Contact-Electrification between Two Identical Materials: Curvature Effect

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Supporting Information

ABSTRACT: It is known that contact-electrification (or triboelectrification) usually occurs between two different materials, which could be explained by several models for different materials systems (Adv. Mater. 2018, 30, 1706790; Adv. Mater. 2018, 30, 1803968). But contact between two pieces of the chemically same material could also result in electrostatic charges, although the charge density is rather low, which is hard to understand from a physics point of view. In this paper, by preparing a contact-separation mode triboelectric nanogenerator using two pieces of an identical material, the direction of charge transfer during contact-electrification is studied regarding its dependence on curvatures of the sample surfaces. For materials such as polytetrafluoroethylene, fluorinated ethylene propylene, Kapton, polyester, and nylon, the positive curvature surfaces are net negatively charged, while the negative curvature surfaces tend to be net positively charged. Further verification of the above-mentioned trends was obtained under vacuum (∼1 Pa) and higher temperature (≤358 K) conditions. Based on the received data acquired for gentle contacting cases, we propose a curvature-dependent charge transfer model by introducing curvature-induced energy shifts of the surface states. However, this model is subject to be revised if the mutual contact mode turns into a sliding mode or more complicated hard-pressed contact mode, in which a rigorous contact between the two pieces of the same material could result in nanoscale damage/fracture and possible species transfer. Our study provides a primitive step toward understanding the basics of contact-electrification.

KEYWORDS: contact-electrification, triboelectrification, triboelectric nanogenerator, curvature, identical material, surface states

It is well known that a contact-separation interaction between two dissimilar materials enables each material surface to accumulate an equivalent amount of net opposite charges, that is, the occurrence of contact-electrification (CE) (or triboelectrification). Generally speaking, CE between distinct materials is attributed to the work function or contact potential difference1,2 and can be attributed to the surface states model or electron-potential well model.3–7 However, CE can also occur between chemically identical materials that have the same contact potential. For instance, it emerges in some natural phenomena such as volcanic plumes,8 sand storms,9 and dust devils,10 and even in industrial processes involving small particles.11 With regard to CE between homologous materials, there is still no reasonable consensus in interpreting and explaining its mechanism. For example, Henry proposed that charge transfer was due to a temperature difference caused by asymmetric rubbing of two surfaces.12 Lowell and Truscott showed that charge transfer occurred during asymmetric rubbing even though temperature and other physical properties remained exactly the same for the two surfaces.13 They proposed that CE was attributed to nonequilibrium electron distributions and transfer of electrons between localized states in insulators. On the other hand, Baytekin et al. assumed that random “mosaics” of oppositely charged regions on each surface led to CE between identical materials, and these charged mosaics were related to the transfer of charged material patches.14

It is noteworthy that CE is a rather sophisticated and complex process since diverse relative motions are likely to occur between the two contacting materials. To simplify, these relative motions can be defined as sliding (or rubbing) and...
contact-separation. There is no doubt that sliding is liable to cause surface damage to materials, especially polymers. The close relation between the surface properties of polymers and CE results in surface damage significantly affecting the ultimate electrical outcome. Moreover, surface damage causes less material transfer to dominate the CE process, altering the authentic direction of charge transfer. However, provided that contact-separation with a gentle force is applied, surface damage can be avoided to some extent, likely reaching reliable conclusions in analyzing CE. Fortunately, the recently invented triboelectric nanogenerator (TENG) can be used to perform precise, real-time quantitative measurements of surface charges and thus produce power for harvesting broad-range energy sources in the ambient environment.\textsuperscript{15−19} In particular, the TENG has various working modes, including a contact-separation mode, and is capable of fine-tuning the magnitude of exerted forces,\textsuperscript{20−23} which provides an ideal platform for in-depth research on the CE mechanism between identical materials. We have previously studied the CE of two dissimilar materials and proposed related models for different materials systems.\textsuperscript{7,24,25}

In this paper, we designed and prepared a TENG using two pieces of a chemically identical material but with surfaces of different macroscale shapes or curvatures and investigated the direction of charge transfer in real time via the TENG operated on the contact-separation mode. It was found that a convex surface with positive curvature was prone to be negatively charged, while a concave surface with negative curvature was inclined to be positively charged. In addition, an increase of applied pressure/force was likely to lead to a reversal of charge transfer direction between the two pieces. Moreover, further verification on the above-mentioned charge trends between identical materials was conducted under vacuum and high temperatures. Based on the research findings, a surface states model was proposed to explain the CE mechanism between identical materials.

