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Title:
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Date:
2020-08-13

Citation:
Sutka, A., Sherrell, P. C., Shepelin, N. A., Lapcinskis, L., Malnieks, K. & Ellis, A. V. (2020). Measuring Piezoelectric Output-Fact or Friction?. Advanced Materials, 32 (32), https://doi.org/10.1002/adma.202002979.

Persistent Link:
https://hdl.handle.net/11343/275988

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DOI: 10.1002/adma.202002979

Article type: Essay

Measuring piezoelectric output – fact or friction?

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Keywords: Piezoelectricity, Triboelectricity, Polymer Composites, Energy Harvesting, Measurement Techniques

Piezoelectric polymers are emerging as exceptionally promising materials for energy harvesting. While the theoretical figures of merit for piezoelectric polymers are comparable to ceramics, the measurement techniques need to be retrofitted to account for the different mechanical properties of the softer polymeric materials. Here, how contact electrification is often mistaken for piezoelectric charge is discussed, through friction and contact separation, and a perspective for how to separate these effects is provided. The state of the literature is assessed, and recommendations are made for

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clear and simple guidelines in reporting, for both sample geometry and testing methods, to enable accurate determination of piezoelectric figures of merit in polymers. Such improvements will allow an understanding of what types of material manipulation are required in order to enhance the piezoelectric output from polymers and enable the next generation of polymer energy harvester design.

1. Introduction

Energy harvesting systems are attracting widespread interest for the conversion of mechanical to electrical energy, with applications ranging from micron-scale vibration to human motion to large-scale energy recovery systems. Of these energy harvesters, polymeric materials are exceptionally promising for human motion and miniaturized systems. This is especially true as they are lightweight, flexible, and can be processed via a large range of solution processing techniques.[1]

At the scale of human motion two fundamental devices dominate the energy harvesting landscape, piezoelectric generators (PEGs) and triboelectric generators (TEGs). While these energy generators produce the same output, namely voltage and charge, the fundamental mechanism that gives rise to the energy generation/harvesting is different.[2] This difference in mechanism of energy generation/harvesting has implications for how PEG or TEG devices are deployed. The output from both PEGs and TEGs is measured in voltage, power, and/or charge, and determining which fundamental process is generating the output is extremely challenging. Many researchers assume that they are only measuring piezoelectric output, which is often not the case. In fact, the triboelectric output is often misreported as a piezoelectric output, resulting in extremely high piezoelectric co-efficients that are not reproducible. In order to understand why triboelectric signals are often present in piezoelectric data, it is important to understand the origin of both processes in polymers. In piezoelectric polymers, most commonly poly(vinylidene difluoride) (PVDF), charge is

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generated by the deformation of aligned polymer chains in a crystallite which in turn deforms aligned dipole moments inducing a net electric field in parallel electrodes (**Figure 1**).[3, 4]

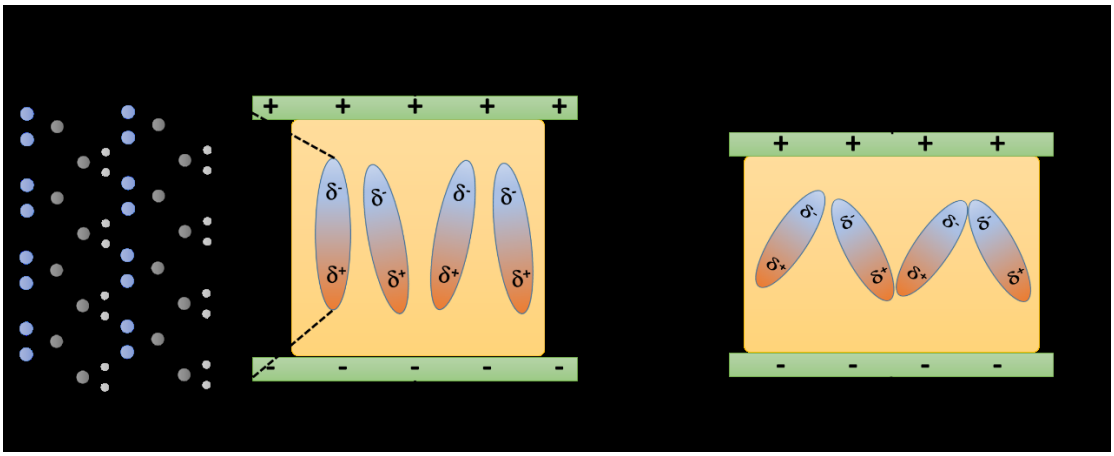


Figure 1. Schematic of the piezoelectric effect in a PVDF PEG, a) chemical structure of PVDF (fluorine atoms shown in blue, hydrogen atoms shown in light grey); b) dipole orientation of PVDF crystallites within the bulk polymer with no applied force; and c) resulting current flow induced by the application of compressive force (electrodes shown in green).

In contrast, triboelectricity is a fundamental property that arises from contact between two dissimilar materials causing opposing charges to form on each surface, called contact electrification (CE).[5-8] In PEGs, CE can result from friction at polymer interfaces, shear forces in composites, and even friction or static discharge from a human finger or rubber glove (both commonly used to test PEGs). Without consideration of CE the electrical output arising from the reported piezoelectric effect is often inflated.[9] Here, we discuss the origins of triboelectric charge in piezoelectric measurements and how the measurement techniques, and reporting in literature, can be improved in order to provide more accurate piezoelectric figures of merit.

2. The Piezoelectric Effect and Contact Electrification in Polymers

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In a PEG device the measured voltage, power, and/or charge arises from electrostatic induction on conductive electrodes placed above and below the piezoelectric polymer (**Figure 1**).[3, 10] As the measurement of the piezoelectric output is driven by electrostatic induction, any other effect that causes charge to flow between the electrodes can add to the measured output, and mistaken for piezoelectricity. In many cases both device design, and testing method, can introduce surface charges which are erroneously recorded as exceptional voltage and charge outputs during piezoelectric testing.[9, 11] Further external circuitry,[12] and the use of low resistance electrical measurement equipment,[13] can dramatically affect the reported values of piezoelectric output. While CE remains poorly understood,[9, 11] there are clear cases of non-piezoelectric charge that arise from friction between polymer-polymer interfaces or electrostatic induction from pre-existing static charge from the testing apparatus. These effects frequently appear unaccounted for in piezoelectric literature. Elucidating non-piezoelectric charge in PEGs is best understood by focussing on the standard modes of operation of TEGs. The standard TEG device configuration consists of one or two chemically distinct polymers which are coated with electrodes **(Figure 2 a)**. In TEG configurations that have two polymers, each polymer is moved against each other in either lateral sliding or contact-separation mode.[14] Alternatively, a single polymer can be rubbed across two electrodes (freestanding mode) or a polymer oscillated with respect to another electrode coated polymer (single electrode mode).[14] Opposing surface charges at the polymer interface arise after initial contact then subsequent separation of the two surfaces, thus inducing charges on the underlying electrodes. The two electrodes in the TEG are connected by an outer electric circuit and upon electrode oscillation an electrical potential is created. This effectively drives electrons between the two electrodes to balance the potential difference. Triboelectric charge is highly material dependant,[15] with commonly used piezoelectric polymers such as PVDF showing exceptionally high triboelectric charge densities (TECDs) (-87.35 ± 2.06 μC m^{-2}). Notably, poly(tetrafluoroethylene)

