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## Electret, piezoelectret, dielectricity and piezoresistivity discovered in exfoliated-graphite-based flexible graphite, with applications in mechanical sensing and electric powering

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#### ABSTRACT

This paper reports the in-plane dielectric, electret, piezoelectret and piezoresistive behavior of exfoliated-graphite-based flexible graphite, with demonstrated feasibility of electret-based electric powering and piezoelectret-based/piezoresistivity-based mechanical stress sensing under elastic tension. The powering is enabled by the inherent DC electric field *E* and DC electrical conductivity (resistivity  $\rho = 7.5 \times 10^{-6} \Omega$  m). *E* is supported by relative permittivity  $\kappa = 1170$  and directionally asymmetric polarization-induced electrical resistance increase. It increases linearly with increasing inter-electrode distance *l*, with  $E = 2.6 \times 10^{-5}$  V/m at l = 40 mm. With increasing stress, *E*,  $\rho$ ,  $\kappa$  and capacitance increase monotonically; *E* and  $\rho$  increase smoothly - totally reversibly for stress  $\leq 1.85$  MPa and slightly irreversibly for stress between 1.85 and 3.18 MPa. The fractional increases in *E* and  $\kappa$  at  $\leq 3$  MPa are  $\leq 110\%$  and  $\leq 73\%$ , respectively. The  $\kappa$ -stress curve abruptly increases in slope at 2.1 MPa, which is accompanied by the onset of some  $\kappa$  increase irreversibility. This 2.1-MPa slope increase is attributed to a microstructural change that does not affect the strain reversibility or  $\rho$ , but increases  $\kappa$ . The change possibly involves interfacial loosening, which promotes polarization without affecting conduction. The piezoelectret coupling coefficient  $d_{33}$  is  $3.7 \times 10^{-8}$  pC/N. The piezoresistivity gage factor is 50.

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#### 1. Introduction

Flexible graphite is a sheet obtained by the compaction of exfoliated graphite in the absence of a binder, as made possible during compression by the mechanical interlocking among the units of exfoliated graphite, which exhibits a cellular structure [1-7]. Each unit of exfoliated graphite (known as a worm) is derived from a graphite flake. Due to the high degree of compaction, the resulting sheet exhibits strong preferred orientation of the carbon layers in the plane of the sheet. The greater is the compaction, pressure used, the higher is the degree of preferred orientation.

Because of the cellular structure and the preferred orientation, flexible graphite is resilient and viscoelastic in the direction

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perpendicular to the plane of the sheet [7-16]. The viscoelasticity is derived from the interfacial frictional sliding mechanism [7]. Due to the resiliency, flexible graphite is used as a gasket material [17-21] that replaces asbestos, which is carcinogenic. The gasket application also benefited from the fact that flexible graphite can withstand high temperatures and harsh chemical environments.

Because of the preferred orientation, flexible graphite exhibits high electrical conductivity in the plane of the sheet. The conductivity enables electrical applications [21–23], such as resistive heating elements [24,25], compliant thermoelectric material [26], fuel cell plates [27,28], flow battery plates [29], lead acid battery cell grids [30], electromagnetic interference (EMI) shielding [31–36] and electrochemical electrodes for batteries, supercapacitors, organic solar cells and sensors [37–56].

Due to the preferred orientation, flexible graphite also exhibits high thermal conductivity in the plane of the sheet. Thus, flexible graphite is used as a heat spreader for microelectronic cooling [57]. Although the thermal conductivity is much lower in the out-ofplane direction than the in-plane direction, the substantial outof-plane thermal conductivity and the out-of-plane resiliency





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enable flexible graphite to be attractive as a thermal interface material for improving thermal contacts, as needed for microelectronic cooling [58–64].

Other applications of flexible graphite include plasma facing [65], nuclear reactor components [66], thermal transistors [67] and photoluminescence [68]. The chemical or physical modification of flexible graphite can be used to enhance selected properties [69–79].

In spite of the numerous electrical applications that exploit the electrical conductivity of flexible graphite, no attention has been given to the dielectric behavior of this material. The dielectric behavior involves electric polarization in the presence of an electric field. The polarization causes an electric field that is in a direction that is opposite to the applied field, thereby hindering the conduction. The main material property that describes the dielectric behavior is the electric permittivity. In case of carbons, the polarization behind the dielectric behavior stems from the movement of the charge carriers [80-82]. This is in contrast to ceramics and polymers, the polarization of which stem from other mechanisms, such as ion movement and molecular reorientation. The permittivity of carbon fibers [80-82] and discontinuous exfoliated graphite (without compression to form flexible graphite) [83–87] has been previously reported by this research group. However, the permittivity has not been previously reported for flexible graphite, which differs from exfoliated graphite in its physical continuity. The continuity allows larger distance of excursion of the electrons or holes during polarization, thus increasing the permittivity. This effect of the continuity has been previously shown by comparing continuous carbon fibers with discontinuous carbons (such as exfoliated graphite and activated carbon). The continuous carbon fibers exhibit relative permittivity  $> 10^3$ , whereas the discontinuous carbons exhibit relative permittivity  $\leq 10^3$  ( $< 10^2$  unless the carbon has been chemically modified).

An electret is a quasi-permanent electric dipole [88–93]). The dipole is associated with a DC electric field. Electrets have long been reported for materials that are essentially not conductive, particularly polymers. However, these materials need to be subjected to a high electric field (a process often referred to as poling) in order to be rendered with the presence of an electric dipole. A particularly common method of poling involves the use of corona discharge. A problem with the poling is that, after the completion of the poling, depoling naturally occurs as time progresses. As a consequence of the depoling, repoling is needed in order to recover substantially the electric dipole.

Due to their essential non-conductivity, the long reported electrets act as capacitors and do not allow DC electric current to flow through them. As a consequence, these electrets cannot serve to provide DC electric power. In contrast, electrets that are conductive act as resistors and allow DC current to flow through them, so that they can serve to provide DC electric power. This is a reason for the importance of studying electrets that are conductive. However, previous work on electrets that are conductive does not exist, except for our parallel work on electrets in the form of steel [94].

The piezoelectret effect pertains to the effect of stress/strain on the electric field in the electret [94–99]. For an electret that is essentially nonconductive, the application of a static (not timevarying) stress/strain affects the capacitance of the electret, so that a DC current pulse flows through the circuit connecting the two electrodes of the electret. Because of its short duration, the pulse is not very useful in relation to providing electric power. On the other hand, for an electret that is essentially nonconductive, the application of a dynamic (time-varying) stress/strain results in a corresponding time-varying current through the circuit connecting the two electrodes. Thus, the mechanical energy input is converted to an electrical energy output. This energy conversion is to be distinguished from the providing of electric power without energy conversion. For an electret that is essentially nonconductive, the providing of electric power without energy conversion is not possible and the electrical energy obtained through the energy conversion cannot be DC. In contrast, an electret that is conductive can provide electrical energy without energy conversion (i.e., without a mechanical energy input) and can provide DC electrical energy.

