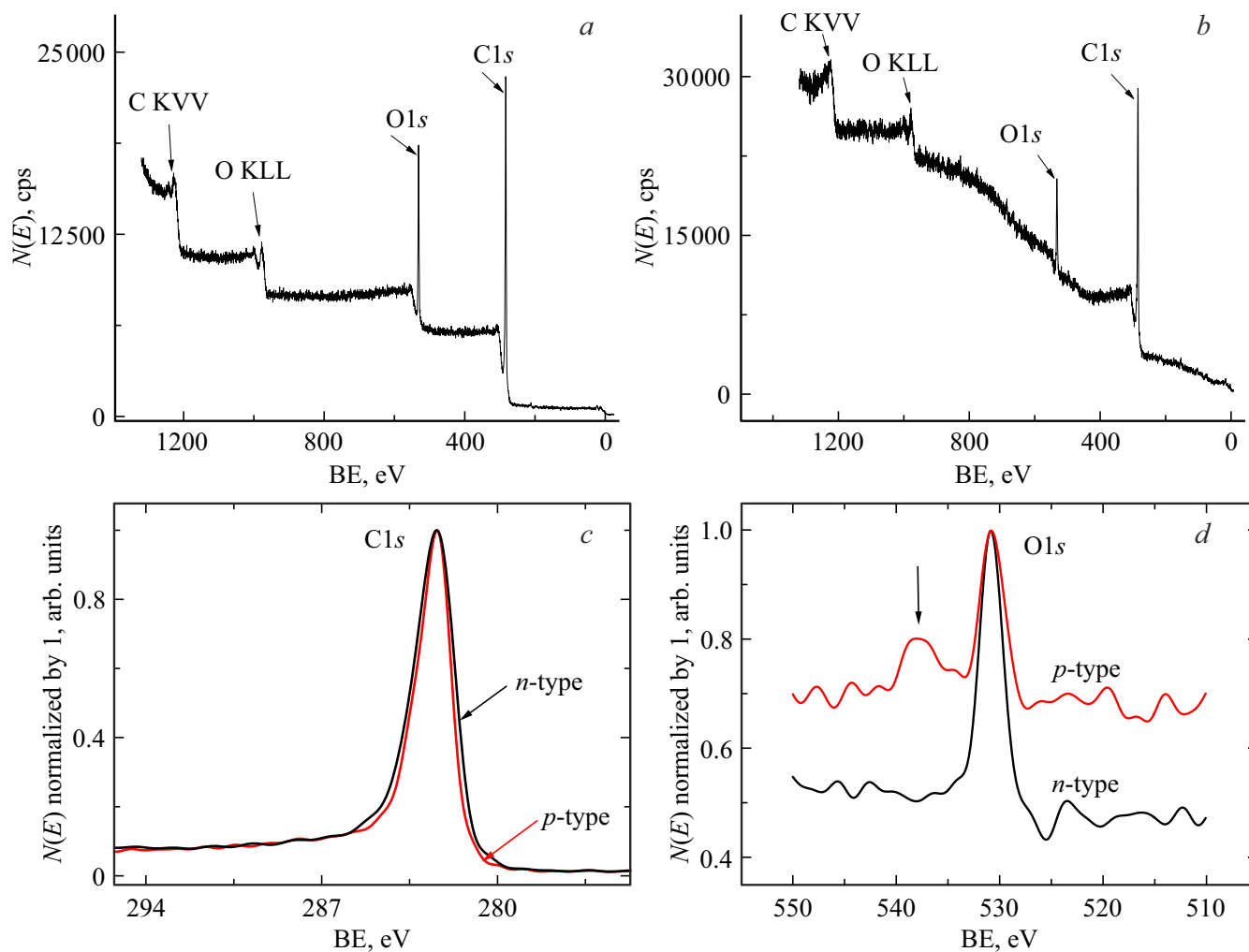


Figure 1. X-ray photoelectron spectra of CF samples, where *a* and *b* — are survey spectra of CF samples with *n*- and *p*-type of conductivity, respectively; *c* and *d* — are spectra of *n*- and *p*-type CF for base peaks C1s and O1s, respectively, measured with high resolution. Electron flux intensity ($N(E)$) is plotted on the vertical axis, binding energy is plotted on the horizontal axis (BE).