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(PTFE) has a higher TECD (-113.06 ±1.14 μC m^{-2}) than the most commonly used triboelectric material, poly(dimethylsiloxane) (PDMS) (-102.05 ± 2.16 μC m^{-2}).[16, 17]

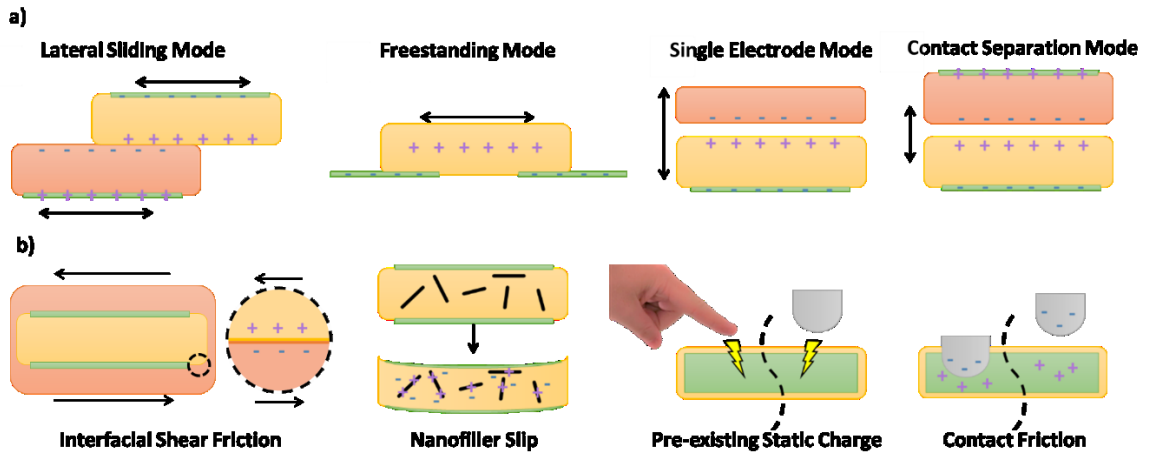


Figure 2. Schematic of a) the operation modes of TEG devices (electrodes shown in green, electrical connections not shown for clarity); [2, 14] and b) sources of CE commonly occurring in PEG devices; friction between an interface of a piezoelectric polymer (yellow) and an insulating polymer (orange) (far left); interfacial slip between rigid fillers and flexible polymers (middle left); contact electrification from the measurement technique in the form of pre-existing static charge (middle right); or friction and contact separation (far right).

In PEGs, force is applied by compression or bending with both the material used to compress, and the rate of compression, playing a crucial role in understanding charge and voltage outputs.[18] The piezoelectric material is often wrapped in an insulating soft polymer shell, for example, PDMS,[18-25] poly(imide) (PI),[26] or poly(ethylene terephthalate) (PET)[26, 27] to protect the active piezoelectric material. Many rigid fillers are also added to PEGs with a goal of boosting the device output and overall performance.[23, 27-29]

Interfacial slip between high TECD polymers in a PEG device generates friction based CE output analogous to the contact sliding mode of TEGs (**Figure 2 b**, interfacial shear). As fluoropolymers themselves are high TECD materials, slip between metallic electrodes and the fluoropolymer during testing induces CE similar to the single polymer shear mode for TEGs. Interfacial slip can also occur between mechanically mismatched rigid fillers (often ceramics)[22, 27, 29] and the piezoelectric polymer

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(**Figure 2 b**, nanofiller slip).[30, 31] This interfacial slip will generate localized CE, however, unless the fillers are highly oriented (such that the net dipole moment is > 0) or bridge the electrodes this charge cannot be measured.

The most ubiquitous source of CE in PEGs is the friction between the loading object and the encapsulating material (or the electrode itself). This friction is highly problematic when attempting to measure piezoelectric output as the triboelectric charges drives electrostatic induction on the electrodes. The contact friction is further exasperated if the repeated application of force results in separation between the loading object and the PEG (**Figure 2**, contact friction, pre-existing static charge). In this case the significant change in distance between the triboelectric charges on the loading object and the PEG induces exceptionally large current and voltage outputs due to the induced variation in field strength.[11, 22] In effect, this friction is analogous to the contact separation mode of TEGs.

2.1. Demonstration and Mitigation of CE in PEGs

To demonstrate a simple process by which CE from the testing object can be eliminated we tested charge output using inherently non-piezoelectric elastomeric PDMS (**Figure 3**).[32] By placing two conductive indium tin oxide (ITO) glass plates (used as electrodes) on either side of a cast PDMS thin film, and applying a known force through a mechanical tester, a response that could easily be misinterpreted as a piezoelectric output was observed (**Figure 3 a and c**). In this work, a cyclic load between 1 N and 10 N was applied to the PDMS via an ITO plate. Without the conductive adhesive tape, a peak-to-peak current of 0.6 nA was observed (**Figure 3c**).

