

Space Charge Drives Electromechanical Conversion in Ion-Implanted Polymers via an Apparent Piezoelectric Effect

Andris Šutka^{1,*†}, Holger Fiedler^{2,*‡}, Artis Linarts¹, Kaspars Mālnieks¹, Kaspars Pudzs³,
Joseph D. Berry⁴, and Peter C. Sherrell^{5,§}

¹*Institute of Physics and Materials Science, Faculty of Natural Sciences and Technology, Riga Technical University, Paula Valdena 3/7, Riga, LV-1048 Latvia*

²*Earth Sciences New Zealand, National Isotope Centre, 30 Gracefield Road, 5010 Lower Hutt, New Zealand*

³*Institute of Solid State Physics, University of Latvia, Kengaraga 8, Riga LV-1063, Latvia*

⁴*Department of Chemical Engineering, The University of Melbourne, Parkville 3010, Australia*

⁵*School of Science, RMIT University, Melbourne 3000, Australia*

 (Received 14 January 2025; revised 13 August 2025; accepted 5 December 2025; published 6 February 2026)

Ion implantation is a powerful tool to modify material chemistry and structure. The implantation process was considered to result in a net-neutral material, due to implanted ionic charge being compensated by the host materials lattice. Here, we show ion implantation into polytetrafluoroethylene (PTFE) results in an uncompensated “space charge” region—requiring a reconsideration of ion implantation into polymers. This is demonstrated via electromechanical testing of Cu implanted PTFE as a triboelectric nanogenerator (TENG). Previously, ion implantation into polymers has been shown to increase TENG performance, attributed to increasing the prevalence of electron transfer during contact-separation testing. This attribution to electron transfer is incorrect, with significant electromechanical conversion being observed in $1 \times 10^{16} \text{ at.cm}^{-2}$ Cu^+ implanted polytetrafluoroethylene (PTFE) in both piezoelectric mode testing and in noncontact induction measurements—where electron transfer cannot occur. These results indicate that the implantation of Cu ions creates a space charge effect in the PTFE matrix, and the subsequent charge asymmetry creates an electric field enhancing TENG performance, analogous to hybrid piezoelectric TENGs. These results demonstrate that ion implanted polymers possess space charge and can be used directly for sensing, creating a new pathway for electromechanical conversion materials.

DOI: 10.1103/th79-cjz6

Introduction—Flexible, polymeric, materials that convert kinetic energy into electricity (or electrical charge) are attracting immense research interest from applications ranging from powering internet-of-things (IoT) microdevices to wearable sensors to enabling green chemical transformations. Materials can achieve this through several phenomena, including ferroelectricity [1], piezoelectricity [2], flexoelectricity [3,4], porous electrets [5], or contact electrification or triboelectricity [6]. Of these phenomena, triboelectricity provides key advantages over other electromechanical conversion phenomena, as it does not require specific materials to generate charge rather the occurrence

of consistent interfacial friction [7]. In particular for triboelectricity, fluoropolymers which are the most common piezoelectric and ferroelectric polymer family, can be avoided [8].

Triboelectricity is exploited through the fabrication of the triboelectric nanogenerator (TENG), whereby two dissimilar (in terms of surface chemistry [9–11,11], mechanical properties [12,13], topography [14,15], or additives [16,17]) [7] undergo cyclic friction, with the produced surface charge causing a Maxwell’s displacement current to flow on nearby electrodes [6]. While the fundamental mechanism of TENGs remains the subject of debate in literature (between electron transfer [18,19] and ionic or molecular fragments [20–22]), significant focus has been devoted to increasing the amount of energy a TENG can produce via directly increasing (and stabilizing [23]) the surface charge produced at the contact interface.

To increase the surface charge, different approaches have been used, such as nanostructuring [14,24], adding fillers [16,25] increasing adhesion, modifying mechanical properties [26,27], or, recently, ion implantation [28,29].

Ion implantation provides a key capability to enhance the surface charge on arbitrary materials. This broad use

*These authors contributed equally to this work.

†Contact author: andris.sutka@rtu.lv

‡Contact author: h.fiedler@gns.cri.nz

§Contact author: peter.sherrell@rmit.edu.au

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International license](#). Further distribution of this work must maintain attribution to the author(s) and the published article’s title, journal citation, and DOI.

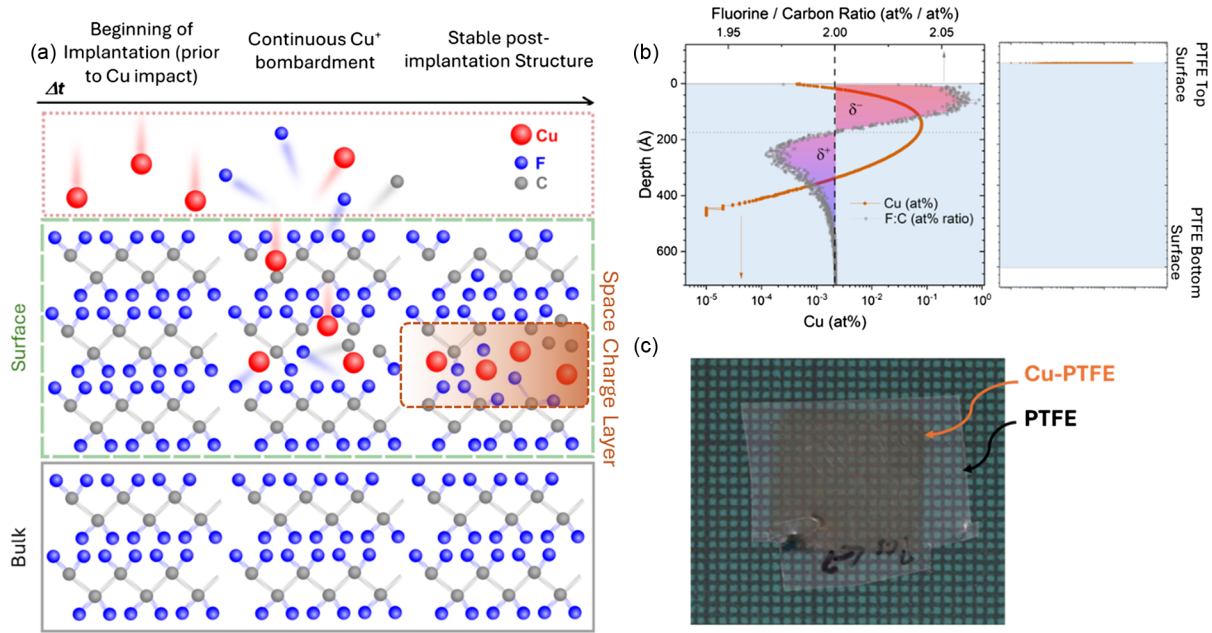


FIG. 1. (a) Schematic of ion implantation methodology; (b) simulated ion implantation depth for copper in PTFE. The fluorine to carbon ratio in the film is highlighted, which causes the formation of a buried space-charge layer (right panel shows the depth over the 0.05 mm thickness of PTFE); and (c) 1×10^{16} ions Cu cm^{-2} sample, showing the implantation area of 13×13 mm.