For the quantitative analysis of relative oxygen and carbon concentrations in CF, monochromatic $AlK\alpha$ source, the database of elemental sensitivity factors and programs included in the electronic spectrometer software package were used. The the CF sample with *p*-type of conductivity contains $97 \pm 3\%$ carbon and $3 \pm 3\%$ oxygen, while the the sample with *p*-type of conductivity contains $95 \pm 3\%$ carbon and $5 \pm 3\%$ oxygen. It is shown that oxygen concentration in various types of CF samples differ within the measurement accuracy and, therefore is not a factor that defines changing the type of conductivity.

For further chemical analysis of various types of samples, the spectra of the carbon and oxygen (peaks). were measured with high resolution. In Figure 1, for convenience of comparison of measured peaks C1s and O1s, *c* and *d* are shown in a normalized form. High-resolution measurements of X-ray photoelectron spectra have shown that the shapes of carbon peaks C1s are almost identical in CF of both types of conductivity (Figure 1, *c*).

However, spectra of oxygen O1s peak are different for samples with *n*- and *p*-type of conductivity (Figure 1, *d*). In the oxygen spectrum for *p*-type CF, an additional peak appears that has the maximum binding energy at 537 eV. This peak shows that the modified CF contains other oxygen-containing functional groups compared with the initial CF. In this case, oxygen always attaches 2 electrons, i.e. it is an acceptor. When O_2 molecules accept electrons from surface carbon atoms, additional charge carriers occur in CF — holes, and the growth of *p*-type carrier concentration results in CF changing the sign of thermal emf. Such process is similar to changing the type of conductivity in CNT when stored in air that has been found before [4,5]. This suggests that a possible reason why CF modified by pulse current changes the type of conductivity is formation of additional bonds in oxygen-containing complexes on a ramified CF surface after modification by pulse current, rather than the amount of oxygen in CF.

3. Thermoelectric properties of the initial CF

Temperature dependences of thermal emf and resistivity were examined and thermoelectric power factor of the initial (*n*-type) and upgraded (*p*-type) CF was calculated. Measurement accuracy was 2% for electrical resistance measurement and 5% for thermal emf measurement. Carbon fibers — porous material whose internal surface area achieves from 50 to 400 m²/g. Therefore, to calculate the CF cross-section, fiber length in the sample was measured first and then its volume was measured using densitometer. The findings were used to calculate the beam cross-section area and determine the CF resistivity. Thermal resistance of CF in oxidizing media is maintained up to 670–720 K, therefore the test temperature range was limited from 300 to 600 K.

Resistivity of initial CF decreases linearly with temperature increase (Figure 2, *a*), and thermal emf grows linearly (Figure 2, *b*). Both these factors have a favorable effect on a giant increase of thermoelectric power factor that achieves an increase by 1600% as the temperature grows from 300 to 600 K (Figure 2, *c*).

The obtained dependences of simultaneous growth of thermal emf and conductance cannot be explained by scattering on acoustic phonons and neutral impurities because the thermal emf in this case grows with temperature, but conductivity decreases because carrier mobility is proportional to $T^{-3/2}$ during scattering on phonons. Favorable variation of physical coefficients of CF observed herein for thermoelectric properties is specific to all common doped semiconductors where carrier scattering dominates on ionized impurities and carrier mobility grows with temperature as $T^{3/2}$ (provided that the band gap and temperature are such that intrinsic conductance has not been manifested yet). In this case, high energy carriers scatter weakly, therefore thermal emf and conductance grow simultaneously as temperature rises. Such situation may occur during carrier scattering (tunneling) on potential barriers [6,7]. Simultaneous growth of conductance and thermal emf is observed in amorphous tellurium and germanium. CF's consist of separate weakly interconnected graphite layers, therefore they may be the equivalent to materials with potential barriers [8].

