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Inversely polarised ferroelectric polymer contact electrodes for triboelectric-like generators from identical materials†

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Although it is known that triboelectric nanogenerators (TENGs) based on ferroelectric polymer films show better performance, the origin of this enhancement remains poorly understood. To date, it has been accepted that enhancement is observed due to shift of the “effective work function” of the ferroelectric polymer insulator, which in turn enhances electron transfer between the TENG electrodes. The present study reveals that this view is incorrect and, in reality, the enhancement is observed due to induction driven by piezoelectric charges. Furthermore a novel piezoelectric-electrostatic generator (PEEG) has been constructed from inversely polarised polyvinylidene films, which exhibits higher performance than TENGs for mechanical energy conversion to electricity.

Triboelectric nanogenerators (TENGs), introduced in 2012 by F. R. Fan *et al.*,¹ are a sustainable solution for converting mechanical energy to electricity by combining electrostatic surface charging and induction effects. TENGs are similar to micro-electro-mechanical system (MEMS) electrostatic generators^{2–4} with the exception that TENGs are not charged by an external voltage, but the source of the charges is surface charge formation upon contacting and separating two materials. TENG devices consist of two conductive electrodes covered with distinct materials – (most commonly) polymer insulator films. In some TENG devices the conductive electrode is not covered with a polymer and plays a dual role simultaneously – acting as an electrode and a contact surface.^{5–7} After contacting–separating two surfaces, opposite net electrostatic charges are created, which then induce charges on the two electrodes. The two electrodes in TENGs are connected by an outer circuit and upon electrode movement (during separation) electric potential

Broader context

Triboelectric nanogenerator (TENG) devices have been considered as a promising solution to harvest mechanical energy. In TENGs, energy is harvested by friction and the device consists of two connected conductive layers covered with distinct materials. After contacting–separating two materials, opposite net surface charges are formed, which in turn induce charges on the conductive layers. During separation, an electric potential is created and electrons are driven to flow between the two conductive material layers in order to balance the electric potential difference. The key parameter which determines TENG performance is the magnitude of electrostatic induction. In the present work we demonstrate that highly efficient TENG devices can be obtained when inversely polarised ferroelectric materials are used as contacting–separating layers. Upon deformation (during contacting–separation), piezoelectric charges are induced on the ferroelectric layers, which in turn drive electrostatic induction and enhance the performance of the TENG. It is suggested to emphasize TENGs based on identical inversely polarised ferroelectric materials as piezoelectric–electrostatic generators (PEEGs), because in this particular case there is a negligible influence of surface charge on performance. We see PEEGs as a competitive solution for mechanical energy conversion to electricity, which will facilitate the further development of novel high-performance mechanical energy harvesting devices.

is created and electrons are driven to flow between the two electrodes in order to balance the electric potential difference.⁸

In order to increase performance of TENG devices, different strategies have been reported. First, it is necessary to choose a proper material combination.⁹ For guidance the so called triboelectric series can be used,¹⁰ where materials are listed in accordance with their tendency to charge positively or negatively when contacted with a distinct material. The highest net surface charge could be expected if materials from the top are contacted with materials from the bottom of a triboelectric series. However, one needs to keep in mind that materials in triboelectric series are empirically ordered and vary from experiment to experiment.¹¹ Another approach to increase the magnitude of net electrostatic surface charge is to modify the surface chemistry^{12–14} or increase the contacting area between the two surfaces, which has been achieved through nanostructuring.^{9,15–20}

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Recently several scientist groups have observed an increase in output voltage generated by TENGs based on ferroelectric polymer insulator films in contact with metals.^{5,21,22} The authors suggested that the increased TENG output voltage is due to the enhanced electron transfer from the metal to the polymer insulator. They suggested that dipoles increase the dielectric constant of the film⁵ or the electric field from the dipoles shifts the so called effective work function of the polymer insulator so that the electrons are easily transferred from metal to polymer.^{5,22}