The electrical energy output (whether DC or AC) is valuable for mechanical energy harvesting and for the sensing of the mechanical energy input. With an electret that is essentially nonconductive, the electrical energy output is feasible only in the presence of a dynamic mechanical energy input. In contrast, with an electret that is conductive, an electrical energy output is feasible, whether a dynamic mechanical energy input is present or not.

Both the piezoelectret effect and the direct piezoelectric effect allow stress/strain sensing through measurement of the electric field or capacitance. Both effects convert mechanical energy to electrical energy. However, the direct piezoelectric effect differs from the piezoelectret effect in that it does not require the presence of an electret in the material.

Piezoresistivity pertains to the effect of stress/strain on the electrical resistivity. No energy conversion occurs. Piezoresistivity allows the sensing of strain/stress through electrical resistance measurement. Piezoresistivity has been widely reported in polymer-matrix composites with electrically conductive fillers, whether the fillers are particles or fibers. The effect usually stems from the effect of stress/strain on the degree of contact of the conductive filler units (e.g., carbon black, carbon nanotubes, graphite nanoplatelet, graphene, etc.) [100]. The effect has also been reported for continuous carbon fiber polymer-matrix composites [101], due to the effect of stress/strain on the composite microstructure (specifically the degree of contact of the fibers in the composite). In addition, piezoresistivity has been reported for a suspended graphene membrane [102] and for a three-dimensional graphene foam [103], due to the effect of deformation of the membrane or foam on the electrical resistance.

The direct piezoelectric effect (more correctly a piezoelectret effect) and piezoresistivity have been previously reported for continuous carbon fibers [82,101] and carbon-carbon composite [104]. However, the direct piezoelectric effect and the piezoelectret effect have not been previously reported for any other carbon material.

The piezoelectret/piezoelectric and piezoresistive effects enable a material to sense its own condition without any embedded or attached sensor. Such capability is known as self-sensing, which is attractive for its high durability, low cost, large sensing volume and absence of mechanical property loss, compared to the use of attached or embedded sensors.

The electret is an aspect of the dielectric behavior of a material. The most basic dielectric property of a material is the electric permittivity, which relates to the tendency for a material to be polarized under the presence of a DC electric field. Therefore, for the purpose of strengthening the science base of electrets, the determination of the permittivity is relevant.

This work is primarily aimed at investigating for the first time the electret, piezoelectret, dielectricity and piezoresistivity of flexible graphite. Along with the investigation is the determination of the permittivity, piezoelectret coupling coefficient and piezoresistivity gage factor. In addition, this work is aimed at understanding the underlying science. Therefore, the effects of (i) loading and subsequent unloading, (ii) stress amplitude and (iii) specimen length on the capacitance (related to the permittivity), resistance (related to the resistivity) and electric field (related to the piezoelectret effect) are studied.

Flexible graphite is widely used as a gasket material for harsh environments [17–21]. The gasket is a sealant that is sandwiched between two surfaces that require sealing. This sandwiching involves the application of stress in the direction perpendicular to the plane of the flexible graphite sheet. Decrease in the stress can occur due to stress relaxation that is associated with the viscoelastic behavior of flexible graphite [9–13]. The stress decrease reduces the effectiveness of the sealing provided by the gasket. Therefore, the ability to sense the stress is desirable.

The secondary objective of this work is to investigate the feasibility of flexible graphite's piezoelectret-based and piezoresistivity-based stress/strain self-sensing in the elastic regime. This capability enables the flexible graphite to sense its own stress or strain, thereby rendering smartness to a gasket made of flexible graphite.

Due to its high in-plane thermal conductivity, flexible graphite is used as a heat spreader for heat dissipation in microelectronics [57]. Electret-based powering is potentially an additional function for the flexible graphite heat spreader. This function would reduce the need for a conventional power source, such as a battery, for the microelectronic device.

The third objective of this work is to investigate the feasibility of electret-based powering by flexible graphite. This capability enables the flexible graphite to be able to serve as a DC power source. The DC power can be converted to AC power by the use of a rectifier.

Damage self-sensing is an additional capability that can be provided by the electret in flexible graphite. This is because the electric field in the electret is expected to be affected by the damage. Damage self-sensing can also be rendered by the piezoelectret in flexible graphite, due to the effect of damage on the degree of the piezoelectret effect. However, damage sensing is beyond the scope of this work.

#### 2. Experimental methods

#### 2.1. Material

The flexible graphite sheet is provided by Polycarbon Inc., currently SGL Technic LLC Polycarbon Division, in Valencia, CA. It is conventionally manufactured by the compaction of exfoliated natural graphite in the absence of a binder. The exfoliated graphite is obtained by the exfoliation of sulfuric-acid intercalated graphite. The material has purity  $\geq$ 98%, ash  $\leq$ 2%, sulfur <500 ppm, chloride  $\leq$ 50 ppm, and tensile modulus 1.38 GPa [105,106]. The density is 0.979 ± 0.033 g/cm<sup>3</sup>, as measured in this work; the material floats on water. The thickness is 1.182 mm, as measured in this work.

#### 2.2. Stress application and mechanical testing methods

Tensile stress is applied by using a stepper-motor-driven mechanical testing system (Mark-10 ESM303, Mark-10 Corp., Copiague, NY). The force is up to 1.5 kN and is increased at the rate 90 N/ min. The specimen is in the form of a rectangular bar, the long direction of which is in the direction of capacitance/resistance measurement. It is gripped at its two ends via adhesively bonded cardboard end tabs that are positioned on the two opposite surfaces of the specimen. The stress is in-plane, in the same direction as the capacitance and resistance. For the purpose of obtaining the tensile stress-strain curve, the strain is measured by using an attached conventional resistance-based strain gage with resistance 120  $\Omega$  (under no load) and gage factor 2.075.

#### 2.3. Capacitance and permittivity measurement methods

The in-plane electric permittivity of the flexible graphite specimen is measured. The method of permittivity measurement is the same as the method used in the prior work of this research group for continuous carbon fibers [80,82,107,108], continuous carbon fiber polymer-matrix composite [109] and carbon-carbon composite [104]. In this method, a dielectric film is positioned between the specimen and each electrode. This film is needed because the LCR meter used for capacitance measurement is not designed for measuring the capacitance of a material system with a low resistance. Furthermore, in this method, the interfacial capacitance is decoupled from the volumetric capacitance, as explained below. The interfacial capacitance refers to the capacitance of the interface between the specimen and the electrode, with the interface including the dielectric film. The specimen is in the form of a rectangular bar, with the long direction of the bar being in the direction of capacitance measurement.