case makes ion implantation a particularly attractive, yet relatively unstudied approach with recent reports should an $8\times$ enhancement compared to equivalent pristine polymers simply be depositing 1×10^{16} at.cm^{-2} He^+ up to a surface charge density of $332 \mu\text{Cm}^{-2}$ [28]. However, in this case the supposed advantage of ion implantation (to enhance arbitrary materials) failed, and only Kapton (polyimide) showed an enhancement [28]. One of the polymers with a degraded performance was PTFE [28,29], which showed an optimum enhancement for a fluence of 10^{14} at.cm^{-2} N^+ . Only a negligible enhancement occurred for the highest (5×10^{15} at.cm^{-2} N^+) and lowest fluence (5×10^{13} at.cm^{-2} N^+) [29].

The mechanism by which ion implantation increased the triboelectric charge remains debated, arising from bond breakage and ionic charges which enable enhanced electron transfer. However, while ion implantation will alter the molecular structure and chemistry of the polymers [28–30], it cannot explain the selective enhancement of only certain polymers. Further, ion implantation is able to convert surface charges into electrets, and while this is well established for inorganic materials [31,32], the formation of stable charged deep-trap states has been demonstrated, but never explored, on polymers [33]. Other methods to introduce charge, such as plasma irradiation [34], radiation (λ rays) [35], corona treatment [36], arc discharge, and even the reported ion implantation methods [28,29] are dominated by electronic stopping [37] which is beneficial for electrets but causes less stable space-charge layers [33].

Excessive electronic charging such as during plasma treatment can also cause radical formation in polymers [38], which is avoided during ion implantation [39].

Here, we demonstrate that the enhanced triboelectric performance of ion-implanted PTFE is due to the introduction of charged ions into the polymer matrix, creating a space charge effect after implantation. Implanting PTFE with 1×10^{16} at.cm^{-2} Cu^+ results in a material which creates significant Maxwell's displacement current during motion near a parallel plate. Cu^+ was chosen for ion implantation as it possesses a relatively high charge density coupled to a heavy mass which guarantees dominant nuclear stopping over electronic effects during implantation, in addition to it being known to have extremely limited passive diffusion through PTFE [40]. The presence of this space charge thus makes the implanted PTFE act as a piezoelectric material, providing an external electric field mimicking the enhancement of TENGs using hybrid piezoelectric TENGs [41]. We demonstrate that this space charge leads to a 28.9-fold improvement in TENG mode testing of implanted PTFE against an indium tin oxide (ITO) electrode proving a tool to significantly enhance electromechanical conversion within polymers for energy harvesting and sensing applications.

Results and discussion—

Ion implantation: To investigate the function of ion implantation into polymers for TENGs, ion implanted polymers were subjected to traditional electromechanical testing processes in piezoelectric mode (oscillatory compression without breaking contact), noncontact oscillation