RESULTS AND DISCUSSION

Polytetrafluoroethylene (PTFE) films were utilized as the tribomaterial of the TENG, in which the left-hand PTFE (PTFE-A) was fixed and the right-hand PTFE (PTFE-B) approached and contacted PTFE-A (Figure S1). If the PTFE-A surface has many initial negative charges before the TENG operation, the results show a positive open circuit voltage ($V_{OC}$) and a negative short circuit transfer charge ($Q_{SC}$). Here, the initial negative charges on PTFE-A were introduced by rubbing it with a Cu foil. Since PTFE-B is the reference to evaluate PTFE-A, a negative sign of $Q_{SC}$ indicates more
negative charges on PTFE-A than those on PTFE-B. However, it is noteworthy that since PTFE-A carries a lot of negative charges prior to the measurement, it is unclear if the negative charge transfer from PTFE-B to PTFE-A or vice versa is in accordance with the sign of $Q_{SC}$. Conversely, provided that more initial negative charges were introduced to the PTFE-B surface with the friction of Cu foil, the results revealed a negative $V_{OC}$ and a positive $Q_{SC}$, indicating more positive charges on PTFE-A or more negative charges on PTFE-B. These aforementioned measurements cannot be used to interpret the actual direction of charge transfer in CE, but only reflect the ultimate charge difference of the material surfaces. Discharge is therefore conducted on both the acrylic substrates and tribomaterials of the TENG prior to measurements to avoid the detrimental effect of the initial residual charges on the surfaces. Meanwhile, the operation of the TENG is categorized into two phases, as shown in Figure 1a. The moment when PTFE-B moves to a very close but inaccessible position with regard to PTFE-A is phase 1, in which the generated $V_{OC}$ and $Q_{SC}$ mainly reflect the induction effect of initial residual charges on the surfaces, but no charge transfer occurs since there is no firm contact between the two surfaces. Once the contact occurs between PTFE-B and PTFE-A (phase 2), the generated $V_{OC}$ and $Q_{SC}$ reflect the combined influence of initial residual charges and transferred charges in CE. Figure 1b,c demonstrate that there are more positive charges on PTFE-A than on PTFE-B before contact; that is, PTFE-B is negatively charged with less electricity after discharging. After contact, the positive charges on PTFE-A increase; in other words, the electrons flow from PTFE-A to PTFE-B. Due to the slight differences of each discharge treatment, another condition of Figure 1d–g is likely to occur. Under that condition, PTFE-A is negatively charged with more electrons than PTFE-B. However, the peak shape of either $V_{OC}$ or $Q_{SC}$ after contact becomes irregular; that is, the peak reverses at the maximum value. Figure 1e,g shows the fitted peaks of peaks A and B in Figure 1d,f, suggesting that the shapes of both peaks are attributed to the superposition of two peaks. The direction of one peak is in accordance with that prior to contact, resulting from the induction of initial charges. Another peak is a reverse one, relying on charge transfer in CE. Here, the negative sign of $V_{OC}$ and positive sign of $Q_{SC}$ indicate more positive charges on PTFE-A, which means the electrons transfer from PTFE-A to PTFE-B, similar to that shown in Figure 1b,c. Figure 1h illustrates the working principle of the TENG with few initial negative charges on the surface of

![Figure 2](image-url)