In order to decouple the interfacial capacitance from the volumetric capacitance, four electrodes are applied to the top surface of the specimen at four points that are essentially equally spaced at a distance of 25.41 mm along the length of the specimen (Fig. 1). Each electrode is in the form of aluminum foil that is adhered to the specimen by using six stacked layers of double-sided adhesive tape (total thickness = 0.462 mm). The tape serves both as the adhesion agent and the dielectric film. Each electrode is 4.76 mm wide in the direction of the specimen length, such that it extends for the entire 5.76-mm width of the specimen. Capacitance measurement is performed along the length of the specimen over distances of L (25.41 mm), 2L (50.81 mm) and 3L (76.21 mm), which correspond to the distance between the 1st and 2nd electrodes, the distance between the 1st and 3rd electrodes, and the distance between the 1st and 4th electrodes, respectively.

A precision LCR meter (Instek LCR-816 High Precision LCR Meter) is used for capacitance measurement at 2.000 kHz, which is the highest frequency that the meter can provide. The kHz range of frequency is widely used and commonly available. The capacitance measurement has error  $\pm 0.0005$  pF. The capacitance corresponds to the meter setting for the equivalent electrical circuit consisting of a capacitance and a resistance in series. The AC voltage (0.500, 1.000 or 1.500 V, as selected from the limited voltage range that the LCR meter can provide) is adjusted so that the electric field (19.7 V/m) is fixed for the three inter-electrode distances (L, 2L and 3L).

The measurement of the capacitance using a pair of electrodes gives a value that corresponds to the series combination of two interfacial capacitances (for the two specimen-electrode interfaces) and the specimen volumetric capacitance. Based on the well-known equation for capacitances in series, the measured capacitance  $C_m$  is given by

$$1/C_m = 1/C + 2/C_i$$
 (1)

where C = the specimen volumetric capacitance, and  $C_i =$  the interfacial capacitance for one interface. The relative permittivity  $\kappa$  of the specimen is related to *C* by the well-known equation

$$C = \varepsilon_0 \kappa A/l, \tag{2}$$

where  $\varepsilon_0$  = the permittivity of free space (8.85 × 10<sup>-12</sup> F/m), l = the inter-electrode distance (L, 2L or 3L), and A = the area of the specimen in the plane perpendicular to the direction of capacitance measurement. The combination of Eqs. (1) and (2) yields the equation

$$1/C_m = l/(\varepsilon_0 \kappa A) + 2/C_i. \tag{3}$$



(c)

**Fig. 1.** Configuration for electric permittivity measurement of flexible graphite. Dimensions are in mm. (a) Top view. (b) Side view, with the vertical scale exaggerated compared to the horizontal scale. (c) Photograph of specimen (horizontal) with a ruler having main divisions in inches. Each electrode (vertical, 2.31 mm wide in the horizontal direction) is much narrower for the region above the specimen than the regions away from the specimen. (A colour version of this figure can be viewed online.)

Based on Eq. (3), with *l* being a variable, a plot of  $1/C_m$  vs. *l* gives a line of slope equal to  $1/(\varepsilon_0 \kappa A)$ . From the slope,  $\kappa$  is obtained.

#### 2.4. Piezoelectret effect characterization method

The permittivity is measured for each level of stress, which is applied as described in Sec. 2.2. The stress is progressively increased and then decreased. For each stress level, the capacitance is measured for specimens with three lengths L, 2L and 3L (Fig. 2) in order to determine the permittivity for the particular stress level.

The electric field output is measured at various stresses. The stress is applied as described in Sec. 2.2. The stress is progressively increased and subsequently decreased. The DC electric field is obtained by dividing the DC voltage output by the distance between the proximate edges of the two electrodes. The voltage measurement involves the same configuration as Fig. 2, except that the dielectric film is replaced by silver paint. A precision digital multimeter (Keithley Model 2002) is used for the voltage measurement. For the relevant voltage range ( $\leq 200 \text{ mV}$ ), this meter

provides voltage resolution 1 nV and input resistance  $>100 \text{ G}\Omega$  [110].

# 2.5. Resistivity measurement and piezoresistivity characterization method

The measurement of the DC electrical resistivity uses the same configuration as Fig. 2, except that silver paint is used in place of the dielectric film. Moreover, the interfacial resistance is decoupled from the volumetric resistance by testing the specimen bar at the three different lengths (L, 2L and 3L). The interface associated with the interfacial resistance is that between the specimen and electrode, with the interface including the silver paint.

The measurement of the resistance using a pair of electrodes gives a value that corresponds to the series combination of two interfacial resistance (for the two specimen-electrode interfaces) and the specimen volumetric resistance. The measured resistance  $R_m$  is thus given by the equation



**Fig. 2.** Configuration for testing the effect of tensile stress on the electrical behavior of flexible graphite. (a) Schematic illustration (top view), with the dimensions shown in mm. (b) Schematic illustration (side view), with the dimensions shown in mm, showing a dielectric film between each electrode and the specimen. The vertical axis is expanded, with the scale being different from that of the horizontal axis. (c) Photograph of three specimens at three lengths shown lined up (with the longest specimen at the left and the shortest specimen at the right). A ruler with major divisions in inch is shown parallel to the three specimens. (A colour version of this figure can be viewed online.)

$$R_m = R + 2R_i,\tag{4}$$

where R = the specimen volumetric resistance, and  $R_i$  = the interfacial resistance for one interface. The resistivity  $\rho$  of the specimen is related to R by the well-known equation

$$R = \rho l / A, \tag{5}$$

where l = the inter-electrode distance (L, 2L or 3L), and A = the area of the specimen in the plane perpendicular to the direction of resistance measurement.

The combination of Eqs. (4) and (5) yields

$$R_m = \rho l/A + 2R_i,\tag{6}$$

Eq. (6) indicates that a plot of  $R_m$  vs. l gives a line of slope =  $\rho/A$ . Thus,  $\rho$  is obtained from the slope. In other words, for each stress level, the resistances corresponding to inter-electrode distances of L, 2L and 3L are used to determine  $\rho$ .

A precision digital multimeter (Keithley Model 2002, two-wire mode) is used for measuring the DC resistance. For the relevant range of resistance, the current provided by the meter is 7.2 mA and the resolution is  $100 n\Omega$  [110].

For characterizing the piezoresistivity, the resistivity is measured for each level of stress, which is applied as described in Sec. 2.2. The stress is progressively increased and then decreased. For each stress level, the resistance is measured for the three lengths (L, 2L and 3L).



Fig. 3. Tensile stress-strain curve of flexible graphite during loading and subsequent unloading, with the stress up to 3.18 MPa.



**Fig. 4.** (a) Plot of  $1/C_m$  vs. distance *l* according to Eq. (3) in the absence of stress for flexible graphite. (b) Plot of  $R_m$  vs. distance *l* according to Eq. (6) in the absence of stress for flexible graphite.