4. Thermoelectric properties of the modified CF

Examination of temperature dependences of thermal emf, resistivity and thermoelectric power factor of the modified CF has shown that all specified parameters vary with temperature growth similar to the dependences of initial CF. Resistivity (Figure 3, *a*) in the room temperature region is approximately by half as low as in the initial CF,

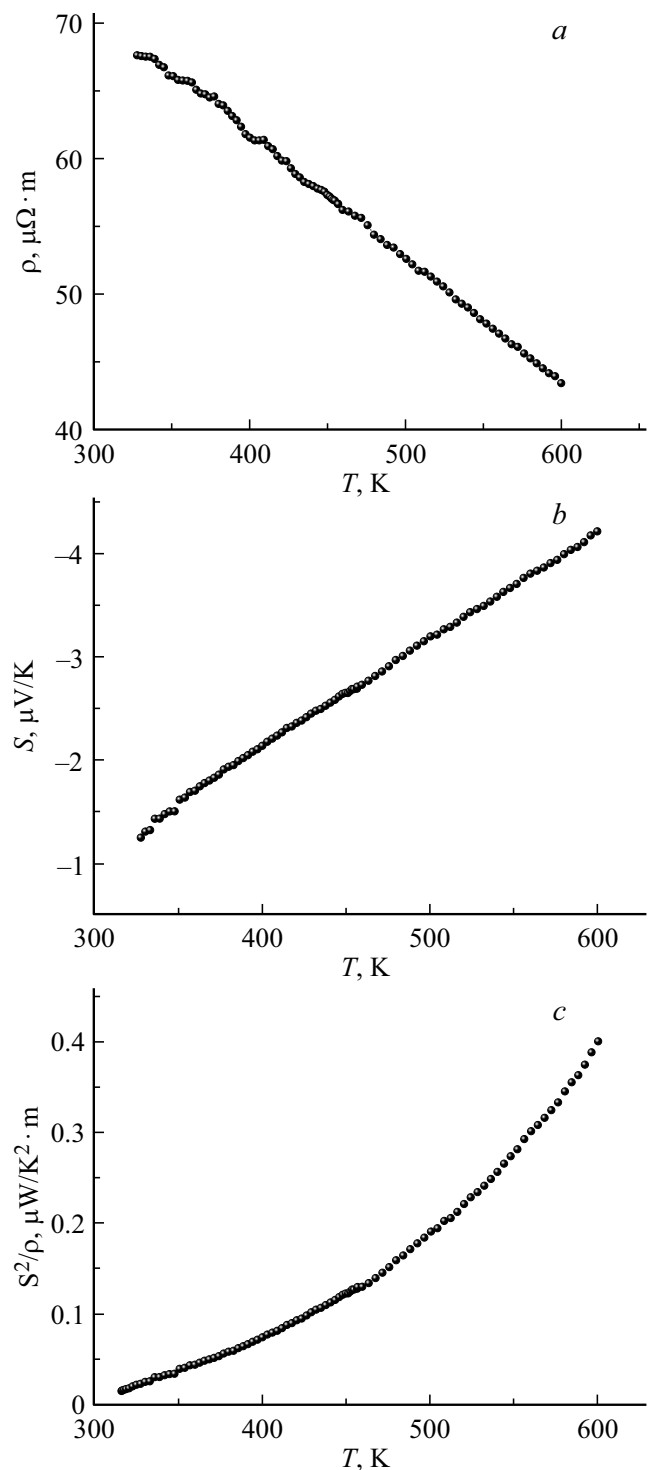


Figure 2. Temperature dependences of resistivity (*a*), thermal emf (*b*) and power factor (*c*) of the initial carbon fiber.

but at temperatures close to $T = 600$ K, ρ of both types of CF is almost equal.

Positive sign of thermal emf throughout the measured temperature range is the main feature of the modified CF. Moreover, thermal emf of the modified CF (Figure 3, *b*) is much higher than S of the initial CF in absolute value.