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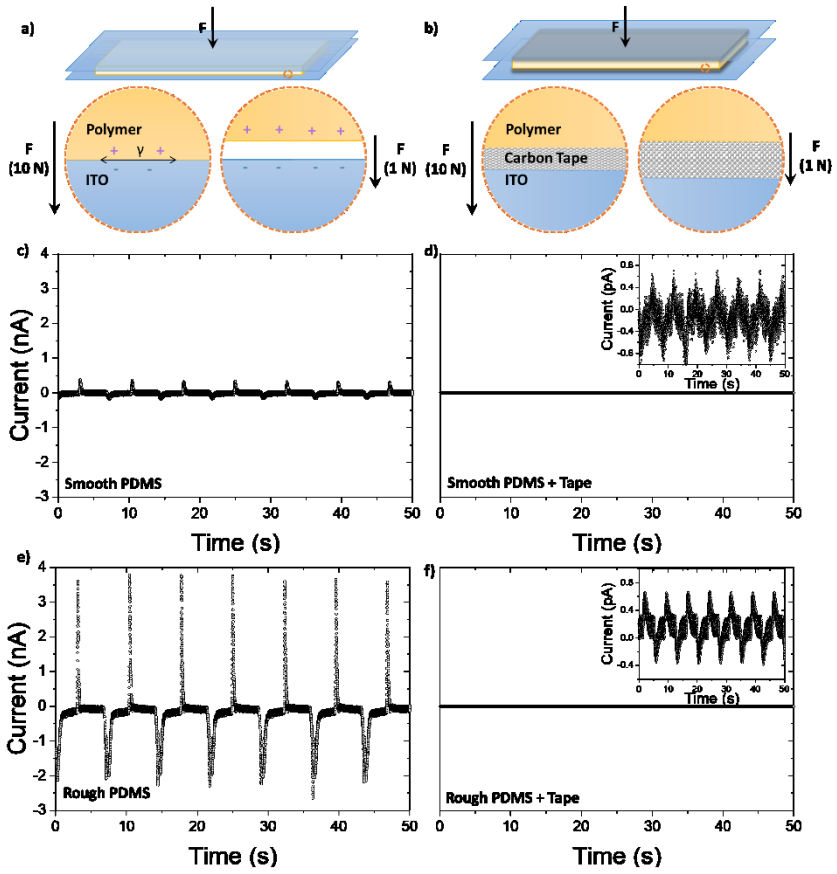


Figure 3. Effect of contact between a PDMS thin film and ITO electrodes on measured electrical output; a) non-piezoelectic polymer sandwiched between two ITO plates (charges shown arise from contact electrification); b) with the addition of carbon tape as a flexible adhesive layer, expanded images show the interface at various times highlighting friction-generated charge due to slip without the carbon tape; c-f) electrical measurements for non-piezoelectric 1 mm thick PDMS films (Sylgard 184, pre-polymer/cross-linking agent – 1/10, cross-linked at 100 $^{\circ}$C for 30 min) with cyclical application of force between 10 N and 1 N; **c)** smooth PDMS film, ITO coated glass slides; d) smooth PDMS film, carbon tape, ITO coated glass slides; **e)** porous PDMS film, ITO coated glass slides; and f) porous PDMS film, carbon tape, ITO coated glass slides.

The addition of conductive adhesive tape in-between the ITO plate and the PDMS (**Figure 3 b**) resulted in virtually no observed current (1.2 pA peak-to-peak, **Figure 3 d**). The trend is more evident when the roughness of the PDMS was increased by the addition of a pore-forming agent (sucrose) followed by phase inversion to generate pores. This roughening resulted in a 6000 pA and 1 pA current being measured for samples without (**Figure 3 e**) and with (**Figure 3 f**) the adhesive tape respectively. The increase in measured current, which arises from friction between the ITO plates and PDMS, is due to the significantly higher roughness at the interface between the ITO and the

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porous PDMS sample (compared to the ITO/smooth PDMS). This higher roughness results in greater friction and therefore a greater degree of contact electrification. The increase in measured current was completely eliminated with the addition of conductive carbon tape (**Figure 3 d and f**), with both samples exhibiting the same piezoelectric output, as expected for a material with the same phase, and geometry. The addition of a flexible, conductive carbon adhesive between the ITO glass plates and the polymer functions to prevent any interfacial friction between the testing device and polymer, and was able to prevent any contact separation modes occurring (**Figure 3 b,d and f**).

There is a simple way to determine if a piezoelectric output would be expected for a sample under compressive testing (**Figure 4 a**), and hence in ascertaining if the measured output is piezoelectric or triboelectric. If a piezoelectric sample is moved (without electrodes) relative to a grounded conductive plate, it will have a flow of charge that can be measured on the grounded conductive plate, whereas a non-piezoelectric material will not induce any current (**Figure 4 b**). To demonstrate this effect we fabricated two unpoled, net polarisation (ΔP) = 0, PVDF films, one of these was subsequently electrically poled aligning the dipoles such that $\Delta P > 0$. These films were tested using ITO plates and conductive carbon tape as described in **Figure 3 b**. As expected, the unpoled sample showed no current output and the poled sample demonstrated a clear piezoelectric response. The lack of current measured for the unpoled sample again confirmed (**Figure 4 c and d**) the lack of triboelectric charge generated by the adhesive tape technique. When the same samples (without electrodes, and never contacted) were moved relative to a grounded metal plate, current (measured on the metal plate) was only observed to flow for the poled PVDF sample (**Figure 4 e and f**). As the poled PVDF sample has an aligned dipole moment, the motion of this sample varies the electric field strength experienced by the grounded plate, resulting in a measurable current by electrostatic induction.

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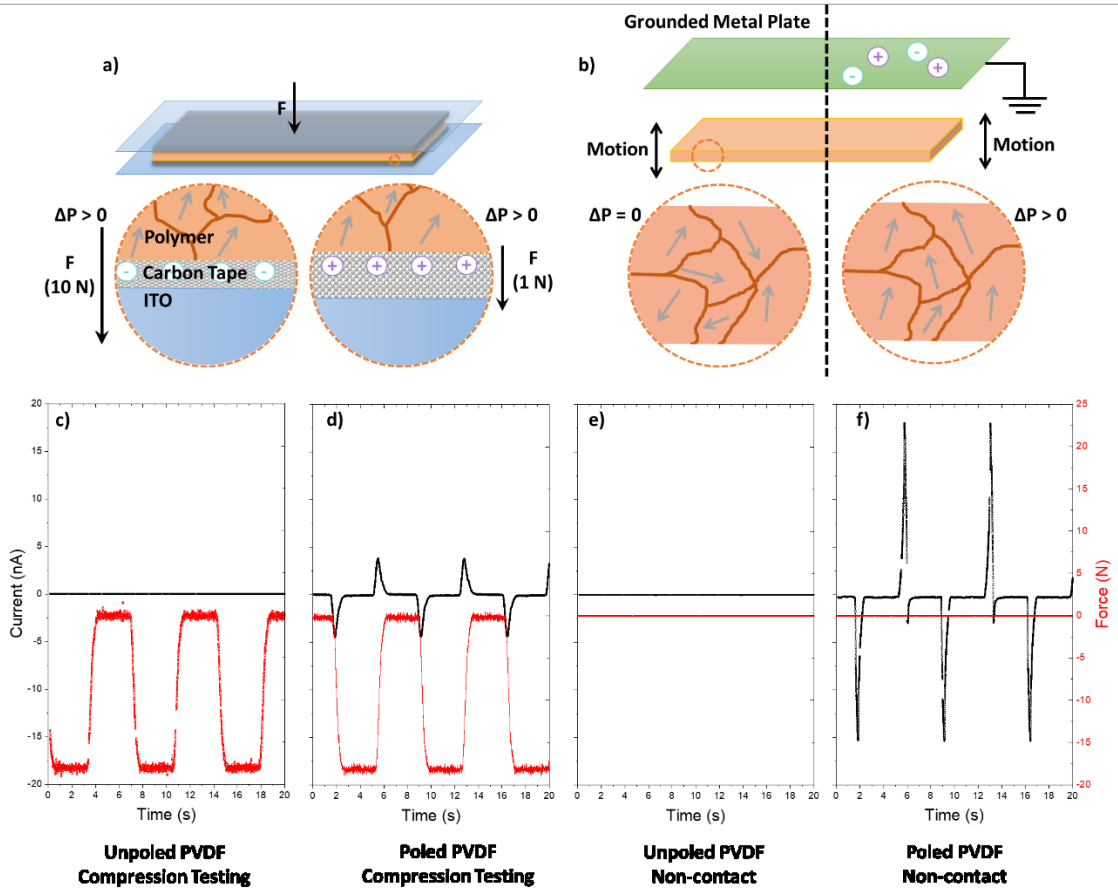