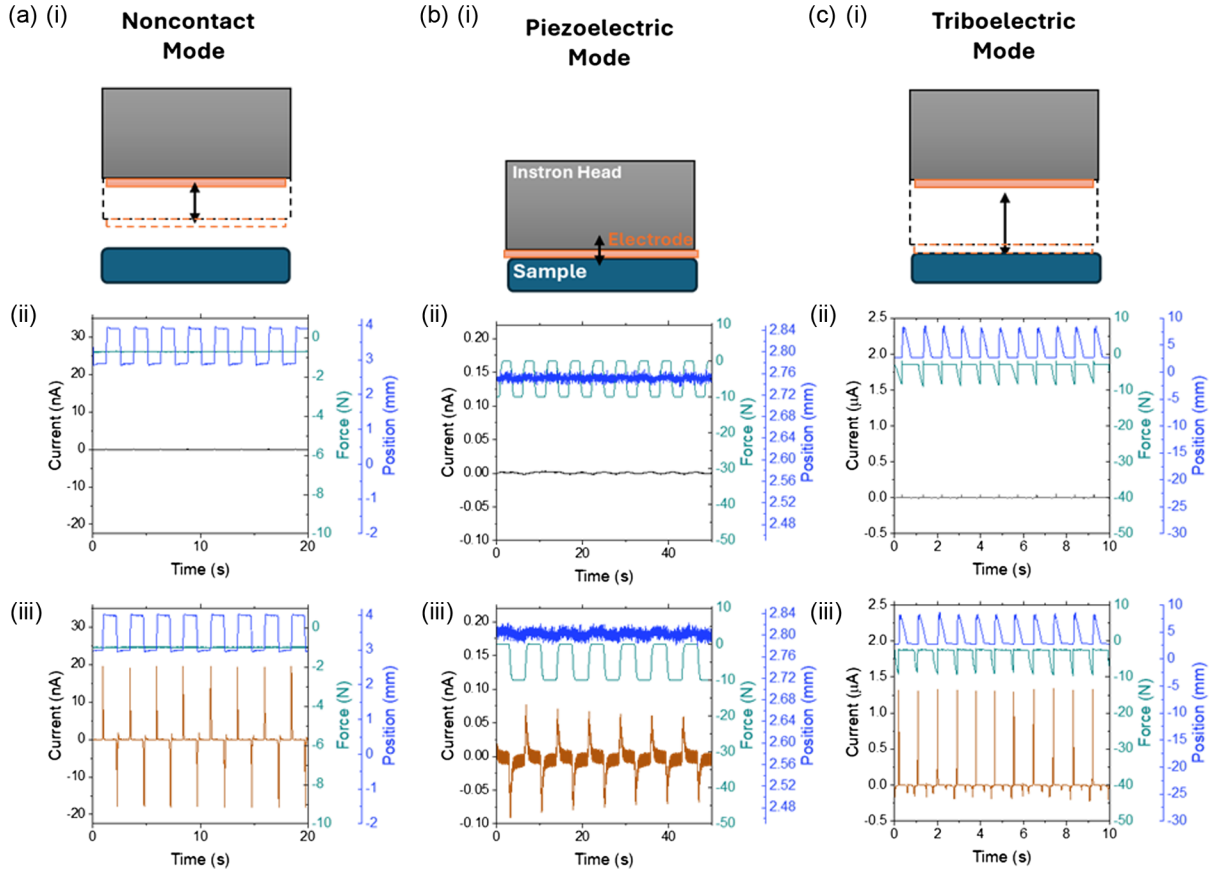


FIG. 2. Measurement of electromechanical conversion in (a) noncontact mode; (b) piezoelectric mode; and (c) triboelectric mode. (i) Schematic of testing mode; (ii) pristine PTFE; and (iii) $1 \times 10^{16} \text{ at.cm}^{-2} \text{ Cu}^+$ implanted PTFE.

near a metal plate, and triboelectric contact-separation mode), please see End Matter for full experimental details [42]. To gain relevant results, from triboelectric testing Cu^+ was chosen as it is known to have extremely limited passive diffusion through PTFE [40].

Cu^+ was implanted into PTFE to a fluence of $1 \times 10^{16} \text{ at.cm}^{-2}$ with an acceleration potential of 20 keV [Fig. 1(a)] [43,44]. The phenomena during ion implantation are shown in Fig. 1(a). Monte Carlo simulations show that for the fluence of $1 \times 10^{16} \text{ at.cm}^{-2}$ the maximum Cu^+ implantation depth occurs at 240 Å, with an atomic concentration of 10^{-21} (corresponding to 1 Cu^+ for every ~ 330 C atoms). This results in a discoloration of the clear PTFE, creating a dull brown (copper) coloration across the $13 \text{ mm} \times 13 \text{ mm}$ implantation area [Fig. 1(c)]. This discoloration may arise from either the copper itself or mild graphitization of the PTFE. The simulations show that within 40 Å of the surface, the Cu^+ atomic concentration drops to 10^{-4} [Fig. 1(b)]. This surface atomic concentration correlates to approximately 1 Cu^+ atoms for every 3×10^5 carbon atoms.

Simulations predict the formation of a space charge layer [Fig. 1(b)]. The charge imbalance emerges from the negatively charged fluorine rich area up to a depth of

174 Å and the positively charged Cu rich and fluorine deficient layer in a depth between 180 to 500 Å. Density functional theory (DFT) confirms the enhanced polarization between defluorinated and pristine PTFE chains, magnified by the presence of Cu [45].

Electromechanical response from ion implanted polymers: To probe the presence of charge within the polymer film post Cu^+ implantation, noncontact oscillation [Fig. 2(a)(i)] of both the PTFE [Fig. 2(a)(ii)] and Cu-PTFE [Fig. 2(a)(iii)] films were performed relative to an ITO electrode. Here, the polymer films were oscillated from between 0.1 and 1.1 mm away from the ITO plate with the short circuit current being recorded. The pristine PTFE shows a negligible 0.2 nA peak-to-peak short circuit current due to the displacement relative to the ITO electrode displacement (Fig. S1, [46]). In contrast, the Cu-PTFE film exhibits a stunning 185-fold increase in the noncontact current, achieving a peak-to-peak current of 37 nA.

This result aligns with the trend observed by Sutka *et al.* [51], where poled ferroelectric poly(vinylidene-difluoride) (PVDF) were found to generate voltage in non-contact mode. These voltages arise due to electrostatic induction from a moving electric field, where the moving electric field corresponds to the permanent dipole within