At the same time, it was found in 2011 by Baytekin *et al.*²³ and confirmed by others¹¹ that electrostatic charge formation on polymer insulators is mainly due to heterolytic covalent bond cleavage and not due to electron transfer, so the contribution of dipoles for enhanced output power described above is doubtful. There are nanoscopic regions with opposite charge on the surface of polymer insulators after contacting and separating where regions with one sign occupy a larger area than regions with the opposite sign, thus forming net electrostatic charge on the surface.²³ The electron transfer is well confirmed for metal-metal contact and depends on the work function,²⁴ but not in metal-polymer contacts, because contact electrification of polymer insulators can't be linked with their atomic properties (ionization energy, electron affinity or electronegativity) or electronic properties (dielectric constant or "effective work function").¹¹

Nevertheless, it is obvious from experimental observations^{5,21,22} that the dipole moment in a TENG electrode enhances its performance. But what is the origin of the observed enhancement? Is it really a shift of "effective work function" on the polymer surface?

In the previous studies mentioned above dielectric polymer films with permanent polarization were tested against metal electrodes to test the theory of electron transfer from metals to polymers. However, even if electron transfer from metals to polymer insulators is possible, the electron transfer should not be possible when contacting and separating insulating polymer-polymers, because there are no available free electrons in insulators.¹¹ In the present work, we demonstrate that there are other underlying effects contributing to the enhanced power output for TENG devices with ferroelectric layers. By contacting PDMS and polarised polyvinylidene fluoride (PVDF) we observed a higher output voltage than that for a TENG based on PDMS and non-polarised PVDF. Even more, we observed high output voltage when contacting identical but inversely polarised PVDF films on opposite TENG electrode layers. Net surface charge on polymer insulators is formed due to heterolytic covalent bond cleavage upon separation, but it was not observed after contacting and separating identical PVDF. Due to the mentioned reasons the origin of the generated power is electrostatic induction driven by piezoelectric charges produced under applied pressure when contacting and separating.

Nanostructured PVDF films were prepared for experiments by using an immersion-precipitation method. PVDF (Sigma Aldrich, $M_w = 530\,000$) was dissolved in *N,N*-dimethylformamide at a concentration of 15 wt%. The solution was spin coated at 3000 rpm on the polyethylene terephthalate (PET) side of ITO-coated PET (sheet resistance $60\ \Omega\ \text{sq}^{-1}$, Kintec) and immersed in antisolvent methanol for 1 minute. The strongly

adhered PVDF films were deposited on the PET side of the ITO covered PET substrate so that the PVDF film is separated from ITO by an insulative $170\ \mu\text{m}$ thick PET layer.

After immersion-precipitation the sample films were removed from methanol and dried in ambient air at room temperature. Before the measurements, the PVDF samples were heat treated at $100\ ^\circ\text{C}$ or poled under constant electric field with strength $2.5\ \text{MV m}^{-1}$. During poling the sample was heated from $20\ ^\circ\text{C}$ to $100\ ^\circ\text{C}$ in 15 min, maintained at $100\ ^\circ\text{C}$ for the next 30 min and cooled down to $20\ ^\circ\text{C}$ for another 30 min under constant electric field strength. Samples were characterised by XRD, AFM, SEM and FTIR, as described in the ESI.†

The TENG performance and piezoelectric characteristics of the poled PVDF films were measured in constant ambient relative humidity (40%) by using an INSTRON E1000 All-Electric Dynamic Test Instrument, which allows precise control of the pressing force and frequency, as well as (important for TENGs) the separation speed and gap between the sample sides. Short circuit current and voltage pulses under different load were measured by a custom-made voltage divider which was used together with a Keithley 6514 electrometer, which was connected to a Picoscope 5444B PC oscilloscope to provide high time resolution, therefore allowing exact peak levels for the generated waveforms to be registered. Due to the necessity to measure precise voltages on high load resistances, a custom voltage divider and cables were made and tweaked to obtain the lowest parasitic impact on the signal shape. Power was calculated by applying Joule's law ($P = U^2/R$) to get instant power at every moment of time, while energy was obtained as an integral $E = \int P dt$. The charge Q induced on the electrode layers or measured on the surface by Faraday cup was calculated by the equation $Q = \int i dt$, where i – instantaneous current. Unless specified, in TENG performance tests we measured the voltage and current under controlled operating conditions (separating distance $0.5\ \text{mm}$, pressing force $10\ \text{N}$ and frequency $1\ \text{Hz}$) to compare different material combinations. In the piezo regime PVDF film was sandwiched between two $170\ \mu\text{m}$ thick PET insulator layers as demonstrated in the ESI,† Fig. S1. The force in piezoresponse measurements was varied from $1\ \text{N}$ to $10\ \text{N}$ at $1\ \text{Hz}$ frequency. Each measurement was repeated for 5 parallel samples. From the measured current in the piezo regime, the piezoelectric charge was found by simulation by using COMSOL software.