Figure 4. Comparison of a) compressive testing (charges shown are piezoelectric in origin); and b) non-contact measurement for ascertaining the piezoelectric response from a material (simplified domains are shown for clarity, in reality polymer crystal structures are notably more complex); c) non-poled PVDF sample under compressive testing; d) poled PVDF sample under compressive testing; and current measured from a grounded metal plate when a e) non-poled PVDF sample; or a f) poled PVDF sample are moved towards then away (between 0.1 mm and 2.0 mm) from the plate.

Above we have described two tools to test the inherent piezoelectricity of piezoelectric polymers and eliminate CE during testing. To accurately analyse assembled PEG devices without measuring CE, the piezoelectric device and sputtered electrodes can be encapsulated within a thin dielectric polymer. This insulating layer should then be coated with a grounded flexible conductor, such as carbon nanotubes, sputtered metal, or conductive polymer composites (**Figure 5 a**).[33] The grounded conductive layers serve to dissipate friction charge measured from the piezopolymer/dielectric interface, such that it cannot induce charge on the electrodes. To quantify the output, compressive mechanical testing should be used where the electrodes are placed on the testing apparatus and the

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force applied, without breaking physical contact with the polymer (**Figure 5 b**).[29] This approach is taken in commercial piezoelectric measurement devices such as the PIEZOTEST d33 Piezometer system, as reported by Wu *et al.*,[29] although conformal contact with no-slip is still required to limit surface charge generation from friction. Through proper testing, that is, eliminating the role of CE and static charge, true piezoelectric figures of merit can be reported. This in turn will enable better elucidation of effective strategies to improve the performance of piezoelectric polymers in device applications.

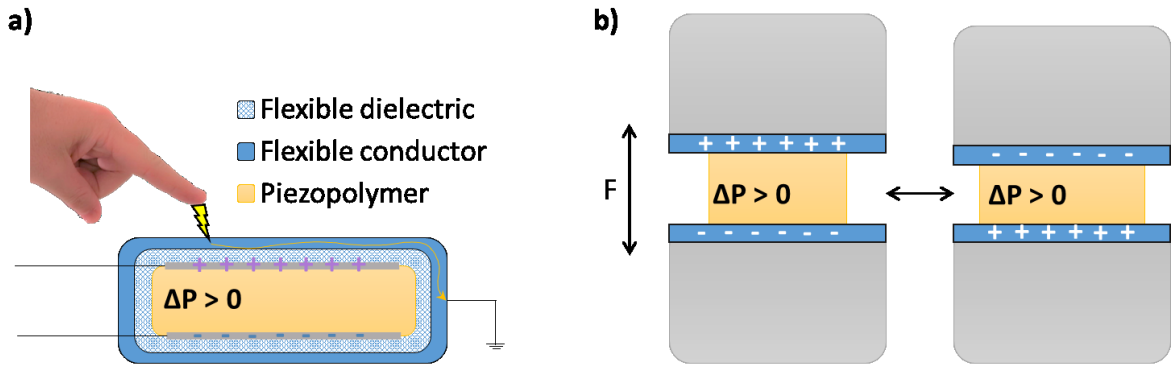


Figure 5. Schematic of potential testing methods to eliminate the generation of surface charge. a) an idealized testing configuration to eliminate static charge and friction effects for a thin piezoelectric polymer sample; and b) a design where the electrodes are on the testing apparatus rather than the sample (charges in a and b arise from the piezoelectric effect), this can be further improved by the addition of adhesive tape between the electrodes and the piezoelectric polymer sample.

3. Evaluating Literature on PEG Outputs

As we have demonstrated, the method of PEG device fabrication (which often introduced polymer interfaces in the device) and testing (friction and contact separation) has a dramatic role on reported piezoelectric output. Thus, a critical assessment of the literature and a context of 'realistic' voltage and charge outputs are crucial to interpreting published data.

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3.1. Realistic Outputs

As has been well reported, and summarized, the perpendicular voltage co-efficient for piezoelectricity (g_{33}), lies between 0.3 V m N^{-1} and 0.4 V m N^{-1} for the highest performance piezoelectric polymers.[1, 34-41] **Equation 1a** shows the dependence of the g_{33} on the electric field and the compressive stress. This can then be expanded (**Equation 1b and c**) and rearranged (**Equation 1d**) (at open circuit potential) to give the voltage dependence on sample testing parameters and geometries.

$$\boldsymbol{g_{33} = -\left(\frac{\partial E_3}{\partial T_3}\right)^D} \qquad \textbf{Equation 1a}$$

$$E_3 = \frac{\Delta V}{t} \qquad \textbf{Equation 1b}$$

$$T_3 = \frac{\Delta F}{A_t} \qquad \textbf{Equation 1c}$$

$$\Delta V = \frac{g_{33} \times \Delta F \times t}{A_t} \propto \frac{t}{A_t} \qquad \textbf{Equation 1d}$$

Where E_3 is the electric field in the direction parallel to the applied force (V m^{-1}), T_3 is the compressive stress of the piezoelectric in the direction of the applied force (N m^{-2}), A_t is the total area under compression, ΔF is the change in force applied to the sample, ΔV is the generated voltage output, and t is the spacing between the electrodes (often approaching the sample thickness). D, in the presence of no external electric field, condenses to the degree of polarization in the z direction (a constant at a given time, and a fraction between 0 and 1).[10]

From **Equations 1a-d**, we can determine that for an applied force of 10 N (an approximate force of a controlled finger tap),[42] the maximum measured voltage that a sample would expect to have is approximately ±80 V for a 100 µm sample thickness (with a 4 cm^2 area of compression, significantly higher than the area of a fingertip). This value represents an 'ideal' generated voltage and is

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expected to reduce dramatically due to environmental factors, such as electrical connections or external (stray) electric fields.