Figure 2. Properties of the PTFE TENG with surfaces of different shapes. (a–d) $V_{OC}$ and $Q_{SC}$ of the TENG with two flat surfaces. (e–h) $V_{OC}$ and $Q_{SC}$ of the TENG with a convex surface (curvature of 0.20 cm\(^{-1}\)) and a flat surface. (i–l) $V_{OC}$ and $Q_{SC}$ of the TENG with a concave surface (curvature of –0.07 cm\(^{-1}\)) and a flat surface. (m–p) $V_{OC}$ and $Q_{SC}$ of the TENG with a convex surface (curvature of 0.20 cm\(^{-1}\)) and a concave surface (curvature of –0.07 cm\(^{-1}\)). The applied force during the contact-separation CE process is 2 ± 0.5 N.

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PTFE-A. When the two PTFE films come into contact, opposite triboelectric charges will be generated on the surfaces. These charges are partly induced by initial residual negative charges on PTFE-A, yielding equivalent positive charges on PTFE-B. Another portion of the negative charges on PTFE-A and equivalent positive charges on PTFE-B are generated because of CE. Overall, PTFE-A is positively charged and PTFE-B is negatively charged. Upon release, the two oppositely charged surfaces start to separate from each other, inducing a potential difference between the two Cu electrodes. This potential difference will drive electrons to flow from the Cu-B electrode to Cu-A electrode. When the separation between the two surfaces reaches a maximum, almost all of the positive charges on the Cu-A electrode will be neutralized. Subsequently, when the PTFE films approach each other again, the reversed potential difference between the two electrodes will be built up, which leads to a back flow of all of the transferred electrons from the Cu-A electrode to the Cu-B electrode. Figure 1 also reveals that, even though complete elimination of the initial charges is impossible, the charge reduction can also assist in the assessment of actual direction of charge transfer for CE at different times using the same set of samples. Therefore, we confirmed the consistency in surface contact position at each time and reassessed sample 5 in Figure 2b,d ten times (Figure S2). It is shown that the direction of charge transfer is the same even though the transferred amount of charges differs each time. This is due to the so-called “memory effect”. Therefore, it is believed that there is a certain regularity of direction of charge transfer for CE between identical materials, which may be relevant to the surface status. Figure 2e–h is the \( V_{OC} \) and \( Q_{SC} \) of the TENG with a convex surface of positive curvature and a flat surface. It is shown that the convex PTFE film is negatively charged in most cases, which indicates that it gains electrons more readily than the flat film. Figure 2i–l is the \( V_{OC} \) and \( Q_{SC} \) of the TENG with a concave surface of negative curvature and a flat surface. The concave PTFE films are positively charged in most cases, which means they are less likely to gain electrons than flat films. Figure 2m–p is the \( V_{OC} \) and \( Q_{SC} \) of the TENG with a convex surface and a concave surface. To improve the quality of contact-separation operation and avoid unintentional contact in other modes, such as sliding, the curvature of the convex PTFE film is set as 0.20 cm\(^{-1}\) and that of the concave PTFE film is set as \(-0.07\) cm\(^{-1}\). In addition, the \( V_{OC} \) and \( Q_{SC} \) results of the TENG that had the PTFE films with opposite but the same magnitude of curvatures as 0.20 cm\(^{-1}\) and \(-0.20\) cm\(^{-1}\) were also measured (Figure S3). These convex–concave pairings reveal that the convex PTFE film is more prone to acquire electrons than the concave film. Figure 2e–p indicate that a surface of larger curvature gains negative charges more easily, which is consistent with the \( V_{OC} \) and \( Q_{SC} \) results of the contact-separation mode fluorinated ethylene propylene (FEP) TENG, Kapton TENG, polyester TENG, and nylon TENG.
with convex−flat, concave−flat, and convex−concave surfaces (Figures S4−7).