Immersion-precipitation yields highly rough and porous PVDF films in one minute or less. Porosity provides high contact area and deformability, which is important to generate piezoelectric charges.²⁵ Immersion-precipitation is a commercially well-known method for production of polymer membranes²⁶ and it has no obvious limitations for size or shape. SEM and AFM images demonstrated in Fig. 1(b and c) reveal that after immersion-precipitation in antisolvent (methanol), highly porous structures are formed. Considering the bulk density, weight and thickness ($10\ \mu\text{m}$, measured by SEM, ESI,† Fig. S2) of the PVDF porous film the porosity was estimated to be 68.3%. The measured AFM root mean square (RMS) surface roughness among five independently prepared samples was $475\ \text{nm}$ with a standard error of $2.85\ \text{nm}$ and deviation of $5.71\ \text{nm}$. RMS surface roughness

Fig. 1 (a) Schematic illustration of the fabrication process of highly porous PVDF contacting layers for the TENG device; (b) SEM image and (c) AFM image for PVDF films obtained by immersion-precipitation with methanol as an antisolvent; (d) a photograph of the 50 cm² sample; (e) schematic representation of the dipole orientation in PVDF. In the PVDF “+” sample, the polar side of the dipole moment is aligned towards the surface while for PVDF “−” it is a negative side of the dipole moment. Graph (f) shows ATR-FTIR spectra of non-polarised as-prepared PVDF, non-polarised PVDF heat treated at 100 °C, PVDF “+” and PVDF “−” at different wavenumbers from 1220 cm^{−1} to 1300 cm^{−1} (top) and from 740 cm^{−1} to 850 cm^{−1} (bottom).

expresses the square root of the mean square of the height deviations of the surface, measured from the mean height of the data plane. The correlation length of the surface irregularities was 2.098 μm, expressing the characteristic size of the surface irregularities in the horizontal direction. Surface roughness measurements for parallel samples confirm that surface roughness is highly repeatable and varies little from sample to sample.

For measurements non-polarised and inversely polarised PVDF films were prepared. Non-polarised PVDF samples were designed with “0”, while polarised PVDF with “+” or “−” depending on the dipole moment orientation towards the sample surface as illustrated in Fig. 1(e). The piezoelectric properties and ferroelectric phases were confirmed by ATR-FTIR measurements (Fig. 1(f)) and the piezoelectric measurements described below. ATR-FTIR measurements showed no crystalline phases in the as-prepared non-polarised PVDF, but after heating or poling (heating in electric field) at 100 °C, the α, β and γ phases appear in the sample. Bands associated with α, β, and γ crystalline phases, as well as the amorphous phase usually appear

simultaneously in PVDF and depend on the preparation conditions.²⁷ The crystalline ferroelectric β phase exhibits an exclusive absorption band at 1275 cm^{−1}, the γ phase at 773 cm^{−1} and 1234 cm^{−1}, and the α-phase at 761 cm^{−1} as it can be seen in Fig. 1(f). The crystalline phases are formed by heating, but an electric field aligns the ferroelectric dipoles.²⁷

In the TENG regime, when samples are contacted and separated as schematically demonstrated in Fig. 2(a), the output voltage and current is proportional to the electrostatically induced charge density on the conductive ITO electrodes below the contacting surfaces²⁸ and thus can be used to directly compare the performance of TENGs based on different sample combinations and to draw important conclusions about electrostatic induction mechanisms. A higher output voltage and current was observed when polarised PVDF was used for contacting with the other material, whatever conductor or insulator was used (Fig. 2 and ESI,[†] Table S1, Fig. S3–S6). As an example, the output voltage (current) from the TENG based on non-polarised PVDF in combination with PET reached 12 V (25 nA), while for the