**Fig. 5.** Effect of tensile stress on the capacitance for lengths L, 2L and 3L during loading for flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

#### 2.6. Polarization-induced apparent resistance measurement

The polarization results in an electric field that opposes the applied electric field, thus hindering conduction and increasing the apparent resistance. Upon sudden polarity reversal, the apparent resistance decreases abruptly, because the polarization does not change instantaneously and this polarization enhances the electric field in the material.

The apparent DC resistance during DC polarization and polarity reversal is measured using the configuration of Fig. 2. However, silver paint is used instead of the dielectric film. There are two scenarios in the testing. In scenario 1, depolarization is conducted immediately prior to testing, as performed by short-circuiting the two outer electrodes for about 6 min. In scenario 2, no depolarization is performed.

For measuring the apparent resistance during polarization, a constant DC current (1 mA) is applied along the length of the specimen using two outer electrodes. The DC current source used is Keithley Model 224. The DC voltage is measured between the two inner electrodes as a function of the time of current application, using a high-precision multimeter (Keithley Model 2002).The apparent resistance is given by the voltage divided by the current. Immediately after current application for 360 s, the polarity of the applied current (i.e., the polarity of the applied electric field) is suddenly reversed, while the voltage measurement continues.

#### 2.7. Power density determination

Let *V* be the voltage provided by the electric field of the electret and let *R* be the resistance of the electret. The power *P* provided by the electret is given by the equation

$$P = V^2/R.$$
 (7)

The electric field E is the voltage gradient, so

$$V = El, \tag{8}$$

where V is the voltage provided by the electret and l is the interelectrode distance of the electret.

The resistance R is given by

$$R = \rho l / A, \tag{9}$$

where  $\rho$  is the resistivity, *l* is the length and *A* is the area. Combining Eqs. (7)–(9) gives the equation

$$P = E^2 l A / \rho. \tag{10}$$

The power density (i.e., power per unit volume) is given by

Power density = 
$$P$$
 /volume =  $E^2/\rho$ , (11)

since the volume is equal to IA.

#### 3. Results and discussion

#### 3.1. Tensile modulus

Based on the completely linear stress-strain curve (Fig. 3), the tensile modulus is  $(1.335 \pm 0.015)$  GPa. This value is close to the literature value of 1.38 GPa (Sec. 2.1). The strain is totally reversible.



Fig. 6. Effect of tensile stress on the capacitance for lengths L, 2L and 3L during loading and subsequent unloading for flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

The stress used in the piezoelectret and piezoresistive testing is within the range in Fig. 3.

#### 3.2. Effect of stress on the capacitance and permittivity

The relative permittivity in the absence of stress is  $1173 \pm 58$ , as obtained from the slope of the linear curve in Fig. 4. Fig. 5 shows that capacitance increases monotonically with increasing tensile stress. The larger is the inter-electrode distance, the lower is the capacitance, as expected. For the maximum stress of 1.85 MPa, the highest fractional increase in capacitance is 10.9% and the fractional increase in capacitance is essentially equal for the three lengths (L, 2L and 3L), as shown by the curves for the three lengths essentially overlapping. For the maximum stress of 3.18 MPa, the highest fractional stress-induced capacitance increase is 26.0%, 45.8% and 53.8% for lengths L, 2L and 3L, respectively. There is an abrupt increase in slope at 2.1 MPa for both the curve of the capacitance vs. stress and the curve of the fractional change in capacitance vs. stress. Below 2.1 MPa, the curves for the three lengths essentially overlap, but they are distinct above 2.1 MPa. Fig. 6 shows that the capacitance increase is completely reversible for the maximum



**Fig. 7.** Effect of stress on the capacitance during loading, with comparison of measured capacitance and calculated capacitance based on the dimensional changes for flexible graphite. Length = L, 2L and 3L. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

stress of 1.85 MPa, but is only partly reversible for stresses between 1.85 and 3.18 MPa. Thus, in spite of the linearity of the stress-strain curve and the total reversibility of the strain up to 3.18 MPa (Fig. 3), the capacitance change is partially irreversible when the stress exceeds 2.1 MPa. Along with the partial irreversibility of the capacitance change is the occurrence of the increase in the fractional stress-induced change in capacitance as the length increases from L to 2L and to 3L. This suggests the occurrence of a microstructural change that does not affect the strain reversibility but reduces the degree of capacitance as the length increases the fractional change in capacitance as the length increases the stress exceeds 2.1 MPa, as further supported below in terms of a similar change in  $\kappa$ .

The capacitance change is calculated based on the dimensional change alone. This calculated capacitance change is negligible compared to the measured capacitance change (Fig. 7). This means that the observed capacitance change is not due to the dimensional change, but is due to another phenomenon, namely the direct piezoelectric effect (Sec. 3.4). Furthermore, with the tensile strain being an elongation, the capacitance is expected to decrease. However, the observed capacitance change is an increase.

For each of the stress levels investigated, the plot of  $1/C_m$  vs.



**Fig. 8.** Effect of tensile stress on the relative permittivity  $\kappa$  during loading for flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

distance *l* in accordance with Eq. (3) is highly linear. The relative permittivity  $\kappa$  is obtained from the slope of the plot, as shown in Fig. 8. The  $\kappa$  values are high for all stress levels, including the value of 1173 at zero stress. The value of  $\kappa$  increases monotonically as the stress increases, with the fractional increase in  $\kappa$  being up to 11% and 73% for the maximum stress of 1.85 MPa and 3.18 MPa, respectively. For the maximum stress of 3.18 MPa, both the curve of  $\kappa$  vs. stress and the curve of the fractional change in  $\kappa$  vs. stress show an abrupt increase in slope at 2.1 MPa. This is consistent with the abrupt increase in slope at 2.1 MPa in the curve of the fractional change in capacitance vs. stress (Fig. 5).

The increase in  $\kappa$  upon loading is totally reversible upon unloading when the maximum stress is 1.85 MPa, but is partially reversible upon unloading when the maximum stress is between 1.85 and 3.18 MPa (Fig. 9). This is consistent with similar behavior of the capacitance (Fig. 6). Since  $\kappa$  is a material property, Figs. 8 and 9 indicate that a change in microstructure occurs at the stress of 2.1 MPa. This microstructural change may be related to the slight loosening of an interface in the flexible graphite, such that this loosening promotes polarization.

The capacitance increase (up to 10.9% and 53.8% for the maximum stresses of 1.85 MPa and 3.18 MPa, respectively, Fig. 5) relates to the increase in  $\kappa$  (up to 11.2% and 73.2% for the maximum stress of 1.85 MPa and 3.18 MPa, respectively, Fig. 8). The fractional increase in  $\kappa$  is greater than the corresponding fractional increase in the capacitance. This is because the measured capacitance  $C_m$  is governed by both the volumetric capacitance  $C_v$  of the specimen and the interfacial capacitance  $C_i$  of the specimen-electrode interface (Eq. (1)). In contrast,  $\kappa$  is governed by  $C_v$  only. The applied tensile stress slightly degrades the quality of the specimen-electrode interface. The greater is the stress, the larger is the intercept  $2/C_i$  in the plot of  $C_m$  vs. distance l (Eq. (3)), and hence the lower is  $C_i$ . Due to the decrease of  $C_i$ ,  $C_m$  decreases (Eq. (3)).