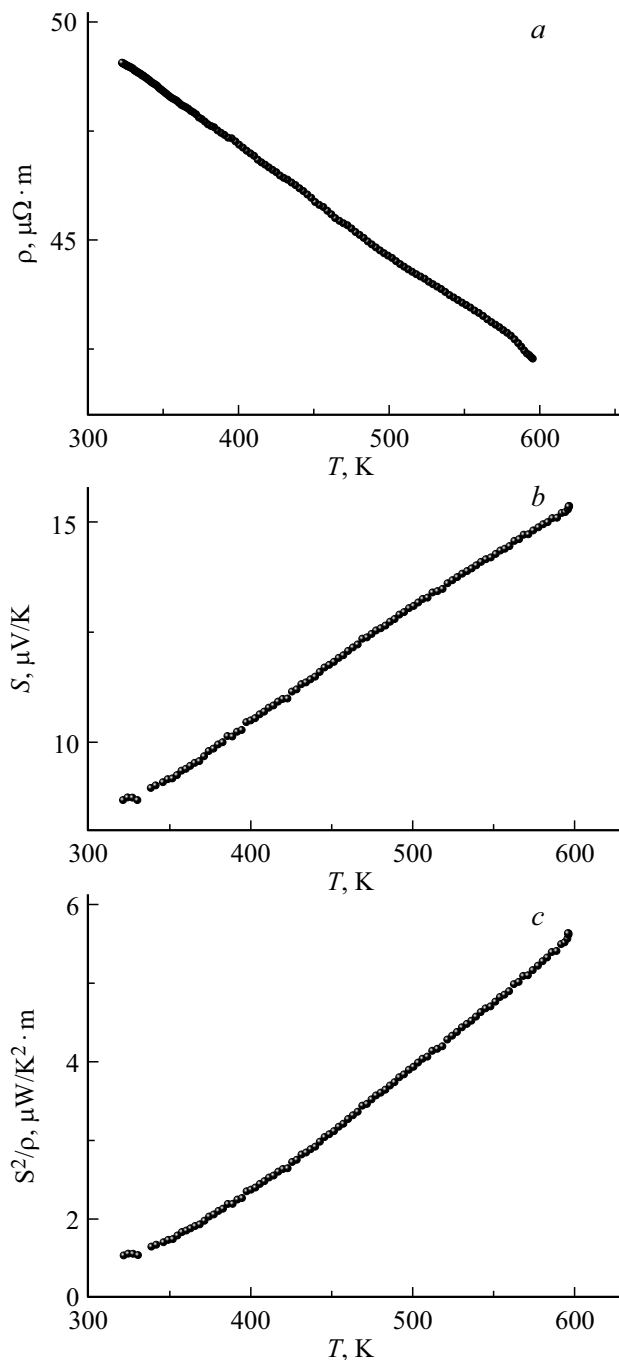


Figure 3. Temperature dependences of resistivity (a), thermal emf (b) and power factor (c) of the modified carbon fiber.

Due to a set of such features favorable for thermoelectric energy conversion with the modified CF, the thermoelectric power factor (Figure 3, c) of this type of CF is by an order of magnitude higher than S^2/ρ of initial CF.

5. Conclusion

Thermal emf sign reversal after CF modification is defined by the formation of additional bonds in oxygen-

containing complexes on ramified surface of CF as detected on the *p*-type sample, rather than by the amount of oxygen in the fiber. The finding suggests that the change of type of carriers in CF modified by pulse current is caused by the formation of additional carbon-oxygen bonds when O_2 molecules accept electrons from surface carbon atoms and generate additional charge carriers — holes. In both types of CF, fast growth of thermoelectric power factor was found in the temperature range 300–600 K. Considering that CF are defined as a chemically pure substance having high chemical resistance, high strength at low coefficient of friction and have almost zero coefficient of linear expansion, it is interesting to use such materials for thermoelectric transducers such as thermocouples and signal sensors operating until extreme operating conditions are achieved.

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Conflict of interest

The authors declare that they have no conflict of interest.

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