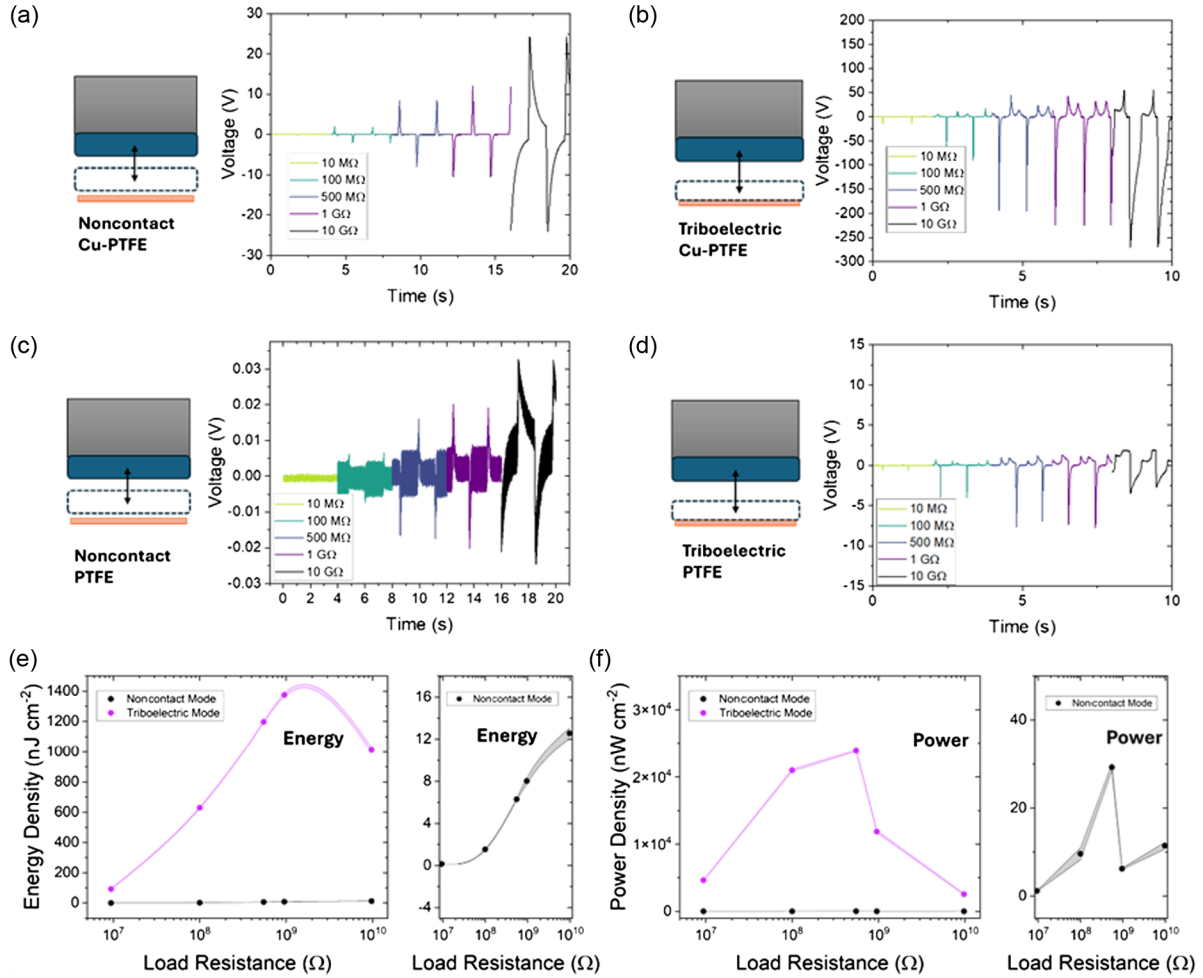


FIG. 3. Voltage outputs under load resistances ranging from 10 MΩ to 10 GΩ for (a) noncontact mode for 1×10^{16} at.cm⁻² Cu⁺-PTFE; (b) triboelectric mode 1×10^{16} at.cm⁻² Cu⁺-PTFE; (c) noncontact mode for pristine PTFE; (d) triboelectric mode for pristine PTFE; (e) energy density; and (f) power density for noncontact and triboelectric mode 1×10^{16} at.cm⁻² Cu⁺-PTFE.

poled PVDF. With Cu-PTFE, the space charge region localized between 100 and 500 Å beneath the surface of the PTFE potentially creates the electric field to cause the measured electrostatic induction. The strength of the electric field generated by the space charge was demonstrated by x-ray photoelectron spectroscopy (Supplemental Material, Fig. S2 [46]), with all peaks shifted to higher binding energies by more than 150 eV (C 1s, F 1s, Cu 2p) due to the presence of the positive Cu⁺ ions hindering the ejection of electrons. COMSOL modeling enabled an estimate of the surface charge density due to the presence of Cu⁺ ions of 1 μC/cm², corresponding to an ion implantation efficiency of ~0.06%.

Piezoelectric-mode testing [Fig. 2(b)(i)], refers to the use of a preload force on the sample, to prevent any contact-separation events occurring [42,52]. When a ΔF of 10 N was applied to both the PTFE [Fig. 2(b)(ii)] and Cu-PTFE samples [Fig. 2(b)(iii)] minimal displacement was observed, indicating no contact-separation events were occurring. For the pristine film, 4 pA of short-circuit

current was measured [Fig. 2(b)(ii)] which is considered negligible. In contrast, the Cu-PTFE demonstrated a considerable pseudopiezoelectric effect with a 40-fold increase in the peak-to-peak short-circuit current value to 165 pA [Fig. 2(b)(iii)]. Given the lack of electrode displacement observed, this pseudopiezoelectric effect is hypothesized to arise from a space charge region between 100 and 500 Å into the PTFE active as a positive region, with the neutrally charged bulk acting as a relatively negative region. Thus, compressing the Cu-PTFE moves the center of charge of the Cu-PTFE creating induction analogous to piezoelectric compression testing. These data yield an *effective* d_{33} coefficient of 3.75 ± 0.81 pC N⁻¹. While this value of pseudopiezoelectric effect is also smaller than reported for other piezoelectric materials [8,53,54], or piezoelectric-like material assemblies [5,55–60] it is higher than those measured during compression of highly charged ionic liquids or solid-polymer electrolytes [61]. The presence of this piezoelectric effect in Cu-PTFE suggests the ability to fabricate hybrid piezoelectric-TENGs (P-TENG)—which

have been often reported to demonstrate exceptional triboelectric performances, far outstripping standard TENG materials [41,51,62–65].

Finally, given the clear demonstration of (1) space charge within the Cu-PTFE via noncontact mode testing; and (2) a permanent dipole within Cu-PTFE giving rise to a pseudopiezoelectric effect from piezoelectric-mode testing, contact-separation “triboelectric” testing was performed to evaluate the observed triboelectrification [Fig. 2(c)(i)].

In triboelectric testing mode, $\Delta 5$ N of force is applied to the PTFE [Fig. 2(c)(ii)] and Cu-PTFE [Fig. 2(c)(iii)] samples by an ITO electrode, before the electrode is separated a distance of 5 mm at a speed of ~ 100 mm s⁻¹. The pristine PTFE film generated a peak-to-peak short-circuit current of 50 nA. However, the Cu-PTFE film produced over 1500 nA of current, corresponding to a 30-fold improvement in electromechanical harvesting. The asymmetric electric signals observed from triboelectric mode testing [Figs. 2(c)(ii) and 2(c)(iii)] occur due to the variations in the speed of the electrode motion during contact and separation steps, as indicated in the experimental section. This enhancement arises as the space charge layer creates an inbuilt electric field within the polymer, leading to more measured electrostatic induction and also more surface charge directly generated from contact electrification (see Supplemental Material, Note S7 [46]).

This comparative improvement was also observed when the voltage curves in noncontact mode [Cu-PTFE, and Figs. 3(a) and 3(c)] and triboelectric mode testing [Cu-PTFE and PTFE, Figs. 3(b) and 3(d)] with a peak-to-peak voltage of noncontact tested Cu-PTFE of 50 V at 10 G Ω increased to 310 V at 10 G Ω in triboelectric mode testing. However, the noncontact tested Cu-PTFE voltage was more than double that of the triboelectric pristine PTFE voltage of 11 V. The resultant energy and power density of the Cu-PTFE film [Figs. 3(e) and 3(f)] in noncontact mode testing and triboelectric testing, respectively, were calculated as 12 nJ cm⁻² and 30 nW cm⁻² (noncontact) and 1.4 μ J cm⁻² and 24 μ W cm⁻² (triboelectric mode) able to power small scale IoT devices [7]. The change in electrical waveform observed in Figs. 3(b) and 3(d) arises due to mechanical vibrations during high speed motion [41], and is not important for understanding the observed effect.