#### 3.3. Effect of stress on the resistance and resistivity

For any of the three inter-electrode distances (L, 2L and 3L), the resistance increases monotonically as the tensile stress increases (Fig. 10). At any of the stress levels, the larger is the inter-electrode distance, the greater is the resistance, as expected. The fractional increase in resistance due to the tensile stress is up to 1.1%, 1.5% and 1.9% for lengths L, 2L and 3L, respectively, for the maximum stress of 1.85 MPa, and is up to 2.7%, 3.6% and 4.5% for lengths L, 2L and 3L, respectively, for the maximum stress of 3.18 MPa.

For either value of the maximum stress and for any of the three lengths, the resistance increases smoothly with increasing stress, such that there is no abrupt change in slope at any stress in the curve of resistance vs. stress or the curve of the fractional change in resistance vs. stress. This smoothness is in contrast to the change in slope at 2.1 MPa for the curve of capacitance (or fractional change in capacitance) vs. stress (Fig. 5) and the curve of  $\kappa$  (or fractional change in  $\kappa$ ) vs. stress (Fig. 8). This means that the microstructural change that occurs above 2.1 MPa is one that affects the capacitance without affecting the resistance.

The increase in resistance upon loading is totally reversible upon unloading for the maximum stress of 1.85 MPa and is almost totally reversible upon unloading for the maximum stress of 3.18 MPa, as shown in Fig. 11. This is in contrast to the partially reversible capacitance increase upon loading for the maximum stress of 3.18 MPa (Fig. 6). This again means that the microstructural change that occurs at 2.1 MPa is one that affects the capacitance without affecting the resistance.

The resistance change is calculated based on the dimensional change caused by the tensile stress. This calculated resistance change is negligible compared to the measured resistance change (Fig. 12). Therefore, the observed resistance increase cannot be explained by the dimensional change. It is attributed to a resistivity increase, which is confirmed below by measuring the resistivity at



Fig. 9. Effect of tensile stress on the relative permittivity  $\kappa$  during loading and subsequent unloading for flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.



**Fig. 10.** Effect of tensile stress on the resistance during loading for length = L, 2L and 3L, with comparison of the measured resistance and calculated resistance based on the dimensional changes alone for flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

each of the stress levels.

For both values of the maximum stress, the fractional increase in resistance due to the stress increases with increasing length from L to 2L and to 3L. However, the fractional change in length due to the stress should be independent of the length in the elastic regime. According to Fig. 3, the strain is totally reversible up to the highest stress of 3.18 MPa, so that the deformation is in the elastic regime. This suggests that, even in the elastic regime, the resistance increase due to the stress (whether up to 1.85 or 3.18 MPa) is not only due to the elastic deformation, but is also due to a reversible microstructural change that increases the resistance reversibly. The occurrence of such a reversible microstructural change is in line with the well-known resiliency of flexible graphite. This same microstructural change also reduces the degree of capacitance reversibility and increases the fractional change in capacitance as the length increases (Sec. 3.2).

The plot of  $R_m$  vs. distance *l* according to Eq. (6) is highly linear for all of the stress levels. The plot at zero stress is shown in Fig. 4(b). Based on the slope of the plot, the resistivity is determined, as shown in Fig. 13. The resistivity increases monotonically with increasing tensile stress. This means that the piezoresistivity is

positive. The fractional increase in resistivity reaches 13.6% and 32.9% for the maximum stresses of 1.85 MPa and 3.18 MPa, respectively. For either value of the maximum stress, the curve of resistivity vs. stress is smooth, with no abrupt change in slope at any stress. This is consistent with the smoothness of the curve of the resistance vs. stress (Fig. 10). This means that the microstructural change that occurs at 2.1 MPa is one that affects  $\kappa$  without affecting the resistivity.

The increase in resistivity upon loading is totally reversible upon unloading for the maximum stress of 1.85 MPa and is almost totally reversible upon unloading for the maximum stress of 3.18 MPa, as shown in Fig. 14. This is in contrast to the partially reversible increase in  $\kappa$  upon loading for the maximum stress of 3.18 MPa (Fig. 9). This means that the microstructural change that affects  $\kappa$  at 2.1 MPa causes a degree of irreversibility in the  $\kappa$  increase, but essentially does not cause any irreversibility in the accompanying resistivity increase.

The resistivity and  $\kappa$  (Sec. 3.2) differ in that  $\kappa$  is more sensitive to the microstructural change at 2.1 MPa than the resistivity. This is probably due to the slight loosening at an interface in flexible graphite (likely the interface between the merged part of the cell wall in the cellular structure of exfoliated graphite [13]) causing an increase in the interfacial resistance, thereby enabling the occurrence of more polarization along the length of the cell wall between the merged parts in the direction of capacitance measurement [13]. The equation that describes piezoresistivity is given by Ref. [111].

$$\delta R/R = \delta \rho/\rho + (\delta \ell/\ell)(1+2\nu), \tag{12}$$

where  $\delta R/R =$  the fractional change in resistance,  $\delta \rho/\rho =$  the fractional change in resistivity,  $\delta Q/Q =$  the longitudinal strain, and  $\nu =$  Poisson's ratio. Eq. (12) applies to the case in which the material is isotropic in the two directions that are transverse to the direction of stress application, i.e.,  $\nu_{12} = \nu_{13}$ . This case is assumed to apply to flexible graphite. The value of  $\nu$  has not been reported for flexible graphite. Hence, the value  $\nu = 0.20 \pm 0.03$  for graphite is used [112]. The gage factor is defined as the fractional change in resistance per unit strain. It is commonly used to describe the severity of the piezoresistivity. In case that a strain sensor is not piezoresistive, but provides resistance change due to the dimensional changes alone, the gage factor is  $1 + 2\nu$ .

Based on Eq. (12) and the initial slope in Fig. 13, the gage factor is determined, as shown in Table 1. The gage factor is higher in the second stress cycle than the first cycle, such that the difference is more significant for the maximum stress of 3.18 MPa than the maximum stress of 1.85 MPa, as shown in Table 1. For the same cycle (either first or second cycle), the gage factor is higher for the maximum stress of 3.18 MPa than the maximum stress of 1.85 MPa. This means that the microstructural change at 2.1 MPa and the slight degree of irreversibility in the resistivity increase after the first cycle in case of the maximum stress of 3.18 MPa contribute to increasing the gage factor. The gage factor is around 50, except for the higher value of 62 for the second cycle and the maximum stress of 3.18 MPa. The gage factor of 50 obtained in this work for flexible graphite under tension is higher than the values ranging from 20 to 38 for three-dimensional graphene foam embedded in an elastomeric polymer matrix and tested under compression [103].

