spectra result from the different resonant behaviors of observed SWNTs with different diameters. Moreover, the Raman intensity of C–C stretching modes of SWNTs is found to be much stronger than of MWNTs. The results indicate that one can distinguish SWNT from MWNT by the intensity analysis of their C–C stretching modes.

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Flexible graphite as a compliant thermoelectric material

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Flexible graphite is a flexible sheet made by compressing a collection of exfoliated graphite flakes (called worms) without a binder [1]. During exfoliation, an intercalated graphite (graphite compound with foreign species called the intercalate between some of the graphite layers) flake expands typically by over 100 times along the *c*-axis. Compression of the resulting worms (like accordions) causes the worms to be mechanically interlocked to one another, so that a sheet is formed without a binder.

Due to the process of exfoliation, flexible graphite has a relatively large specific surface area (e.g. 15 m^2/g [2]). As a result, flexible graphite is used as an adsorption substrate. Because of the absence of a binder, flexible graphite is essentially entirely graphite (other than the residual amount of intercalate in the exfoliated graphite). As a result, flexible graphite is chemically and thermally resistant, and has a low coefficient of thermal expansion (CTE). Due to its microstructure involving graphite layers that are preferentially parallel to the surface of the sheet, flexible graphite has high electrical and thermal conductivities in the plane of the sheet. Because graphite layers are somewhat connected perpendicular to the sheet (i.e. the honeycomb microstructure of exfoliated graphite), flexible graphite is electrically and thermally conductive in the direction perpendicular to the sheet (although not as conductive as the plane of the sheet). These in-plane and out-of-plane microstructures result in resilience and impermeability to fluids perpendicular to the sheet. The combination of resilience, impermeability and chemical and thermal resistance makes flexible graphite attractive for use as a gasket material for high temperature or chemically harsh environments.

Gasketing (i.e. packaging, sealing) [3–7] is by far the main application of flexible graphite, which can replace asbestos. Other than gasketing, a number of applications have emerged recently, including adsorption, electromagnetic interference (EMI) shielding, vibration damping, electrochemical applications and stress sensing [1,2,8–10].

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This paper provides yet another application, namely the use of flexible graphite as a compliant thermoelectric material.

Thermoelectric behavior pertains to the conversion between thermal and electrical energy. In particular, the Seebeck effect is a thermoelectric effect in which a voltage results from a temperature gradient, which causes the movement of charge carriers from the hot point to the cold point. This voltage (Seebeck voltage) is useful for temperature sensing and pertains also to the generation of electrical energy. The negative of the change in Seebeck voltage (hot minus cold) per degree C in temperature rise (hot minus cold) is called the thermoelectric power, the thermopower, or the Seebeck coefficient.

The thermal stress between a thermoelectric cell and the wall of a heat exchanger of a thermoelectric energy conversion system affects the thermal coupling as well as the durability. To reduce the thermal stress, compliant pads are used at the interface, although the pad acts as a barrier against thermal conduction [11,12]. If the thermoelectric material is itself compliant, a compliant pad will not be necessary. Compliant polymer–matrix composites containing a thermoelectric filler suffer from their inability to withstand high temperatures, as encountered in thermoelectric power conversion systems with a high thermal energy density. Flexible graphite is compliant and resistant to high temperatures, in addition to being a thermoelectric material [13].

Metals are in general more compliant than semiconductors, but their Seebeck effect is relatively weak and they tend to suffer from corrosion. Polymers can be more compliant than metals, but they are usually electrically insulating and do not exhibit the Seebeck effect. Flexible graphite is quite unusual in its combination of compliance and strong thermoelectric behavior.

The Seebeck effect tends to be weaker in metals than in semiconductors, but metals are more conductive electrically than semiconductors. This means that attaining a large Seebeck effect is not simply a matter of increasing the carrier concentration or mobility. A low thermal conductivity helps, as it enables a steep temperature gradient to occur, thereby decreasing the flow distance of the carrier.

Flexible graphite is much more conductive thermally in the in-plane direction than in the out-of-plane direction. The high in-plane thermal conductivity, together with the resilience in the out-of-plane direction, help the attaining of a good thermal contact between flexible graphite and a hot/cold surface. On the other hand, the low out-of-plane thermal conductivity is favorable for the Seebeck effect in the out-of-plane direction.

The Seebeck effect in the through-thickness direction of flexible graphite can be used for the generation of electrical energy, as a Seebeck voltage is generated between the two opposite in-plane surfaces of a flexible graphite sheet when the sheet is placed on a hot object (such as a human body) or a cold object (such as the window of an aircraft). The flexibility of the sheet facilitates the placement on a surface which is not flat. A related application is the sensing of the temperature of the hot or cold object.