Space charge and electromechanical mechanisms: Here, we demonstrate that this space charge is significant enough to induce a piezoelectriclike dipole within a PTFE film, and thus achieve improved TENG performance through hybrid P-TENG principles (Fig. 4). This space charge arises from the addition of charged species into a material, as opposed to electrets which typically are polarized voids produced during production. While space charge typically has a shorter lifetime compared to electrets, they are rarely studied in dielectric materials, and indeed, the Cu-PTFE sample shows analogous

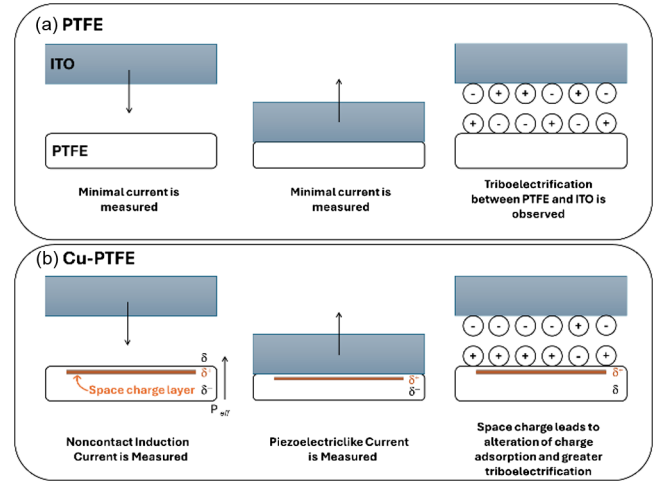


FIG. 4. Phenomenon occurring during triboelectric mode testing of (a) PTFE and (b) Cu-PTFE. In the Cu-PTFE case, electromechanical conversion occurs during all stages of triboelectric testing, however, the magnitude of noncontact induction and piezoelectriclike response is significantly smaller than the space charge induced coupling to triboelectric charge separation.

electromechanical performance 1.5 yrs after production (Supplemental Material, Fig. S8 [46]). The consideration of these ion implanted polymers as P-TENGs explains why some polymers do not see an improved triboelectrification after ion implantation, where the direction of the piezoelectriclike dipole is in opposition to the triboelectric charge of the polymer itself. This occurs, for example, during ion implantation of helium into PTFE (see Supplemental Material [46]). In pristine PTFE, minimal electromechanical response is observed during approach and compression stages of triboelectric testing, due to the lack of space charge in the structure, and triboelectrification occurs due to typical charge transfer across the interface [Fig. 4(a)]. In contrast, for Cu-PTFE the approach and compression phases of triboelectric testing do produce electromechanical output, however, the primary enhancement in triboelectric performance arises from the piezoelectric field-triboelectric coupling phenomenon driving enhanced charge separation [Fig. 4(b)]. This Letter provides a tool to induce an inbuilt electric field into a dielectric polymer, raising the possibility to improve the electromechanical performance of any contact-separation triboelectric device.

Conclusions—Ion implantation of polymers is a relatively unexplored tool to produce electromechanical conversion materials. The implantation of 1×10^{16} at.cm⁻² Cu⁺ resulted in a material with embedded space charge, able to induce current flow in a nearby moving electrode, and also demonstrating a weak piezoelectriclike effect. The space charge and subsequent electric field-triboelectric interfacial coupling led to an enhancement in the triboelectrification of Cu-PTFE with ITO of 30 $\times$. These first investigations on noncontact and piezoelectric

electromechanical conversion from ion implanted polymer films enable a clear assessment of the enhancement mechanisms for ion implanted polymer-based TENGs, with guiding principles based on hybrid P-TENG systems (that is, using additive dipole directions rather than opposing), being able to be adopted broadly for study in the future.

Acknowledgments—P. C. S. would like to acknowledge support from RMIT University via the RMIT Vice-Chancellor's Fellowship Scheme (2023). A. S., H. F., and P. C. S. would like to acknowledge support from Catalyst: seeding funding provided by the New Zealand MBIE and administrated by the Royal Society Te Aparangi (CSG-GNS2303). J. D. B. is the recipient of an Australian Research Council Future Fellowship (FT220100319) funded by the Australian Government. The authors acknowledge the facilities, and the scientific and technical assistance of the RMIT University's Microscopy & Microanalysis Facility (RMMF), a linked laboratory of the Microscopy Australia, enabled by NCRIS, as well as the Materials Characterisation and Fabrication Platform (MCFP) at the University of Melbourne. H. F. acknowledges funding from the New Zealand Ministry of Business Innovation and Employment Low Carbon Future programme (Strategic Science Investment Fund, Grant No. C05X1702). The authors are grateful for access to and technical assistance associated with the use of the equipment and facilities in the RMIT School of Science and RMMF, particularly Dr. Billy Murdoch. The authors thank Chi Nghiep Le for their assistance with contact angle measurements. A. Š acknowledges funding by the Central Finance and Contracting Agency (Latvia) under Contract No. 1.1.1.5/2/24/A/007, ERC Project TriboCharge: Controlling and exploiting triboelectric effect in polymers for mechanical-to-electrical-chemical conversion.

Data availability—The data that support the findings of this article are openly available [66].

- [1] R. G. Kepler and R. Anderson, Ferroelectric polymers, *Adv. Phys.* **41**, 1 (1992).
- [2] N. A. Shepelin, A. M. Glushenkov, V. C. Lussini, P. J. Fox, G. W. Dicoski, J. G. Shapter, and A. V. Ellis, New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting, *Energy Environ. Sci.* **12**, 1143 (2019).
- [3] M. Marvan and A. Havránek, in *Relationships of Polymeric Structure and Properties*, edited by I. Chudáček, Progress in Colloid & Polymer Science Vol. 78 (Steinkopff, Darmstadt, 1988), pp. 33.
- [4] S. Huang, L. Qi, W. Huang, L. Shu, S. Zhou, and X. Jiang, Flexoelectricity in dielectrics: Materials, structures and characterizations, *J. Adv. Dielectr.* **08**, 1830002 (2018).