Both resistivity and  $\kappa$  increase with increasing stress. This means that the resistivity and  $\kappa$  are correlated. The sense of the correlation is attributed to the fact that a high resistance helps support polarization. The presence of correlation is consistent with the fact that the resistivity and permittivity are not independent of one another. This dependence is embodied in the Kramers-Kronig relationship [113].



Fig. 11. Effect of tensile stress on the resistance for lengths L, 2L and 3L during loading and subsequent unloading for flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

#### 3.4. Electret behavior

In the absence of stress, the electric field is  $2.58 \times 10^{-5}$  V/m at the inter-electrode distance *l* of 40 mm. The electric field increases linearly with increasing *l*, as shown in Fig. 15(a). When *l* is increased from 40 mm to 120 mm, the electric field is increased by 0.698%. The linear relationship between *E* and *l* over large distances up to 1280 m has been shown for copper [94]. Based on Eq. (11), the volumetric power density is obtained. The value is 0.44 W/m<sup>3</sup> for l = 40 mm × 30000 = 1200 m.

The meaning is given below for the fact that the fractional increase in electric field when the inter-electrode distance l is tripled is 0.698%. Consider two inter-electrode distances (L and 3L). For length L, the magnitude of charge at each end of the length is Q. For length 3L, based on the relationship between the electric field and polarization, the magnitude of charge at each end of the interelectrode distance is 1.00698Q. The voltage across length L is given by Q/C, where C is the capacitance across length L. The electric field across length L is the voltage divided by L, i.e., Q/(CL). The voltage across length 3L is given by 1.00698 Q/(C/3), since the capacitance across 3L is 1/3 of that across L. Hence, the electric field across length 3L is the voltage divided by 3L, i.e., 1.00698 Q/(CL), which is equal to 1.00698 times the electric field across length L, as consistent with the abovementioned consideration of 0.698% increase in the electric field when l is tripled. Fig. 15(b) shows the decrease of this factor with increasing *l*.

The presence of an electret is supported the apparent resistance increase during DC polarization and abrupt apparent resistance decrease during subsequent polarity reversal. During polarization, the apparent resistance increases with time, such that the rate of increase decreases with increasing time. The decreasing rate is because the polarization results in an electric field which make further polarization more difficult. Upon sudden polarity reversal of the applied electric field, the apparent resistance decreases suddenly, since the polarization cannot change instantaneously. Without prior depolarization, the apparent resistance immediately before and immediately after the polarity reversal is asymmetrical about the true resistance, due to the electret present, as shown in Fig. 15(c). However, with immediately prior depolarization, the apparent resistance change upon polarity reversal is essentially symmetrical, as shown in Fig. 15(d), due to the electret by the depolarization. These results on the apparent resistance support the existence of the electret.

Flexible graphite is commercially available in the form of rolls of length up to 1200 m and width up to 1.5 m [114]. Furthermore, a flexible graphite sheet may be cut along lines that are parallel to the direction of the electric dipole in order to form a continuous serpentine conductor pattern that enables an electret to be much longer than the material length. For example, through the making of 20 cuts (so that the width of the electret is 1.5 m/20 = 1.5 cm), a roll of the abovementioned dimensions can provide an electret of length 24000 m. The fractional change in electric field for tripling *l* from 40 mm to 120 mm is 0.698% (Table 2). This means that factor of 600000, increasing 1 by а so that  $l = 40 \text{ mm} \times 600000 = 24000 \text{ m}$  will increase the electric field to 0.0360 V/m, thus increasing the power density to  $171 \text{ W/m}^3$ . The linearity in the relationship between the electric field and *l* has



**Fig. 12.** Effect of stress on the resistance during loading of flexible graphite, with comparison of measured resistance and calculated resistance based on the dimensional changes. Length = L, 2L and 3L. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

been shown up to l = 1280 m for copper [94].

#### 3.5. Piezoelectret behavior

The electric field increases monotonically as the tensile stress increase, as shown in Fig. 16 for the length 3L. The fractional increase in electric field reaches 45.0% and 109% for maximum stresses of 1.85 MPa and 3.18 MPa, respectively. The length (L, 2L and 3L) affects the electric field negligibly. The electric field without stress is  $2.576 \times 10^{-5}$ ,  $2.581 \times 10^{-5}$  and  $2.587 \times 10^{-5}$  V/m for lengths L, 2L and 3L, respectively. This negligible dependence of the electric field on the length is in contrast to the dependence of the capacitance (Sec. 3.2) and resistance (Sec. 3.3) on the length. It is expected since the electric field corresponds to the voltage gradient rather than the voltage. The electric field increases smoothly with increasing stress, with no abrupt change in slope in the curve of the electric field vs. stress. The electric field increase is totally reversible upon unloading for the maximum stress of 1.85 MPa, but is slightly irreversible upon unloading for the maximum stress between 1.85 and 3.18 MPa, as shown in Fig. 17. The finding that the electric field is nonzero  $(2.6 \times 10^{-5} \text{ V/m})$  when the stress is absent suggests



**Fig. 13.** Effect of tensile stress on the resistivity  $\rho$  during loading of flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

electret behavior.

A change in stress results in a change in polarization  $\Delta P$  according to the equation [111].

$$\Delta P = (\kappa - 1) \left( \Delta Q / A \right) + (\Delta \kappa) \left( Q / A \right) + \Delta \kappa \Delta Q / A, \tag{13}$$

where Q = the stored charge in the absence of the change in stress,  $\Delta Q =$  the change in the stored charge due to the change in stress  $\Delta \sigma$ ,  $\kappa =$  the relative permittivity in the absence of the change in stress,  $\Delta \kappa =$  the change in  $\kappa$  due to the change in stress, and A = the area of the capacitor. The first term on the right side of Eq. (13) is a description of the classical piezoelectret effect that is due to the change in Q; the second term is a description of the less classical piezoelectret effect (akin to as reverse electrostrictive effect) that is due to the change in  $\kappa$ ; the third term is a description of the even less classical piezoelectret effect (typically neglected effect) that is due to the changes in both  $\kappa$  and Q. By definition, the longitudinal piezoelectret coupling coefficient d (i.e.,  $d_{33}$ ) is given by

$$d = \Delta P / \Delta \sigma. \tag{14}$$

In case that the piezoelectret effect is solely due to  $\Delta Q$  (i.e., the first term on the right side of Eq. (8)), *d* is given by Ref. [111].