Fig. 2 The average output voltage (measured at load resistance $1 \times 10^9 \Omega$) and short circuit peak values for polarised and non-polarised PVDF measured in the TENG (a) and piezo (b) regime as demonstrated by schematic images in the insets. The voltage and current measured from the TENG based on PVDF "+" is demonstrated in graphs (c and e), but in the piezo-regime in graphs (d and f), respectively. Measurement curves for other samples are demonstrated in the ESI.†

TENG based on PVDF "+" and PVDF "-" in combination with PET the output voltage 100 V (300 nA) and 55 V (145 nA) was observed, respectively (Fig. 2 and ESI,† Fig. S3). The same relationship was observed when different PVDFs were contacted with polydimethylsiloxane on ITO, poly(methyl methacrylate) on ITO or copper, as demonstrated in the ESI,† Table S1 and Fig. S4–S6.

To understand the origin of the observed higher voltage and current from TENGs based on a ferroelectric polymer layer, the piezo-regime measurement (Fig. 2(b)) was performed; it demonstrates induction driven by piezoelectric charges through an insulative layer, because both sides of PVDF were insulated from ITO by 170 μm thick PET as schematically demonstrated in Fig. 2(b). Piezovoltage and piezocurrent were observed from polarised PVDF (Fig. 2(b), ESI,† Fig. S7), while there was negligible piezoelectric behaviour for non-polarised PVDF (Fig. 2(b) and ESI,† Fig. S7). It is important to note that the polarity of both the piezocurrent and piezovoltage (Fig. 2(c), (d) and ESI,† Fig. S7) is changing during the loading and unloading of PVDF "+" and PVDF "-" in the piezo-regime. The experiment clearly demonstrates that induction can be driven by piezocharges even through thick insulator layers. The electrostatic charge induced

by piezocharges from 10 μm thick PVDF film sandwiched between two 170 μm thick PET layers was 0.082 nC cm^{-2} from PVDF "-" and 0.104 nC cm^{-2} from PVDF "+". Small induced charge (0.008 nC cm^{-2}) was observed also from nonpolarised PVDF. The piezoresponse from a non-polarised sample may come from crystalline phases observed in non-polarised PVDF after heating, as described above. From the measured charge we simulated piezoelectric charge on a ferroelectric layer necessary to drive electrostatic induction through 170 μm thick PET layers, as well as verified that piezoelectric charge-driven induction is possible. Simulation shows that for positively poled PVDF, in order to observe an induced charge of 0.104 nC cm^{-2} , the piezocharge surface density must be 8.45 nC cm^{-2} . In this case the electric field strength inside the PVDF layer is $1.291 \times 10^6 \text{ V m}^{-1}$ and in the PET layer it is $3.798 \times 10^4 \text{ V m}^{-1}$ as demonstrated in the ESI,† Fig. S8. For negatively poled PVDF, in order to observe an induced charge of $0.0816 \text{ nC cm}^{-2}$, the piezocharge surface density must be 6.63 nC cm^{-2} and the electric field strength inside the PVDF layer is $1.013 \times 10^6 \text{ V m}^{-1}$ and in the PET layer it is $2.980 \times 10^4 \text{ V m}^{-1}$. In general, the induced charge on ITO, in this particular geometry, is ~ 80 times smaller than the piezoelectric charge. The piezoelectric

charge obtained from the simulation is realistic for PVDF based piezoelectric materials.²⁵ In comparison, the surface charge, measured by Faraday cup, on non-polarised PVDF in contact with PET is $-0.014 \text{ nC cm}^{-2}$, but in contact with PDMS it is $+0.17 \text{ nC cm}^{-2}$, which is in good agreement with the measured performance for different TENGs based on PVDF in contact with different materials (ESI†, Table S1 and Fig. S3–S6).