- [5] Y. Zhang, C. R. Bowen, S. K. Ghosh, D. Mandal, H. Khanbareh, M. Arafa, and C. Wan, Ferroelectret materials and devices for energy harvesting applications, *Nano Energy* **57**, 118 (2019).
- [6] F.-R. Fan, Z.-Q. Tian, and Z. L. Wang, Flexible triboelectric generator, *Nano Energy* **1**, 328 (2012).
- [7] A. Šutka *et al.*, Engineering polymer interfaces: A review toward controlling triboelectric surface charge, *Adv. Mater. Interfaces* **10**, 2300323 (2023).
- [8] P. C. Sherrell, A. Sutka, M. Timusk, and A. Sutka, Alternatives to fluoropolymers for motion-based energy harvesting: Perspectives on piezoelectricity, triboelectricity, ferroelectrets, and flexoelectricity, *Small* **20**, 2311570 (2024).
- [9] P. C. Sherrell, A. Sutka, N. A. Shepelin, L. Lapčinskis, O. Verners, L. Germane, M. Timusk, R. A. Fenati, K. Malnieks, and A. V. Ellis, Probing contact electrification: A cohesively sticky problem, *ACS Appl. Mater. Interfaces* **13**, 44935 (2021).
- [10] S. Li, J. Nie, Y. Shi, X. Tao, F. Wang, J. Tian, S. Lin, X. Chen, and Z. L. Wang, Effects of interfacial acid–base on the performance of contact–separation mode triboelectric nanogenerator, *Adv. Mater.* **32**, 2001307 (2020).
- [11] Y. Liu, G. Liu, T. Bu, and C. Zhang, Contributions of different functional groups to contact electrification of polymers, *Mater. Today Energy* **20**, 100686 (2021).
- [12] A. Šutka *et al.*, The role of intermolecular forces in contact electrification on polymer surfaces and triboelectric nanogenerators, *Energy Environ. Sci.* **12**, 2417 (2019).
- [13] D. W. Kim, J. H. Lee, J. K. Kim, and U. Jeong, Material aspects of triboelectric energy generation and sensors, *NPG Asia Mater.* **12**, 6 (2020).
- [14] O. Verners, L. Lapčinskis, L. Germane, A. Kasikov, M. Timusk, K. Pudzs, A. V. Ellis, P. C. Sherrell, and A. Šutka, Smooth polymers charge negatively: Controlling contact electrification polarity in polymers, *Nano Energy* **104**, 107914 (2022).
- [15] B. N. J. Persson, On the role of flexoelectricity in triboelectricity for randomly rough surfaces, *Europhys. Lett.* **129**, 10006 (2020).
- [16] L. Lapčinskis *et al.*, Triboelectrification of nanocomposites using identical polymer matrices with different concentrations of nanoparticle fillers, *J. Mater. Chem. A* **9**, 8984 (2021).
- [17] J. Zhang, Y. He, C. Boyer, K. Kalantar-Zadeh, S. Peng, D. Chu, and C. H. Wang, Recent developments of hybrid piezo–triboelectric nanogenerators for flexible sensors and energy harvesters, *Nanoscale Adv.* **3**, 5465 (2021).
- [18] C. Xu *et al.*, On the electron-transfer mechanism in the contact-electrification effect, *Adv. Mater.* **30**, 1706790 (2018).
- [19] Z. L. Wang and A. C. Wang, On the origin of contact-electrification, *Mater. Today* **30**, 34 (2019).
- [20] O. Verners, L. Lapčinskis, P. C. Sherrell, and A. Šutka, Contact electrification at dielectric polymer interfaces: On bond scission, material transfer, and electron transfer, *Adv. Mater. Interfaces* **10**, 2300562 (2023).
- [21] L. S. McCarty and G. M. Whitesides, Electrostatic charging due to separation of ions at interfaces: Contact electrification of ionic electrets, *Angew. Chem., Int. Ed.* **47**, 2188 (2008).
- [22] Y. Fang, C. K. Ao, Y. Jiang, Y. Sun, L. Chen, and S. Soh, Static charge is an ionic molecular fragment, *Nat. Commun.* **15**, 1986 (2024).