Many of the best reported values of PE output arise from ultra-thin samples that contain either a high-surface area of polymer nanofibers,[20] or ceramic nanofillers that bridge the electrodes, both of which can lead to CE contributions in reported measurements.[43]

According to **Equation 1d,** polymer samples should show a voltage output proportional to their thickness, so these ultra-thin samples, having the highest outputs, is somewhat surprising.[20, 27] Further, the most common ceramic nanofillers used in PVDF-based polymers are barium titanate ($BaTiO_2$ (BTO)),[23] zinc oxide (ZnO),[43] or lead zirconate titanate (PZT).[22, 27] While the charge co-efficient (d_{33}) is significantly higher for these ceramic nanofillers, the voltage co-efficient (g_{33}) is typically an order of magnitude lower (g_{33}(BTO) = 0.013 V m N^{-1}; g_{33}(PZT) = 0.026 V m N^{-1}; g_{33}(PVDF) = 0.32 V m N^{-1}).[1] Hence, even with exceptional interface engineering between the ceramic and the fluoropolymer, the voltage output would be expected to decrease with ceramic nanofiller addition. There are two exceptions to this rule: 1) for high aspect ratio nanofillers such as carbon nanotubes[44] or ceramic nanorods[22] the nanofillers can act as local stress concentrators, effectively giving a nanoscale A_t, and hence much larger ΔV; and 2) when the ceramic nanofillers have a greater degree of freedom to move within the polymer matrix. In this case the strong dipole moment of the ceramic experiences a relatively higher misalignment (compared to the dipole of the fluoropolymer crystallite) under compressive stress. The higher degree of misalignment leads to subsequent greater change in the electric field and subsequent induction of charge on the electrodes. Overall in cases where the g_{33} of the nanofiller is lower, any increase in voltage output would only be expected from changes in polymer crystallization (i.e., the percentage or alignment of the ferroelectric crystal phase) from polymer/nanofiller interactions,[44] or cases where the ceramic nanofillers are free to rotate.[45] Based on these concepts, it is expected that ultra-thin piezoelectric polymers containing

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ceramic nanofillers have a lower voltage output, unless the ceramic fillers are free to move and deform, and the fact this is not the case suggests the measurement of surface charge.

Similarly, the d_{33} for fluoropolymers ranges between 28 pC N^{-1} and 140 pC N^{-1},[44] however, determining the maximum reasonable current is impossible as charge is a time dependent property. Therefore, the generated induced current on the electrodes is dependent on the rate of change of applied stress, a parameter that is exceptionally poorly defined and reported in literature.

Film thickness, applied stress (for g_{33}), the rate of change of applied stress and the total compressed area (for d_{33}), are crucial when comparing literature values within the field.[46] Unfortunately, many publications cite testing methods in which one or all of these values are omitted rendering the results irreproducible, thus removing any ability to establish figures of merit for the materials being tested.

The full derivation and explanation of piezoelectric properties is beyond the scope of this report, and there are excellent explanations of these already in the literature, most notably by Wang.[10] Equally, there are excellent reviews in literature on triboelectric outputs,[15, 16] yet there remains a large gap in literature around discussions of these two effects occurring simultaneously during device testing. In the next section we strive to understand factors effecting PE and TE measurements, and comment on how critical interpretation of piezoelectric data can strengthen the field moving forward.

3.2. Towards Standardization

The three most common reported tests carried out in piezoelectric literature are piezo-force microscopy (PFM),[28] unimorph cantilever beam testing,[47] and tapping with a human finger.[17] These techniques each have limitations, PFM measures only nanoscale response, unimorph cantilever beam testing only considers one mode of motion, and human finger tapping results in an undefined force and can introduce static charge.[43] lack of standardization in many PEG tests, where

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the rate of change of applied stress or compressed area is not report, for example, driving over a sample with car tires,[18] or tapping with a human finger (as the sole measurement technique),[43] make the accurate evaluation of PEG output impossible to determine. These non-standard types of testing also are prone to measuring CE from friction or static charge. Further, charge and/or voltage outputs are often reported without area or thickness normalization.[48] Both induction (by moving a poled piezoelectric material with respect to a grounded metal plate, **Figure 4 b**) and reporting of the field loop hysteresis can provide context to the reported charge and/or voltage output.[49]

The challenge here is not that the values measured and reported are incorrect, it is that the data cannot be reproduced by other researchers. To highlight this challenge, we have collated several key publications and classified them by testing method that was used to record the figure of merit (**Figure 6 a)**. There is no implication here that the reports are incorrect, simply that there are design parameters which could be improved in the future.

Compression with a human hand or finger, remains the most commonly used testing method. Over recent years the use of the human hand has been slowly replaced by bending and cyclical compression testing as a testing method. Taking the data from **Figure 6 a**, and assessing the literature for potential sources of surface charge (**Figure 6 b**) demonstrates that both polymer interfaces and testing methodologies, not designed for the elimination of surface charge, are present in the majority of papers. This representation of the data (**Figure 6 a and b**) is not normalized to area, nor converted to d_{33} (or g_{33}) figures of merit as the manuscripts often lack the context needed to calculate or compare these values (for instance, missing thickness, missing surface area, undefined force application). These basic values are crucial for clear reporting and comparison within piezoelectric literature.