The measurements in the TENG- and in piezo-regime allow conclusions to be drawn about the working principle of TENGs from ferroelectric materials. The electrostatic charges on the underlying electrode layers are induced by piezocharges in the ferroelectric film, when it is pressed in the TENG by contacting two sides as it is demonstrated in Scheme 1. When two sides are separated, the polarity of the piezoelectric charges is switched in the opposite direction and electron flow is induced in the external circuit. The polarity switching is supported by piezoelectric current and piezoelectric voltage measurements described above. It must be concluded that the output voltage enhancement in TENG devices from ferroelectric materials is not due to the shift of the polymer insulator “effective work function”, as reported before.^{5,22}

To support our hypothesis we contacted PDMS with PVDF and measured the surface charge on PDMS by Faraday cup. We contacted polarized/non-polarized PVDF with a freestanding PDMS film to avoid any influence of the conductive substrate and measured the resulting surface charge on PDMS. The net surface charge on PDMS after contacting with the different PVDFs was negative: $-0.17 \pm 0.01 \text{ nC cm}^{-2}$. The negative surface charge on PDMS after contacting and separating with different materials is commonly observed.²⁹ Nevertheless, we did not observe any influence of the PVDF polarisation direction on either the sign or magnitude of net surface charge, in contrast, to expectations reported previously.³⁰

Further we contacted and separated non-polarised and inversely polarised PVDF films mutually at different combinations. The results are demonstrated in Fig. 3 and the ESI† (Table S2 and Fig. S9, S10). When pressing non-polarised PVDF films against each other, almost no output voltage was measured, showing that there is no surface charge or piezoelectric charge formation which

Fig. 3 The average output voltage (measured at load resistance $1 \times 10^9 \Omega$) and short circuit peak values for the TENG device based on PVDF. Non-polarised and inversely polarised PVDF films were contacted and separated mutually at different combinations. The schematic image demonstrates the working mechanism for the TENG-like PEEG based on inversely polarised PVDF layers.

could drive induction on underlying electrode layers. Surface charge formation is usually not observed by contacting identical materials, but exceptions have been demonstrated.³¹ When non-polarised PVDF was contacted with polarised PVDF we observed high open circuit voltage (short circuit current) -71 V (135 nA) and 67 V (126 nA) in the case of PVDF “−” and PVDF “+”, respectively. Almost the sum of these output voltages -119 V (180 nA) was observed when PVDF “−” and PVDF “+” were pressed against each other. Upon contacting, the measured value was stable for many cycles as shown in the ESI†, Fig. S11. During 1000 cycles no decrease in the measured output voltage was observed. Negligible voltage and current was generated when PVDF films, polarised in the same direction, were contacted and separated (Fig. 3 and Table S2, Fig. S9, S10, ESI†).

We also considered the influence of surface and piezoelectric charges in PVDF based TENGs by measuring the output voltage and current from combinations of different materials when moving two films towards each other in contact and non-contact modes without making physical contact. First, the output voltage and current from TENGs was measured in non-contact mode, and then the TENG was switched to contact mode and then again to non-contact mode. There is no output voltage and current when freshly prepared never contacted PDMS and non-polarised PVDF are moved back and forth towards each other in non-contact mode, but by switching to contacting mode, a voltage and current is generated as usual (see Fig. 4(a and b)). The voltage and current is also generated when switching back from contact to non-contact mode, because surface charges on the polymer

Scheme 1 Working mechanism for a TENG-like piezoelectric-electrostatic generator (PEEG). At first, electrostatic charge is induced on both underlying conductive electrode layers by piezoelectric charge forming during the contacting polarised PVDF film, thus observing electron flow in the external circuit. Upon releasing two the PEEG sides, the polarity of the piezocharges is changed, opposite sign electrostatic charges are induced on the electrode layers and current flow in the opposite direction is observed in the external circuit.