- [23] S. Im, E. Frey, D. J. Lacks, J. Genzer, and M. D. Dickey, Enhanced triboelectric charge stability by air-stable radicals, *Adv. Sci.* **10**, 2304459 (2023).
- [24] A. Šutka, J. Ruža, M. Järvekülg, A. Linarts, K. Mālnieks, V. Jurkāns, I. Gorņevs, J. Blūms, K. Rubenis, and M. Knite, Triboelectric nanogenerator based on immersion precipitation derived highly porous ethyl cellulose, *J. Electrostat.* **92**, 1 (2018).
- [25] L. Lapčinskis, A. Šutka, M. Kinka, F.-K. Shieh, L. Ģermane, S. Balčiūnas, A. Linarts, and R. Grigalaitis, Controlling the magnitude and polarity of surface charges in PEBA polymers by adding UIO-66 MOFs, *Mater. Sci. Eng. B* **5**, 4242 (2024).
- [26] L. Lapčinskis, K. Mālnieks, J. Blūms, M. Knite, S. Oras, T. Käämbre, S. Vlassov, M. Antsov, M. Timusk, and A. Šutka, The adhesion-enhanced contact electrification and efficiency of triboelectric nanogenerators, *Macromol. Mater. Eng.* **305**, 1900638 (2020).
- [27] A. Šutka *et al.*, The role of intermolecular forces in contact electrification on polymer surfaces and triboelectric nanogenerators, *Energy Environ. Sci.* **12**, 2417 (2019).
- [28] S. Li, Y. Fan, H. Chen, J. Nie, Y. Liang, X. Tao, J. Zhang, X. Chen, E. Fu, and Z. L. Wang, Manipulating the triboelectric surface charge density of polymers by low-energy helium ion irradiation/implantation, *Energy Environ. Sci.* **13**, 896 (2020).
- [29] Y. Fan *et al.*, Negative triboelectric polymers with ultrahigh charge density induced by ion implantation, *Nano Energy* **90**, 106574 (2021).
- [30] J. Leveneur, Y. Zhang, H. Fiedler, S. Prabakar, E. C. Le Ru, and J. Kennedy, Surface modification of collagen using low-energy noble gas ion implantation, *Surf. Coat. Technol.* **468**, 129768 (2023).
- [31] N. Yuan and J. Li, SiO₂ film electret with high surface potential stability, *Appl. Surf. Sci.* **252**, 455 (2005).
- [32] V. S. Remizovich and A. I. Rudenko, The effect of space charge electric field on ion implantation in dielectrics, *J. Electrostat.* **6**, 259 (1979).
- [33] M. Olszowy, Electret state in the polyethylene terephthalate films implanted by oxygen and bismuth ions, *Phys. Status Solidi (a)* **113**, 609 (1989).
- [34] X. Sun, Y. Liu, N. Luo, Y. Liu, Y. Feng, S. Chen, and D. Wang, Controlling the triboelectric properties and tribological behavior of polyimide materials via plasma treatment, *Nano Energy* **102**, 107691 (2022).
- [35] Y. Pan, M. Li, T. Huang, X. Hao, M. Lu, S. Chen, K. Zhang, and A. Qin, Dynamic co-irradiation techniques: A new method improving the electrical output of TENG by optimizing the charge capture capacity of polypropylene membrane, *Appl. Mater. Today* **35**, 101979 (2023).
- [36] H.-w. Lo and Y.-C. Tai, Parylene-based electret power generators, *J. Micromech. Microeng.* **18**, 104006 (2008).
- [37] D. W. Vance, Surface charging of insulators by ion irradiation, *J. Appl. Phys.* **42**, 5430 (1971).
- [38] M. Bertin, H. Fiedler, E. M. Leitao, S. Bickerton, and C. J. R. Verbeek, Characterization of modified low-density polyethylene by cold atmospheric pressure plasma jet treatment in the melt state, *J. Appl. Polym. Sci.* **142**, e56388 (2025).
- [39] M. A. Booth, J. Leveneur, A. S. Costa, J. Kennedy, and J. Travas-Sejdic, Tailoring the conductivity of polypyrrole films using low-energy platinum ion implantation, *J. Phys. Chem. C* **116**, 8236 (2012).
- [40] E. W. Lees, B. A. Mowbray, F. G. Parlange, and C. P. Berlinguette, Gas diffusion electrodes and membranes for CO₂ reduction electrolyzers, *Nat. Rev. Mater.* **7**, 55 (2022).
- [41] A. Šutka, K. Mālnieks, A. Linarts, P. C. Sherrell, X. Yu, and E. Bilotti, High-performance hybrid triboelectric generators based on an inversely polarized ultrahigh β -phase PVDF, *ACS Appl. Energy Mater.* **6**, 9300 (2023).
- [42] A. Šutka, P. C. Sherrell, N. A. Shepelin, L. Lapčinskis, K. Mālnieks, and A. V. Ellis, Measuring piezoelectric output—fact or friction?, *Adv. Mater.* **32**, 2002979 (2020).
- [43] H. Fiedler, P. Gupta, J. Kennedy, and A. Markwitz, 28Si⁺ ion beams from Penning ion source based implanter systems for near-surface isotopic purification of silicon, *Rev. Sci. Instrum.* **89**, 123305 (2018).
- [44] H. Fiedler, N. Malone, D. R. G. Mitchell, M. Nancarrow, V. Jovic, G. I. N. Waterhouse, J. Kennedy, and P. Gupta, Room temperature ion beam synthesis of ultra-fine molybdenum carbide nanoparticles: Toward a scalable fabrication route for earth-abundant electrodes, *Small* **20**, 2304118 (2024).
- [45] A. Ciniero, G. Fatti, M. Marsili, D. Dini, and M. C. Righi, Smart flexible fabrics for energy storage, self-heating, energy harvesting, and self-powered motion sensing at low temperatures, *Nano Energy* **112**, 108502 (2023).
- [46] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.136.056203> for (i) electrical waveforms; (ii) XPS; (iii) discussion on COMSOL simulations; implantation of He⁺; (iv) energy diagram; (v) kelvin probe; (vi) long term stability testing; (vii) water contact angle; (viii) discussion of electromechanical enhancement via space charge; and included Refs. [47–50].
- [47] J. D'Errico, Movingslope, MATLAB central file exchange, 2024, <https://www.mathworks.com/matlabcentral/fileexchange/16997-movingslope>, Retrieved January 15, 2025.
- [48] J. M. Colwell, E. Wentrup-Byrne, J. M. Bell, and L. S. Wielunski, Advanced electrospun fiber-based triboelectric nanogenerators: From diversified designs to customized applications, *Surf. Coat. Technol.* **168**, 216 (2003).
- [49] I. Kondyurina, I. Shardakov, G. Nechitailo, V. Terpugov, and A. Kondyurin, From Fiber to Power: Recent Advances Toward Electrospun-Based Nanogenerators, *Appl. Surf. Sci.* **314**, 670 (2014).
- [50] V. N. Popok, Defects drive the tribocharging strength of PTFE: An *ab-initio* study, *Radiation effects in polymeric materials*, edited by V. Kumar, B. Chaudhary, V. Sharma, and K. Verma, Springer Series on Polymer and Composite Materials (Springer, Cham, 2019).
- [51] A. Šutka, K. Mālnieks, A. Linarts, M. Timusk, V. Jurkāns, I. Gorņevs, J. Blūms, A. Bērziņa, U. Joost, and M. Knite, Inversely polarised ferroelectric polymer contact electrodes for triboelectric-like generators from identical materials, *Energy Environ. Sci.* **11**, 1437 (2018).
- [52] R. T. Leon, P. C. Sherrell, A. Šutka, and A. V. Ellis, Decoupling piezoelectric and triboelectric signals from PENGs using the fast fourier transform, *Nano Energy* **110**, 108445 (2023).