4. Outlook

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In this essay, we have discussed methods in which CE can be excluded from measurements designed to evaluate piezoelectric materials. In general, ceramic piezoelectric devices are better understood and are less prone to reporting CE as piezoelectric output due to their higher proportion of ferroelectric (piezoelectric) phase compared to polymers. Yet even for piezoelectric ceramics, device design and infiltration with polymers can still lead to erroneous CE measurement.. In the future, this discussion will enable the development of improved piezoelectric performance from polymer architectures. With improved polymer PEGs, hybrid PE-TEGs that harvest energy from both piezo- and tribo-electric processes, thus attaining a much broader energy harvesting capability, can be developed effectively.[11, 45, 50-54] There is excellent emerging research focussed on the development of such hybrid PE-TEG devices.[2, 11, 45, 51, 52, 55] In particular, Woo-Suk Jung *et al.* have shown clear evidence of the impact in optimizing both piezo- and tribo-electric components in PE-TEGs (**Figure 6 c and d**). They successfully deconvoluted the voltage generated by a PE-TEG device into individual piezo- and tribo-electric components (**Figure 6 e**). This deconvolution showed the peak-to-peak voltage arising from triboelectricity is double that from piezoelectricity.[11] It is important to note here that the polymer surfaces did not undergo any roughening,[11] which we have shown (**Figure 3 e and f**) can increase the output current by an order of magnitude.

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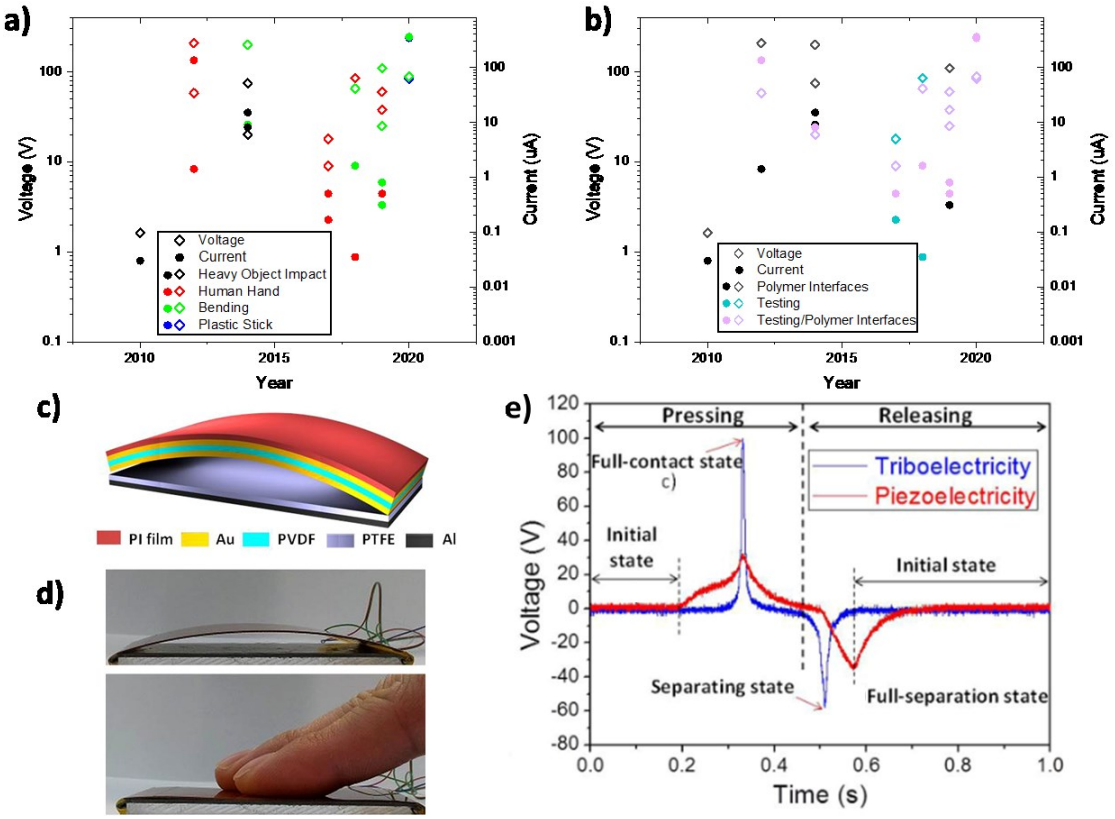


Figure 6. a) Literature comparison of voltage and current output with variable testing systems; and; b) sources of non-piezoelectric charge in the sampe dataset;[18, 20-23, 27, 43, 48, 52, 56-59] c) hybrid PE-TEG schematic; d) photograph of a hybrid PE-TEG device under human finger testing; and e) deconvolution of the piezo- and tribo-electric outputs from (c,d). c–e) Adapted under the terms of the CC-BY 4.0 open access license.[11] Copyright YEAR, COPYRIGHT HOLDER, Published by PUBLISHER.

Finally, the path forward relies on developed a stronger understanding of the origins of CE within energy harvesting devices, coupled to complete reporting of device components and geometries within research articles. Most importantly, the testing methods need to be fully and clearly described to provide readers, with confidence that the reported piezoelectric figures of merit do not arise from CE. Building confidence in reported values, by consideration of CE in device fabrication and testing method, will help hasten the development of PEGs into the commercial market.

5. Conclusion

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Polymer piezoelectric materials are a field complicated by the complexities of device fabrication, and confusion between the measurement of the piezoelectric effect and contact electrification from interfacial slip and friction. It is of crucial importance for literature to be reported with PE material thicknesses and applied forces that are normalized to the total area under compression. The field needs to address overlap of piezoelectric with triboelectric effects, and we have provided key measurement protocols and conceptual guidance to aid in the elucidation of where triboelectric charge influences measurements. Energy harvesting devices are crucial for powering next-generation electronics, and therefore appropriately understanding how they capture and convert energy most efficiently will enable better advanced materials to be developed that can be more readily progressed into commercial applications.

6. Experimental Section

6.1 PDMS Film Fabrication

To demonstrate contact electrification in piezoelectric testing, non-piezoelectric films of PDMS (Sylgard 184) approximately 1 mm thick and 5 cm^2 were fabricated. The pre-polymer and cross-linking agent ratio was 1:10 (wt/wt). The PDMS films were cross-linked at 100 ºC for 30 min. To prepare rough PDMS films, a sugar cube (sucrose) was used as a pore-forming template. The PDMS was first infiltrated into the sugar cube, degassed, and then cross-linked (at 100 ºC for 30 min) inside the pores of the sugar cube. The PDMS/sugar cube was then immersed in water, with the sugar dissolving leaving a highly porous, rough, PDMS template.

6.2 PVDF Film Fabrication

PVDF films were prepared to demonstrate both the expected piezoelectric output from compressive testing and the non-contact method of proving a samples piezoelectricity. A stock solution of PVDF (20 wt%) in dimethylformamide (DMF) was spin-coated onto the PET side of an ITO/PET substrate.