Fig. 4 Graphs (a and b) show the output voltage and current for a combination of PDMS vs. non-polarised PVDF during switching between non-contact to contact mode measurements. There is no output voltage and current when freshly prepared never contacted PDMS and non-polarised PVDF are moved back and forth towards each other in non-contact mode, but by switching to contacting mode voltage and current are generated. The voltage and current are also generated when switching back from contact to non-contact mode, because surface charges on the polymer films have been formed which drive electrostatic induction on the conductive electrode layers. Graphs (c and d) show the same measurements but for a combination of PVDF “+” and PVDF “−” where a stable output voltage and current can be observed in non-contact mode even for the PEEG from freshly polarised and never contacted PVDF “+” and PVDF “−”. By switching to contacting mode, high voltage and current are observed as usual, but switching back to non-contact mode turns the voltage down to the same level as observed from fresh samples, showing no contribution from surface charges.

films have been formed which drive electrostatic induction on conductive electrode layers. Further output voltage and current in non-contact mode vanishes slowly in 5 minutes. The annihilation time of surface charges is comparable with those measured by Faraday cup in previous studies.³²

As demonstrated in Fig. 4(c and d), completely different behaviour is observed for the TENG with PVDF “+” and PVDF “−” contacting materials. Stable output voltage (up to 15 V depending from separating distance, ESI,† Fig. S12) and current can be observed in non-contact mode even for the device from freshly polarised and never contacted PVDF “+” and PVDF “−”. By switching to contacting mode, high voltage and current (at around 120 V and 210 nA) are observed as usual, but switching back to non-contact mode turns the voltage down to the same level observed from fresh samples, showing no contribution from surface charges. The voltage is generated in non-contact mode due to the electrostatic induction in the underlying conductive electrodes that is driven by the electric field arising from the permanent dipole moment in the poled PVDF ferroelectric film.

Measurements show that the output voltage increase of the TENG based on ferroelectric materials is due to electrostatic induction driven by piezoelectric charges produced under applied pressure when contacting. When contacted films are separated the polarity of the piezoelectric charges is switched in the opposite direction thus driving electrons through the external

circuit. When PVDF polarised in the same direction is contacted and separated almost no voltage and current can be measured because inversely oriented dipoles induce charges with the same sign on opposite conductive electrode layers.

We have to suggest that it is not entirely correct to use the term TENG in the case of triboelectric nanogenerators that are based on ferroelectric films, because there is a negligible influence of the contact (tribo-) charge on the generated power. It is more appropriate to call our TENG-like device a “piezoelectric-electrostatic generator” (PEEG). The output power, voltage and current generated by electrostatic generators (TENG, MEMS and PEEG) are dependent mainly on the load resistance and several other factors, such as the separation distance between the two electrode layers,³³ contacting area,³⁴ contacting force,³⁴ contacting-separating (vibration) frequency^{35–37} and materials used.⁹ Under the most extreme experimental conditions and abilities of the testing machine (5 mm gap and separating speed 0.5 m s^{-1}), an open circuit voltage up to 240 V was measured from the PEEG with a 5 cm^2 size (ESI,† Fig. S13). The contacting force also influences the output voltage of our device, but it reaches the maximum output already at the contacting force 10 N (ESI,† Fig. S14). Production of high voltage under low applied pressure upon contact is beneficial for mechanical energy harvesting generators, because even low intensity ambient vibrations could be used for energy production. The power density generated by the PEEG from one contact-separating cycle reached 30 mW m^{-2} and energy 4.53 mJ m^{-2} . The calculated powers reported for TENG devices vary in a broad range from microwatts³⁸ to hundreds of watts per square meter.^{16,37,39,40} For power calculations here we used instantaneous voltage in every measurement point of the voltage pulse, not a maximum peak voltage value. We prepared contact layers with two different sizes 5 cm^2 and 30 cm^2 and the observed power density was the same (ESI,† Fig. S15), but it is not the case if the peak value is used for power density calculations by using equation $P = U^2/R$. Overall, the value of generated power that we demonstrate can be considered remarkably high. For reference, a 50 cm^2 TENG that exhibited two orders of magnitude smaller output power density (0.5 mW m^{-2}) was reported to be able to light up 40 diodes.⁴¹

Conclusions

Triboelectric nanogenerator (TENG) devices from ferroelectric polymers exhibit higher performance due to electrostatic induction by piezoelectric charges, not due to enhanced electron transfer between contacted layers as reported before. Taking this into the account it is possible to construct highly efficient TENG-like piezoelectric-electrostatic generators (PEEGs) consisting of two inversely polarised ferroelectric polymer films from the same material. The proposed energy harvesting device has great potential for self-powering applications.

Conflicts of interest

There are no conflicts to declare.

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