Figure 3a,b are the typical $V_{OC}$ and $Q_{SC}$ of the PTFE TENG with surfaces of different positive curvatures. In addition, the measurement is conducted on five sets of samples five times each, in which the surface curvatures of the TENG are 0.26 and 0.07 cm$^{-1}$ (Figure S8). These results coincide with those in Figure 2, suggesting that larger curvature leads to a more negatively charged surface. It is intriguing that similar findings were shown in studies on CE of particles; that is, a particle with a smaller radius was more likely to be negatively charged when contacted with another chemically identical larger particle.28−30

Illustrated in Figure 3c,d is the effect of applied forces on the performance of the TENG with a surface curvature of 0.10 and 0.26 cm$^{-1}$. Because it is difficult to precisely measure the $Q_{SC}$ when a miniscule contact force is applied, only the variation of $V_{OC}$ with increasing force is investigated to estimate the direction of charge transfer. Figure 3c shares the same findings as previous results, demonstrating that the increased applied force results in a gradual increase of $V_{OC}$.31,32 This is mainly attributed to the fact that the increased force enlarges the contact area between the two surfaces of the TENG. However, it is interesting that the increased applied force also results in another situation as shown in Figure 3d, which has not been previously reported in the TENG studies. The increase of applied force to 3 N inversely leads to the reduction of $V_{OC}$, and the further increase of the force to 10 N results in a complete reversal of $V_{OC}$ (i.e., the direction of charge transfer reverses). What is more, the CE of the TENG with surface curvatures of 0.26 and 0.07 cm$^{-1}$ creates a more complicated case; that is, two separated reversals in $V_{OC}$ occur with the increase of applied force (Figure 3e). The $V_{OC}$ variation along with a gradual increase of the applied forces in CE of the TENG with two flat surfaces is measured to compare the results (Figure 3f). It indicates that $V_{OC}$ gradually increases with the increase of the applied forces in most cases. The above findings suggest that the CE of two convex surfaces is prone to reverse the direction of charge transfer as applied force increases, while flat surfaces undergoing CE of increasing force do not tend to reverse the direction of charge transfer. Here, as for the mutual contact between two convex surfaces, the increase of applied forces is more likely to change the mode of relative motions rather than merely an increase in contact area, such as the transformation from contact-separation mode to sliding mode. The continuous increase of applied forces may generate some surface damage and even lead to material transfer. All of the above reasons probably account for the results of Figure 3e,f. To summarize the results from Figures 2 and 3, it is believed that some regularities exist: the initial driving force for CE is induced by curvature differences under the contact-separation mode (smaller applied forces), in which

Figure 4. Temperature effects on the properties of Kapton TENG. (a) Setup of the vacuum chamber and high-temperature test platform. (b, c) $V_{OC}$ and $Q_{SC}$ of the TENG with a convex surface (curvature of 0.20 cm$^{-1}$) and a flat surface at different temperatures. (d, e) $V_{OC}$ and $Q_{SC}$ of the TENG with two flat surfaces at different temperatures. (f) Maximum $V_{OC}$ and $Q_{SC}$ of the TENG with two flat surfaces at different temperatures. (g−i) SEM images of the Kapton surface before and after 358 and 388 K measurement, respectively. The scale bar is 10 μm.
a surface of larger curvature obtains negative charges more easily. Increasing the applied force is likely to result in irregular surface deformations and surface damage or even material transfer due to relative sliding. All these complicate the predictability of the direction of charge transfer.

Among the influential factors of CE, temperature is a crucial element aside from applied force.\textsuperscript{33,34} Since the surfaces of PTFE used in TENGs are likely to be changed/damaged at a temperature of 353 K or above,\textsuperscript{35} Kapton with better heat stability is adopted as the tribomaterial to prepare the TENG in this study. Moreover, since the increase of temperature leads to dramatic changes in humidity in the environment, a vacuum and high-temperature testing platform is designed and shown in Figure 4a. This platform can provide relatively low vacuum (∼1 Pa) to exclude humidity effects in high-temperature measurements. Figure 4b,c are the results of $V_{\text{OC}}$ and $Q_{\text{SC}}$ obtained from the TENG with a convex surface and a flat surface under a temperature from 298 to 358 K. The charge transfer under vacuum and high temperature is in accordance with the results in Figures 2 and 3, which is that convex Kapton films of larger curvature are prone to be negatively charged. Additionally, $V_{\text{OC}}$ and $Q_{\text{SC}}$ are 0.6 V and 0.25 nC under vacuum and 298 K, three times larger than those under atmospheric pressure and at the same temperature (Figure S5).