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The film was then immersed in methanol for 1 min, allowing the DMF to leach out into the methanol phase, leaving the PVDF remaining as a solid film adhered to the ITO/PET substrate. The thickness of the resulting PVDF film was estimated at approximately 20 µm (by cross-sectional scanning electron microscopy using a TESCAN MIRA microscope, data not shown), and the geometric area was 5 cm^2. To align the dipoles in a single PVDF film, electric field poling was used at a field strength of 5 MV/m for 1 h at 115 $^{\circ}C$.

6.3 Electrical Measurements

Double-sided adhesive tape (100 µm thick) was used to eliminate friction during the electromechanical response measurements. Electrical measurements were performed by a custom-made voltage divider in combination with a Keithley 6514 electrometer connected to a Picoscope 5444B PC oscilloscope. An INSTRON E1000 All-Electric Dynamic Test Instrument was used in the experiments to apply force and precise sample movement. The pressing force during the compressive electromechanical response measurements was varied from 2 to 20 N.

7. Acknowledgements

This research was supported by the Australian Government through the Australian Research Council's Linkage Projects funding scheme (LP160100071). Linards Lapčinskis and Andris Šutka acknowledge Riga Technical University's Doctoral Grant and Research Excellence grant programs. Kaspars Mālnieks acknowledge the European Regional Development Fund within the Activity 1.1.1.2 "Post-doctoral Research Aid" of the Specific Aid Objective 1.1.1 "To increase the research and innovative capacity of scientific institutions of Latvia and the ability to attract external financing, investing in human resources and infrastructure" of the Operational Programme "Growth and Employment" (Grant No. 1.1.1.2/VIAA/3/19/404). Andris Šutka and Peter C. Sherrell equally contributed to this work.

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Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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References

[1] N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicinoski, J. G. Shapter, A. V. Ellis, *Energy & Environmental Science* **2019**, 12, 1143.

[2] F. R. Fan, W. Tang, Z. L. Wang, *Advanced Materials* **2016**, 28, 4283.

[3] E. Fukada, *Ultrasonics* **1968**, 6, 229.

[4] C. Wan, C. R. Bowen, *Journal of Materials Chemistry A* **2017**, 5, 3091.

[5] J. Henniker, *Nature* **1962**, 196, 474.

[6] Z. L. Wang, *Advanced Energy Materials*, n/a, 2000137.

[7] Z. L. Wang, *ACS Nano* **2013**, 7, 9533.

[8] A. Šutka, K. Mālnieks, L. Lapčinskis, P. Kaufelde, A. Linarts, A. Bērziņa, R. Zābels, V. Jurķāns, I. Gorņevs, J. Blūms, M. Knite, *Energy & Environmental Science* **2019**, 12, 2417.

[9] S. Mishra, L. Unnikrishnan, S. K. Nayak, S. Mohanty, *Macromolecular Materials and Engineering* **2019**, 304, 1800463.

[10] Z. L. Wang, *Materials Today* **2017**, 20, 74.

[11] W.-S. Jung, M.-G. Kang, H. G. Moon, S.-H. Baek, S.-J. Yoon, Z.-L. Wang, S.-W. Kim, C.-Y. Kang, *Scientific Reports* **2015**, 5, 9309.

[12] M. B. Khan, D. H. Kim, J. H. Han, H. Saif, H. Lee, Y. Lee, M. Kim, E. Jang, S. K. Hong, D. J. Joe, T.-I. Lee, T.-S. Kim, K. J. Lee, Y. Lee, *Nano Energy* **2019**, 58, 211.

[13] Y. Su, C. Dagdeviren, R. Li, *Advanced Functional Materials* **2015**, 25, 5320.

[14] A. Ahmed, I. Hassan, M. F. El-Kady, A. Radhi, C. K. Jeong, P. R. Selvaganapathy, J. Zu, S. Ren, Q. Wang, R. B. Kaner, *Advanced Science* **2019**, 6, 1802230.

[15] S. Pan, Z. Zhang, *Friction* **2019**, 7, 2.

[16] H. Zou, Y. Zhang, L. Guo, P. Wang, X. He, G. Dai, H. Zheng, C. Chen, A. C. Wang, C. Xu, Z. L. Wang, *Nature Communications* **2019**, 10, 1427.

[17] S. Cherumannil Karumuthil, S. P. Rajeev, S. Varghese, *Nano Energy* **2017**, 40, 487.

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Author Manuscript

[18] K. Y. Lee, D. Kim, J.-H. Lee, T. Y. Kim, M. K. Gupta, S.-W. Kim, *Advanced Functional Materials* **2014**, 24, 37.

[19] G. Zhang, P. Zhao, X. Zhang, K. Han, T. Zhao, Y. Zhang, C. K. Jeong, S. Jiang, S. Zhang, Q. Wang, *Energy & Environmental Science* **2018**, 11, 2046.

[20] L. Gu, N. Cui, L. Cheng, Q. Xu, S. Bai, M. Yuan, W. Wu, J. Liu, Y. Zhao, F. Ma, Y. Qin, Z. L. Wang, *Nano Letters* **2013**, 13, 91.

[21] S. Maiti, S. Kumar Karan, J. Lee, A. Kumar Mishra, B. Bhusan Khatua, J. Kon Kim, *Nano Energy* **2017**, 42, 282.

[22] X. Chen, S. Xu, N. Yao, Y. Shi, *Nano Letters* **2010**, 10, 2133.

[23] S.-H. Shin, Y.-H. Kim, M. H. Lee, J.-Y. Jung, J. Nah, *ACS Nano* **2014**, 8, 2766.

[24] Y. Zhang, H. Sun, C. K. Jeong, *ACS Applied Materials & Interfaces* **2018**, 10, 35539.

[25] Y. Zhang, C. K. Jeong, J. Wang, H. Sun, F. Li, G. Zhang, L.-Q. Chen, S. Zhang, W. Chen, Q. Wang, *Nano Energy* **2018**, 50, 35.

[26] E. J. Lee, T. Y. Kim, S.-W. Kim, S. Jeong, Y. Choi, S. Y. Lee, *Energy & Environmental Science* **2018**, 11, 1425.

[27] K.-I. Park, J. H. Son, G.-T. Hwang, C. K. Jeong, J. Ryu, M. Koo, I. Choi, S. H. Lee, M. Byun, Z. L. Wang, K. J. Lee, *Advanced Materials* **2014**, 26, 2514.

[28] S. Dunn, *Journal of Applied Physics* **2003**, 94, 5964.

[29] Y. Wu, F. Ma, J. Qu, Y. Luo, C. Lv, Q. Guo, T. Qi, *Applied Surface Science* **2019**, 469, 283.