- [53] P. C. Sherrell, M. Fronzi, N. A. Shepelin, A. Corletto, D. A. Winkler, M. Ford, J. G. Shapter, and A. V. Ellis, A bright future for engineering piezoelectric 2D crystals, *Chem. Soc. Rev.* **51**, 650 (2022).
- [54] M. Habib, I. Lantgios, and K. Hornbostel, A review of ceramic, polymer and composite piezoelectric materials, *J. Phys. D* **55**, 423002 (2022).
- [55] A. Šutka *et al.*, Recycled polystyrene waste to triboelectric nanogenerators: Volumetric electromechanically responsive laminates from same material contact electrification, *Adv. Ener. Sus. Res.* **5**, 2300259 (2024).
- [56] A. Linarts, P. C. Sherrell, K. Mālnieks, A. V. Ellis, and A. Šutka, Electrospinning Triboelectric Laminates: A Pathway for Scaling Energy Harvesters, *Small* **19**, 2205563 (2023).
- [57] L. A. Zhang, S. Liu, J. Wen, X. Huo, B. Cheng, Z. Wu, L. Wang, Y. Qin, and Z. L. Wang, Collecting the space-distributed Maxwell's displacement current for ultrahigh electrical density of TENG through a 3D fractal structure design, *Energy Environ. Sci.* **16**, 3781 (2023).
- [58] X. Zhang, P. Pondrom, G. M. Sessler, and X. Ma, Ferroelectric nanogenerator with large transverse piezoelectric activity, *Nano Energy* **50**, 52 (2018).
- [59] S. K. Ghosh, T. K. Sinha, B. Mahanty, and D. Mandal, Self-poled efficient flexible “Ferroelectric” nanogenerator: A new class of piezoelectric energy harvester, *Energy Technol.* **3**, 1190 (2015).
- [60] X. Zhang, X. Zhang, G. M. Sessler, and X. Gong, in *Proceedings of the 2013 Annual Report Conference on Electrical Insulation and Dielectric Phenomena* (IEEE, Shenzhen, 2013), p. 579.
- [61] Ž. Simon, B. Dharmasiri, T. Harte, P. C. Sherrell, and L. C. Henderson, From stress to charge: investigating the piezoelectric response of solvate ionic liquid in structural energy storage composites, *Mater. Horizons* **11**, 4321 (2024).
- [62] H. Patnam, B. Dudem, S. A. Graham, and J. S. Yu, High-performance and robust triboelectric nanogenerators based on optimal microstructured poly(vinyl alcohol) and poly(vinylidene fluoride) polymers for self-powered electronic applications, *Energy* **223**, 120031 (2021).
- [63] Y. Pang, Y. Cao, M. Derakhshani, Y. Fang, Z. L. Wang, and C. Cao, Hybrid energy-harvesting systems based on triboelectric nanogenerators, *Matter* **4**, 116 (2021).
- [64] C. Zhao, Q. Zhang, W. Zhang, X. Du, Y. Zhang, S. Gong, K. Ren, Q. Sun, and Z. L. Wang, Hybrid piezo/triboelectric nanogenerator for highly efficient and stable rotation energy harvesting, *Nano Energy* **57**, 440 (2019).
- [65] M. Han, X. Chen, B. Yu, and H. Zhang, Coupling of piezoelectric and triboelectric effects: From theoretical analysis to experimental verification, *Adv. Electron. Mater.* **1**, 1500187 (2015).
- [66] A. Šutka, H. Fiedler, A. Linarts, K. Mālnieks, K. Pudzs, J. Berry, and P. Sherrell, Dataset for: Space charge drives electromechanical conversion via a piezoelectric-like effect in ion implanted polymers, 2025, 10.25439/rmt.30716912.
- [67] A. Mutzke, R. Schneider, W. Eckstein, and R. Dohmen, Max Planck-Institut für Plasmaphysik (2011), <https://hdl.handle.net/11858/00-001M-0000-0026-EAF9-A>.
- [68] H. Fiedler, V. Jovic, D. R. G. Mitchell, J. Leveneur, E. Anquillare, K. E. Smith, and J. Kennedy, Tuning the electromechanical properties and polarization of Aluminium Nitride by ion beam-induced point defects, *Acta Mater.* **203**, 116495 (2021).

End Matter

Methods—

Ion implantation of Cu in PTFE: Ion implantation was performed using a Penning sputter ion source [43,44]. Cu was implanted into 50 μm thick PTFE to a fluence of $1 \times 10^{16} \text{ at.cm}^{-2}$ with an acceleration potential of 20 keV. A raster scanner ensures homogeneous implantation into the substrate of the implanted area with a size of $13 \text{ mm} \times 13 \text{ mm}$. During implantation carbon tape the PTFE surface is contacted to the sample holder stage with conductive tape to minimize charging of the sample. To limit potential heating the current density is limited to $1 \mu\text{A cm}^{-2}$.

Monte Carlo simulation to evaluate the ion-beam-polymer interaction were performed using the program SDTRIM.SP version 5.07 [67]. The simulation used a Krypton-Carbon (KrC) potential with surface binding energies of 3.49, 4.79, and 0.82 eV for Cu, C, and F, respectively. The calculations are based on a substrate density of 2.2 g cm^{-3} . The changes of the implanted area are taken into dynamic consideration to analyze the change of the implanted area such as surface sputtering of the already implanted Cu. The accuracy of the implantation profile has been described by Fiedler *et al.* [68] for ceramic systems, however, analysis of soft polymer samples via

cross-sectional techniques typically deforms the interface limiting precise validation in these materials.

COMSOL Multiphysics (v. 6.3) was used to model the induced charge in the moving ITO electrode due to the presence of charge implanted in the PTFE, allowing an estimate of the ion implantation efficiency (see Supplemental Material [46] for more details).

Electromechanical testing: Electromechanical response in noncontact mode, piezoelectric mode, and contact-separation mode was measured under controlled testing conditions using an Instron E1000 material testing machine.

In *noncontact mode*, ITO electrode plates with an area of 6.25 cm^2 were oscillated in the distance between 0.1 to 1.1 mm.

In *piezoelectric mode*, sample films were compressed and released in a range from 0 to 10 N. The sample film was fixed between ITO electrodes by conductive double adhesive tape to eliminate other parasitic triboelectric signals from friction [42,52].

In *triboelectric mode*, the films were contacted with ITO by 10 N force and separated at a distance of 5 mm with a separation speed of 0.1 ms^{-1} . All triboelectric measurements were carried out at 22°C and a humidity of 45% RH.

For electrical *measurements*, the generated current and voltage signals were recorded by Keithley 6514 electrometer connected to a Picoscope 5444B PC oscilloscope system. The surface charge, Q (nC), was calculated from the measured current peaks using the equation $Q = \int i dt$, where i is the instantaneous current (nA) and dt is the differential of time (s).

Kelvin probe measurements were performed using the scanning Kelvin probe system SKP5050. The surface potential of the sample was scanned by oscillating a 2 mm radius tip over a scan area of approximately 10×10 mm. This area was chosen to cover most of the contact-separated sample. Scanning was done with a step of around 0.5 mm, with 20×20 scan points in total for each sample.