The relative humidity under vacuum in this experiment is far lower than 1%, indicating the reduction of water in the air benefits the increase of charge transfer in CE. This notion is in contrast to previous studies on ions generated from the water in humid air being the primary medium of charge transfer in CE.\textsuperscript{36} Therefore, it is possible to exclude the ion transfer mechanism of water as the basis for charge transfer in CE between identical materials. Additionally, the increase of temperature results in the decrease of electrification, as shown in Figure 4b,c. Since high temperature may change the surface nature of polymer films and decrease the electrification in effect, we retested the TENG three times with repetitively increasing and decreasing the temperature. It shows that the quantity of electrification can return to the original level following surface changes at high temperature, suggesting that the decrease in electrification is not attributed to film surface damage but lies in the deleterious effect of high temperatures. This is consistent with previous results that the CE between two different materials always decreased with a temperature increase, which could be partly attributed to the thermionic electron emission.\textsuperscript{7,23,33,37} Figure 4d,e shows the $V_{\text{OC}}$ and $Q_{\text{SC}}$ at surfaces in Figure 5a. When the two convex and concave surfaces contact each other (Figure 5c), electrons show charge transfer before contact, in contact, and after contact between the identical materials A and B with different surface curvatures (depicted by orange shapes) explained by the surface states models. LUMO, lowest unoccupied molecular orbital; $E_n$, neutral level of surface states; HOMO, highest occupied molecular orbital.

Figure 5. Mechanism of CE between identical materials. (a) Surface states model of the identical materials A and B with ideal flat surfaces. (b–d) Charge transfer before contact, in contact, and after contact between the identical materials A and B with different surface curvatures (depicted by orange shapes) explained by the surface states models. LUMO, lowest unoccupied molecular orbital; E_n, neutral level of surface states; HOMO, highest occupied molecular orbital.

Despite the increase of temperature decreasing the electrification, temperature is not a determining factor in the direction of charge transfer in CE between identical materials, echoing the findings of Lowel et al.\textsuperscript{13}

Based on the above experimental results, a surface states model is proposed to explain the mechanism of CE between identical materials in Figure 5. When two ideal flat surfaces composed of chemically identical materials A and B contact each other, no electron transfer occurs in that the neutral levels of surface states ($E_n$) are equivalent and horizontally matched (Figure 5a). However, CE emerges even when two flat surfaces mutually contact each other in the present experiment. This is probably due to the fact that flat surfaces are less likely to be absolutely smooth at the nano-microscale, and curvature differences determine the direction of charge transfer in terms of microstructures. Figure 5b–d show charge transfer before contact, in contact, and after contact between two identical materials A and B with different surface curvatures, within which there is a convex surface in A (i.e., larger curvature) and a concave surface in B (i.e., smaller curvature). The curvature difference may result in different surface energy, which may lead to a shift of surface states $E_n$. As shown in Figure 5b, the $E_n$ shifts to a lower level for the convex surface, whereas it shifts to a higher level for the concave surface than that of flat surfaces in Figure 5a. When the two convex and concave surfaces contact each other (Figure 5c), electrons located at high-energy states in B will transfer to the low-energy states of the surface of A. To some extent, this is a similar concept to that of charge density in conductors being
greater at regions of large curvature and lower in small curvature regions. In other words, the contact position on surfaces of large curvature can accommodate more electrons than that on small curvature surfaces when in contact, resulting in the flow of electrons from the latter to the former. Figure 5d shows that the separation between the two identical materials results in negative charges on A and an equivalent amount of positive charges on B. Even though the research findings are obtained on the macrosurfaces, it may well be available on microsurfaces on considering the relationship between CE and micro/nanostructures of surfaces, which certainly needs to be further validated using other techniques such as atomic force microscopy (AFM). It is worth noting that the prerequisite for the above mechanism is the utilization of a contact-separation mode with a gently applied force that is not expected to cause surface damage. In addition, the micro/nanosurface roughness may change and the local stain/stress generated in the films may vary, according to the curvature difference. Both of these are likely to influence the direction of charge transfer, which still needs further study.