[30] A. S. Rahman, D. W. Radford, *Composite Interfaces* **2017**, 24, 817.

[31] S. Vivekchand, U. Ramamurty, C. Rao, *Nanotechnology* **2006**, 17, S344.

[32] K. K. Sappati, S. Bhadra, *Sensors (Basel)* **2018**, 18, 3605.

[33] Z. Zhu, S.-Z. Guo, T. Hirdler, C. Eide, X. Fan, J. Tolar, M. C. McAlpine, *Advanced Materials* **2018**, 30, 1707495.

[34] S. Crossley, R. A. Whiter, S. Kar-Narayan, *Materials Science and Technology* **2014**, 30, 1613.

[35] C. Jean-Mistral, S. Basrour, J. J. Chaillout, *Smart Materials and Structures* **2010**, 19.

[36] Z. Li, J. Wang, X. Wang, Q. H. Yang, Z. C. Zhang, *Rsc Advances* **2015**, 5, 80950.

[37] Z. M. Li, Y. H. Wang, Z. Y. Cheng, *Applied Physics Letters* **2006**, 88.

[38] K. S. Ramadan, D. Sameoto, S. Evoy, *Smart Materials and Structures* **2014**, 23.

This article is protected by copyright. All rights reserved.

Author Manuscript

[39] F. P. Wang, P. Frubing, W. Wirges, R. Gerhard, M. Wegener, *Ieee Transactions on Dielectrics and Electrical Insulation* **2010**, 17, 1088.

[40] Y. Wang, B. Neese, Q. M. Zhang, C. Huang, J. West, Ieee, in *2007 Ieee Ultrasonics Symposium Proceedings, Vols 1-6*, 2007, 2606.

[41] E. Klimiec, W. Zaraska, K. Zaraska, A. Cichocki, K. Gąsiorwski, T. Sadowski, M. Pajda, *Elektronika : konstrukcje, technologie, zastosowania* **2006**, Vol. 47, nr 12, 11.

[42] K. Shima, Y. Tamura, T. Tsuji, A. Kandori, M. Yokoe, S. Sakoda, "Estimation of human finger tapping forces based on a fingerpad-stiffness model", presented at *2009 Annual International Conference of the IEEE Engineering in Medicine and Biology Society*, 3-6 Sept. 2009, 2009.

[43] G. Zhu, A. C. Wang, Y. Liu, Y. Zhou, Z. L. Wang, *Nano Letters* **2012**, 12, 3086.

[44] N. A. Shepelin, P. C. Sherrell, E. Goudeli, E. N. Skountzos, V. C. Lussini, G. W. Dicinoski, J. G. Shapter, A. V. Ellis, *Energy & Environmental Science* **2020**, 13, 868.

[45] L. Lapčinskis, K. Mālnieks, A. Linarts, J. Blūms, K. n. Šmits, M. Järvekülg, M. r. Knite, A. Šutka, *ACS Applied Energy Materials* **2019**, 2, 4027.

[46] C. R. Bowen, J. Taylor, E. LeBoulbar, D. Zabek, A. Chauhan, R. Vaish, *Energy & Environmental Science* **2014**, 7, 3836.

[47] C. Mo, S. Kim, W. W. Clark, *Smart Materials and Structures* **2009**, 18, 055017.

[48] S. He, W. Dong, Y. Guo, L. Guan, H. Xiao, H. Liu, *Nano Energy* **2019**, 59, 745.

[49] Y. Zhang, J. Roscow, R. Lewis, H. Khanbareh, V. Y. Topolov, M. Xie, C. R. Bowen, *Acta Materialia* **2018**, 154, 100.

[50] X. Chen, M. Han, H. Chen, X. Cheng, Y. Song, Z. Su, Y. Jiang, H. Zhang, *Nanoscale* **2017**, 9, 1263.

[51] C. Zhao, Q. Zhang, W. Zhang, X. Du, Y. Zhang, S. Gong, K. Ren, Q. Sun, Z. L. Wang, *Nano Energy* **2019**, 57, 440.

[52] C. Sun, Q. Shi, D. Hasan, M. S. Yazici, M. Zhu, Y. Ma, B. Dong, Y. Liu, C. Lee, *Nano Energy* **2019**, 58, 612.

[53] C. Rodrigues, A. Gomes, A. Ghosh, A. Pereira, J. Ventura, *Nano Energy* **2019**, 62, 660.

[54] X.-S. Zhang, M.-D. Han, R.-X. Wang, F.-Y. Zhu, Z.-H. Li, W. Wang, H.-X. Zhang, *Nano Letters* **2013**, 13, 1168.

[55] A. Šutka, K. Mālnieks, L. Lapčinskis, M. Timusk, K. Pudzs, M. Rutkis, *iScience* **2020**, 23, 101011.

[56] D. Y. Hyeon, K.-I. Park, *Advanced Materials Technologies* **2019**, 4, 1900228.

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[57] L. Zhang, J. Gui, Z. Wu, R. Li, Y. Wang, Z. Gong, X. Zhao, C. Sun, S. Guo, *Nano Energy* **2019**, 65, 103924.

[58] X. Yuan, X. Gao, J. Yang, X. Shen, Z. Li, S. You, Z. Wang, S. Dong, *Energy & Environmental Science* **2020**, 13, 152.

[59] A. S. Dahiya, F. Morini, S. Boubenia, K. Nadaud, D. Alquier, G. Poulin-Vittrant, *Advanced Materials Technologies* **2018**, 3, 1700249.

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Author Photograph(s) ((40 mm broad, 50 mm high, gray scale))



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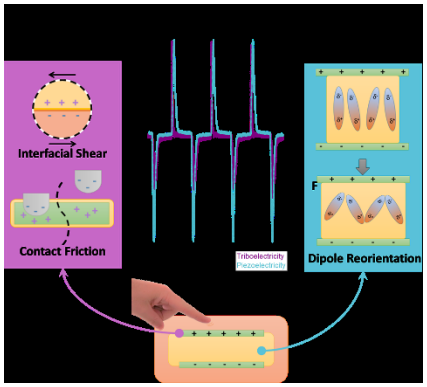
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Enhancing piezoelectric polymers energy harvesting capabilities is a key challenge for next-generation wearable and remote technologies. Enhancement of piezoelectric polymers is challenging given that many literature reports confuse measured charge from contact electrification and triboelectricity with the piezoelectric effect. Here, how to simply avoid this confusion and a framework to enable a robust literature discussion about the field moving forward are provided.



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