Fig. 14. Effect of tensile stress on the resistivity  $\rho$  during loading and subsequent unloading of flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

Table 1	
Electromechanical properties of flexible graphite, based on initial slope of the relevant cur	ves

Phenomenon	Property	Up to 1.85 MPa		erty Up to 1.85 MPa		Up to 3.18 MPa	
		First cycle	Second cycle	First cycle	Second cycle		
piezoelectret piezoelectret piezoelectret piezoelectret Piezoresistivity	$d_{33}$ (pC/N), Eq. (15) $d_{33}$ (pC/N), Eq. (16) $d_{33}$ (pC/N), Eq. (17) $d_{33}$ (pC/N), Eq. (17) $d_{33}$ (pC/N), total Gage factor	$\begin{array}{c} (2.98\pm 0.22)\times 10^{-8} \\ (7.27\pm 0.61)\times 10^{-9} \\ (3.04\pm 0.12)\times 10^{-10} \\ (3.74\pm 0.28)\times 10^{-8} \\ 45.8\pm 3.2 \end{array}$	$\begin{array}{c} (3.28\pm0.25)\times10^{-8}\\ (7.72\pm0.83)\times10^{-9}\\ (3.66\pm0.13)\times10^{-10}\\ (4.09\pm0.33)\times10^{-8}\\ 51.3\pm2.1 \end{array}$	$\begin{array}{c} (2.97\pm0.19)\times10^{-8} \\ (7.35\pm0.48)\times10^{-9} \\ (3.11\pm0.15)\times10^{-10} \\ (3.71\pm0.24)\times10^{-8} \\ 51.4\pm5.4 \end{array}$	$\begin{array}{c} (6.35\pm0.42)\times10^{-8}\\ (2.86\pm0.14)\times10^{-8}\\ (2.30\pm0.08)\times10^{-9}\\ (9.44\pm0.57)\times10^{-8}\\ 61.8\pm3.2 \end{array}$		

$$d = (\kappa - 1) \varepsilon_0 \,\Delta E / \Delta \sigma, \tag{15}$$

where  $\Delta E$  = the change in electric field caused by the change in stress  $\Delta \sigma$ . The value of *d* based on Eq. (15) is obtained by using the initial slope of the curve in Fig. 16 and the zero-stress  $\kappa$  of 1173 ± 34. These values are listed in Table 1. In spite of the large values of  $\kappa$ , the *d* values are small in magnitude. This is due to the small value of  $\Delta E$  caused by the large value of  $\Delta \sigma$ .

In case that the piezoelectret effect is solely due to  $\Delta \kappa$  (i.e., the second term on the right side of Eq. (13)), *d* is given by

$$d = (\Delta \kappa) (Q/A) / \Delta \sigma = (\Delta \kappa / \Delta \sigma) \varepsilon_0 E$$
(16)

where E = the electric field when there is no change in stress. The values obtained by using Eq. (16) are shown in Table 1. The values obtained by using Eq. (16) are smaller than those obtained using Eq. (15).

In case that the piezoelectret effect is solely due to the last term on the right side of Eq. (13), *d* is given by

$$d = (\Delta \kappa / \Delta \sigma) \varepsilon_0 \Delta E.$$
(17)

The values obtained based on Eq. (17) are shown in Table 1. The values obtained by using Eq. (17) are smaller than those obtained using Eq. (15) or (16), as typically expected.

All three terms on the right side of Eq. (13) contribute to the observed overall piezoelectret effect. Although both the change in  $\kappa$  (Fig. 8) and the change of Q contribute to the effect, the change of Q is most influential. The sum of the contributions from the three terms gives the total *d*, as shown in Table 1. The values of the total *d* are smaller than those of well-known piezoelectrets by orders of magnitude. Nevertheless, the piezoelectret effect is adequate for self-sensing that involves measurement of the electric field or voltage (Figs. 16 and 17) and for self-sensing that involves measurement of the capacitance (Fig. 5).

#### 3.6. Comparison of flexible graphite with carbon fiber

Flexible graphite (this work) and PAN-based carbon fiber [108] are both monolithic single-phase carbons with high preferred orientation of the carbon layers in the direction of the electrical measurements. Therefore, comparison of flexible graphite with carbon fiber (Table 2) is more suitable than comparison of flexible graphite with carbon composites.



**Fig. 15.** Electret behavior. (a) Effect of inter-electrode distance *l* on the electric field. (b) Effect of the inter-electrode distance *l* on the factor by which the fraction of carriers that participate is decreased when the inter-electrode distance *l* is tripled from 40 mm to 120 mm. (c) Effect of polarization and polarity reversal for flexible graphite without prior depolarization. (d) Effect of polarization and polarity reversal for flexible graphite with immediately prior depolarization.

#### Table 2

Comparison of the properties of flexible graphite and PAN-based carbon fiber.

Properties	Flexible graphite	Carbon fiber [105]
$d_{33} (pC/N), Eq. (15)$ $d_{33} (pC/N), Eq. (16)$ $d_{33} (pC/N), Eq. (17)$ $d_{33} (pC/N), total$ Electric field (V/m) at inter-electrode distance 40 mm The fractional increase in electric field when length is tripled from 40 mm	$(2.98 \pm 0.22) \times 10^{-8}$ $(7.27 \pm 0.61) \times 10^{-9}$ $(3.04 \pm 0.12) \times 10^{-10}$ $(3.74 \pm 0.28) \times 10^{-8}$ $2.58 \times 10^{-5}$ $0.698\%$	$\begin{array}{c} (1.7 \pm 0.3) \times 10^{-8} \\ (1.3 \pm 0.2) \times 10^{-8} \\ (9.3 \pm 0.6) \times 10^{-9} \\ (3.9 \pm 0.6) \times 10^{-9} \\ 1.28 \times 10^{-5} \\ 1.408\% \\ 0.2300 \end{array}$
Factor Relative permittivity at 2 kHz Resistivity $(10^{-5} \Omega m)$ Power density <sup>b</sup> $(W/m^3)$ Gage factor	$\begin{array}{c} 0.3337\\ 1.17 \times 10^3\\ 0.756\\ 0.44\\ 45.8 \pm 3.2\end{array}$	0.3380 $1.25 \times 10^4$ 1.55 1.14 $-376 \pm 23$

<sup>a</sup> The factor refers to that by which the fraction of carriers that participate is decreased when the inter-electrode distance *l* is tripled from 40 mm to 120 mm. A larger factor means less decrease.

<sup>b</sup> The power density is calculated based on Eq. (11) for  $l = 40 \text{ mm} \times 30000 = 1200 \text{ m}$ , with *E* adjusted in accordance with the fractional change in electric field for increasing *l* and the data in Fig. 15(a), which gives the fractional change in electric field for tripling *l*. For example, for flexible graphite, the fractional change in electric field for tripling *l* is 0.698%. This means that increasing *l* by a factor of 30000 will increase the electric field by 6980%. The linear relationship between *E* and *l* over large distances up to 1280 m has been shown for copper [94].