CONCLUSION

In summary, we introduce the same material made TENG to investigate the CE between identical materials. The results show no apparent tendency of the direction of charge transfer between two flat films. However, for the curved surface to be contacted, the films with a convex surface (larger curvature) are prone to be negatively charged, while the films with a concave surface (smaller curvature) are inclined to be positively charged. The performance of the TENG with surfaces of different positive curvatures also suggests that larger curvature leads to more electrons negatively charging the surface. In addition, an increase of applied force is likely to lead to a reversal of charge transfer direction between the two surfaces. Further verification on the above-mentioned charge trends between identical materials is conducted under a vacuum of \( \sim 1 \) Pa and at a temperature as high as 358 K. On the basis of these experimental results, we propose a curvature-dependent charge transfer model for CE by introducing the curvature-induced energy shifts of the surface states. The prerequisite for the above model is the utilization of a contact-separation mode with a gentle applied force, since increasing the force is likely to result in irregular surface deformations and surface damage or even material transfer due to relative sliding. All of these complicate the predictability of the charge transfer direction. Our study may provide a possibility for the unification of the mechanisms of CE between different materials and between the identical materials in the future.

EXPERIMENTAL SECTION

Fabrication of the TENG. PTFE film with a thickness of 0.05 cm\(^{-1}\), FEP film with a thickness of 0.025 cm\(^{-1}\), Kapton film with a thickness of 0.025 cm\(^{-1}\), polyester film with a thickness of 0.025 cm\(^{-1}\), Nylon film with a thickness of 0.05 cm\(^{-1}\), and acrylic sheets with different curvatures were purchased from McMaster-Carr. For the preparation of the TENG, a Cu coating with a thickness of 200 nm was deposited on the back of each tribomaterial film as the electrode by using a Denton Explorer e-beam evaporator. Then, the films with a Cu coating were bonded to the acrylic sheet with a mechanical feedthrough with a steel rod, and a vacuum system. The pressure was about 1 Pa\(^{-1}\) and the relative humidity was less than 1% in the chamber. Nickel wires were attached to the Cu electrodes and extended out of the chamber. The steel rod was connected with a linear motor, which provided an accurate control of position and speed for the mechanical stimulation. The separation distance between the two tribomaterial surfaces of the TENG was 1 cm. To eliminate the initial charges, the discharge treatment was carried out in two processes. First, once the TENG was prepared, both the acrylic substrates and tribomaterial films were rinsed with anhydrous ethanol and 2-propanol three times and then dried in ambient air for 48 h. Second, before each measurement, the surface of the tribomaterial film was rinsed with anhydrous ethanol three times and then dried in ambient air for at least 8 h. The open-circuit voltage \( V_{OC} \) and short-circuit transfer charge \( Q_{SC} \) of the TENG were measured by a Keithley 6514 electrometer. The relative humidity was measured by a Shaw Superdew 3 hygrometer. The forces applied to the TENG were measured by a Vernier LabQuest Mini dynamometer. The microscope images of the surface of Kapton films were measured by a Hitachi SU8010 field-emission SEM.

ASSOCIATED CONTENT

Supporting Information

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Properties of the PTFE TENG with many initial surface charges, \( V_{OC} \) and \( Q_{SC} \) of the PTFE TENG when the contact position is kept the same each time, properties of the FEP TENG, Kapton TENG, polyester TENG, and nylon TENG, \( V_{OC} \) and \( Q_{SC} \) of the PTFE TENG with different surface curvatures, properties of the Kapton TENG under atmospheric pressure and at room temperature, SEM images of the Kapton surface (PDF)

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Notes

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