This work provides a study of the thermoelectric behavior of flexible graphite. In addition to its relevance to applications, the study is relevant to basic understanding of the electrical conduction in this material.

Flexible graphite sheet (Grade GTB) was provided by EGC Enterprises, Inc. (Mentor, OH). The specific surface area is 15 m^2/g, as determined by nitrogen adsorption and measurement of the pressure of the gas during adsorption using the Micromeritics (Norcross, GA) ASAP 2010 instrument. This specific surface area corresponds to a crystallite layer height of 0.18 μm within a sheet, if the crystallite surface is considered to be the dominant contribution to the observed surface area. According to the manufacturer, the ash content of flexible graphite is $<5.0\%$; the density is 1.1 g/cm^3; the tensile strength in the plane of the sheet is 5.2 MPa; the compressive strength (10% reduction) perpendicular to the sheet is 3.9 MPa; the thermal conductivity at 1093°C is 43 W/m K in the plane of the sheet and 3 W/m K perpendicular to the sheet; the coefficient of thermal expansion (CTE) (21–1093°C) is -0.4×10^{-6}/°C in the plane of the sheet.

The thermoelectric behavior in the through-thickness direction was investigated using the following method. A specimen of size 25.9×24.9×1.17 mm was placed on an insulator-lined hot plate. Thus, a temperature gradient was generated in the through-thickness direction. The hot plate was controlled by a temperature controller, which provided a heating rate of 0.174°C/min and a cooling rate of 0.167°C/min. The voltage difference between the top and bottom surfaces was measured by using electrical contacts in the form of silver paint in conjunction with copper wire. The temperatures of the top and bottom surfaces were simultaneously measured by using two T-type thermocouples. The temperature of the hot side ranged from 21 to 111°C; that of the cold side ranged from 21 to 49°C. The temperature difference was up to 62°C. The cold side was cooled by using air, which was blown through a steel pipe in the direction perpendicular to the specimen surface. The extent of cooling depended on the air flow conditions.

Fig. 1 shows the measured voltage difference vs. the temperature difference during heating. The hundreds of data points essentially fall on a straight line through the origin. The slope of the line gives a thermoelectric power (relative to that of copper) of −0.65 μV/°C. This Seebeck coefficient minus the absolute thermoelectric power of copper (+1.94 μV/°C at 300 K) [14] is the absolute thermoelectric power of the specimen. The absolute thermoelectric power is thus −2.6 μV/°C. The behavior was quantitatively similar during cooling; the slope of the curve was the same.

The thermoelectric power has been previously reported for flexible graphite [13], kish graphite [15,16], highly

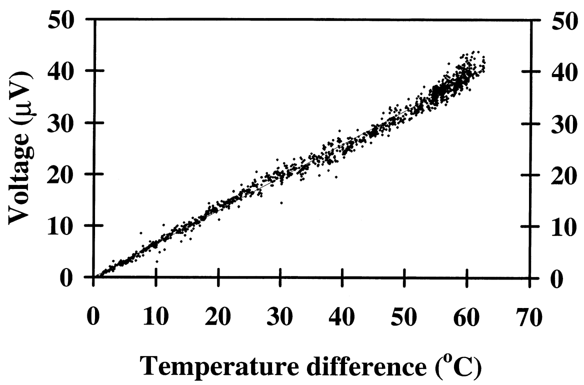

Fig. 1. Measured voltage difference vs. temperature difference between the top and bottom surfaces of a flexible graphite sheet during heating.

oriented pyrolytic graphite [15,17], carbon fibers [18,19] and graphite intercalation compounds [20,21]. For carbons that have not been intercalated, both positive and negative values of the absolute thermoelectric power at room temperature have been reported. The value depends on the crystallinity, defects, phonons and impurities, in addition to depending on the carrier type and concentration.

The value of −2.6 μV/°C reported here for flexible graphite in the through-thickness direction near room temperature in the absence of a magnetic field is comparable to but more negative than that previously reported for flexible graphite of density 0.82 g/cm^3 [13]. The difference in density is a factor that contributes to the difference in thermoelectric power.

Relative to other carbons, the value reported here is attributed to the combination of crystallinity, *c*-axis electrical connectivity and in-plane preferred orientation of the carbon layers. In particular, the unique microstructure of flexible graphite compared to other carbons is probably a factor.

In summary, the through-thickness absolute thermoelectric power of flexible graphite is −2.6 μV/°C near room temperature. The effect, together with the flexibility of the material, make the thermoelectric phenomenon potentially useful for temperature sensing and electric power generation.

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