**Fig. 16.** Effect of tensile stress on the electric field during loading of flexible graphite for length 3L. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

Flexible graphite is essentially the same as PAN-based carbon fiber in the magnitude and sign of  $d_{33}$ , but it is lower than the carbon fiber in both the relative permittivity and electrical resistivity. The fact that low permittivity and low resistivity correlate is consistent with the notion that both polarization and conduction involve the movement of the mobile charge carriers in the carbon.

For an inter-electrode distance of 40 mm, the electric field is higher for flexible graphite than the carbon fiber (Table 2). However, the fractional increase in electric field when the interelectrode distance is tripled from 40 mm to 120 mm is higher for the carbon fiber than flexible graphite (Table 2). Therefore, for a large enough inter-electrode distance, the electric field is higher for the carbon fiber than flexible graphite. The lower fractional increase in electric field when *l* is increased from 40 mm corresponds to a lower factor by which the fraction of carriers that participate is decreased when *l* is increased (Table 2). In other words, the fraction of carriers that participate decreases with increasing *l* more significantly for flexible graphite than the carbon fiber. This difference between the two carbons is consistent with the cellular structure of flexible graphite and the consequent increase in the number of interfaces as *l* increases.

In spite of its lower resistivity and Eq. (11), flexible graphite gives lower power density than the carbon fiber. This is because of

the lower fractional increase in electric field when the interelectrode distance *l* is increased from 40 mm (Table 2).

The gage factor is opposite in sign between flexible graphite and the carbon fiber, with the magnitude being much smaller for flexible graphite. The positive sign of the gage factor of flexible graphite is attributed to the reversible loosening of an interface in the flexible graphite upon tension. This interface is probably that between the merged parts of the cell wall in the cellular structure of exfoliated graphite [13]. The negative sign of the gage factor of carbon fiber is probably due to the increase in the preferred orientation of the carbon layers upon tension [107]. In other words, the difference in piezoresistivity between flexible graphite and the carbon fiber is attributed to the difference in microstructure and the consequent difference in how stress affects the microstructure. The microstructure obviously affects the resistivity.

The power density, as calculated for a length of 1200 m, is lower for flexible graphite than PAN-based carbon fiber (Table 2). For a given electret material, the electric field increases linearly with the length. The effect of the length on the electric field is stronger for carbon fiber than flexible graphite.

With stainless steel as the electret material, the corresponding power density for a length of 1200 m is  $41.8 \text{ W/m}^3$  [94]. With coldworked copper as the electret material, the corresponding power density for a length of 1200 m is  $510 \text{ W/m}^3$  [115]. Thus, for the same length, both flexible graphite and carbon fiber are much less effective than these metals for serving as power sources. The low resistivity of the metals and Eq. (11) contribute to the effectiveness of the metals. Nevertheless, this work provides the foundation for the future development of electret-based power sources in the form of carbons.

#### 4. Conclusion

This paper provides the first report of the dielectric, electret, piezoelectret and piezoresistive behavior of flexible graphite, which is fabricated commercially and conventionally by the compaction of exfoliated graphite. The in-plane tensile modulus is 1.34 GPa. The in-plane tensile stress used is within the elastic regime, with the strain being totally reversible.

The relative permittivity  $\kappa$  (2 kHz) at zero stress is  $1173 \pm 34$ . Both  $\kappa$  and the capacitance increase monotonically with increasing tensile stress, in spite of the dimensional changes expected to cause a capacitance decrease. The fractional increase in  $\kappa$  is up to 11.2% and 73.2% for the maximum stress of 1.85 MPa and 3.18 MPa, respectively. For the maximum stress of 3.18 MPa, the curve of  $\kappa$  vs. stress shows an abrupt increase in slope at 2.1 MPa, above which a degree of irreversibility of the  $\kappa$  increase occurs. For the maximum stress of 1.85 MPa, there is no abrupt change in slope and the smooth  $\kappa$  increase is totally reversible.

In the absence of stress, the electric field is  $2.58 \times 10^{-5}$  V/m at the inter-electrode distance *l* of 40 mm. The value is comparable to but higher than the value of  $1.28 \times 10^{-5}$  V/m for PAN-based carbon fiber [108]. The electric field increases linearly with increasing *l*. When *l* is increased from 40 mm to 120 mm, the electric field is increased by 0.698%. This is explained in terms of the fraction of carriers that participate decreasing with increasing *l*. The factor by which the fraction of carriers that participate is decreased when the inter-electrode distance *l* is tripled from 40 mm to 120 mm is 0.3357.

The power density is  $0.44 \text{ W/m}^3$  for l = 1200 m. This value is lower than the corresponding value of  $1.14 \text{ W/m}^3$  for PAN-based carbon fiber [108].

The DC electric field output of the piezoelectret effect increases monotonically and smoothly with increasing stress, with the electric field increase being totally reversible for the maximum stress of



Fig. 17. Effect of tensile stress on the electric field during loading and subsequent unloading of flexible graphite. (a) Stress up to 1.85 MPa. (b) Stress up to 3.18 MPa.

1.85 MPa and slightly irreversible for the maximum stress between 1.85 and 3.18 MPa. The piezoelectret coupling coefficient  $d_{33}$  is  $3.7 \times 10^{-8}$  pC/N, which is close to the value of  $3.9 \times 10^{-8}$  pC/N for PAN-based carbon fiber. The DC electrical resistivity also increases monotonically and smoothly with increasing stress. The resistivity increase is totally reversible for the maximum stress of 1.85 MPa and is almost totally reversible for the maximum stress between 1.85 and 3.18 MPa. The gage factor is 50, which is very different from the value of -380 for PAN-based carbon fiber [108].

The tensile stress causes  $\kappa$ , the resistivity and the electric field to increase. The abrupt increase in slope of the curve of  $\kappa$  vs. stress at 2.1 MPa is attributed to a microstructural change that does not affect the strain reversibility but affects  $\kappa$  when the stress exceeds 2.1 MPa. Although this microstructural change affects  $\kappa$ , it has little effect, if any, on the electric field output or the resistivity. Both the resistivity and electric field increase smoothly with increasing stress.

In spite of the linearity of the stress-strain curve and the total reversibility of the strain up to 3.18 MPa, the capacitance change due to the stress is partially irreversible when the stress exceeds 2.1 MPa. Along with the partial irreversibility is the occurrence of the increase in the fractional change in capacitance as the length increases from L to 2L and to 3L. For both values of the maximum stress (1.85 and 3.18 MPa), the resistance increase due to the stress is reversible and the fractional increase in resistance due to the stress increases with increasing length from L to 2L and to 3L. The effect of length on the fractional stress-induced change in capacitance or resistance is attributed to a reversible microstructural change that increases the resistance reversibly, but increases the capacitance in a manner that is not totally reversible. The occurrence of such a reversible microstructural change is in line with the well-known resiliency of flexible graphite. The microstructural change possibly involves the loosening of an interface in the cellular structure of exfoliated graphite, such that this loosening promotes polarization without affecting conduction.

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