

Electrostatics

Contact Electrification between Identical Materials**

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Contact electrification (CE),^[1–3] the transfer of charge between two surfaces that are brought into contact and then separated, plays a central role in several useful technologies, such as photocopying,^[4] laser printing,^[5] and electrostatic separation methods,^[6] but is also responsible for the build-up of charge leading to electrical shocks, explosions, mechanical jams, or damage of electronic equipment.^[7,8] Despite a long history of investigation that dates back to antiquity,^[9] the fundamental understanding of the phenomenon remains elusive, and the nature of charge carriers transferred during CE is a subject of ongoing scientific debate.^[1,10–15] On the other hand, existing theories generally accept that 1) CE requires a difference in material properties^[1,6,16] and/or of the chemical potentials of the charge carriers on the contacting surfaces (the latter, in the case of grains of the same material but of different diameters),^[17] and 2) that the magnitude of charge separation is proportional to the effective/real area of contact.^[1,15,18] Herein, we demonstrate that neither of these long-held beliefs is necessarily true. Specifically, we show that atomically flat pieces of identical insulators can separate charge by contact electrification and can continue to charge when contacted multiple times (Figure 1). Remarkably, the magnitude of charge Q that develops scales not with the contact area A , but rather with its square root, $Q \propto \sqrt{A}$ (Figure 2). These observations—supported by theoretical considerations—suggest that CE between identical materials is driven by the inherent, molecular-scale fluctuations in the surface composition or structure of the material.

Charge separation was observed when pieces of the same material were contacted: in our experiments, we confirmed this phenomenon for poly(propylene), poly(styrene), Teflon, poly(vinyl chloride), and poly(dimethylsiloxane) (PDMS). Whilst the qualitative features of CE were similar for all these

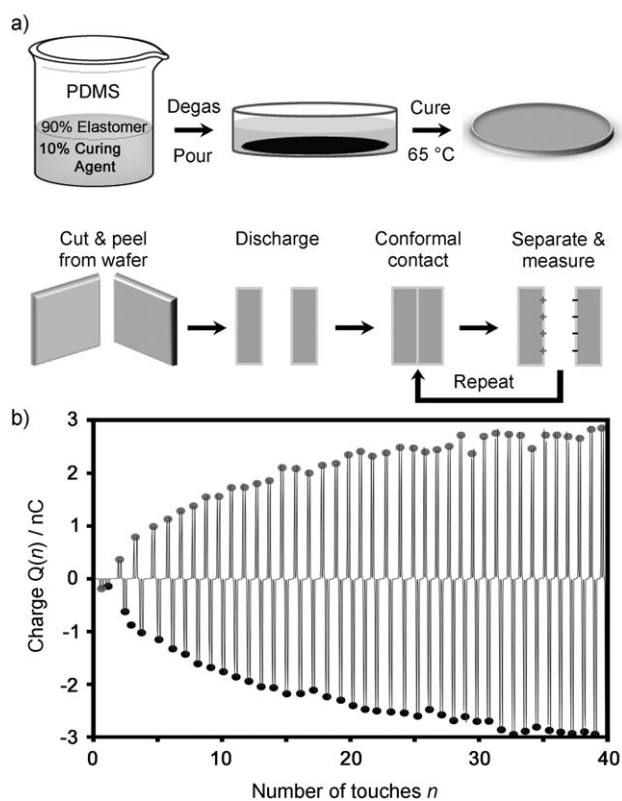


Figure 1. a) Experimental procedure. b) Typical raw data of the charges Q developed on two contacting PDMS pieces as a function of the number of touches n . Q is measured by placing the pieces in a Faraday cup (twice for each piece and condition, hence the splitting of the individual peaks). Note that one piece continues to charge positively whilst the other charges negatively.

systems (see the Supporting Information, Section 4), most quantitative studies were performed using PDMS, because it can be cast and cured against atomically flat masters and when cured, it is known to come into conformal contact with many types of surfaces, including that of PDMS itself.^[19,20] To prepare PDMS blocks for CE experiments (Figure 1a), a degassed PDMS/crosslinker (Sylgard 184, Dow) was cast against disjoint regions of an atomically flat [100] silicon wafer (Montco Silicon Technologies, Inc.), either silanized with 1H,1H,2H,2H-perfluorooctyltrichlorosilane or unsilanized, and was cured at 65 °C for times between 24 and 96 h. Once cured, the PDMS pieces were gently peeled off the wafer. PDMS casting, curing, peeling, and all subsequent manipulations were performed in a glove-box under an inert atmosphere (nitrogen or argon) and in the presence of Drierite desiccants (W. A. Hammond Drierite Co. Ltd). Prior to CE experiments, any adventitious charge that might have

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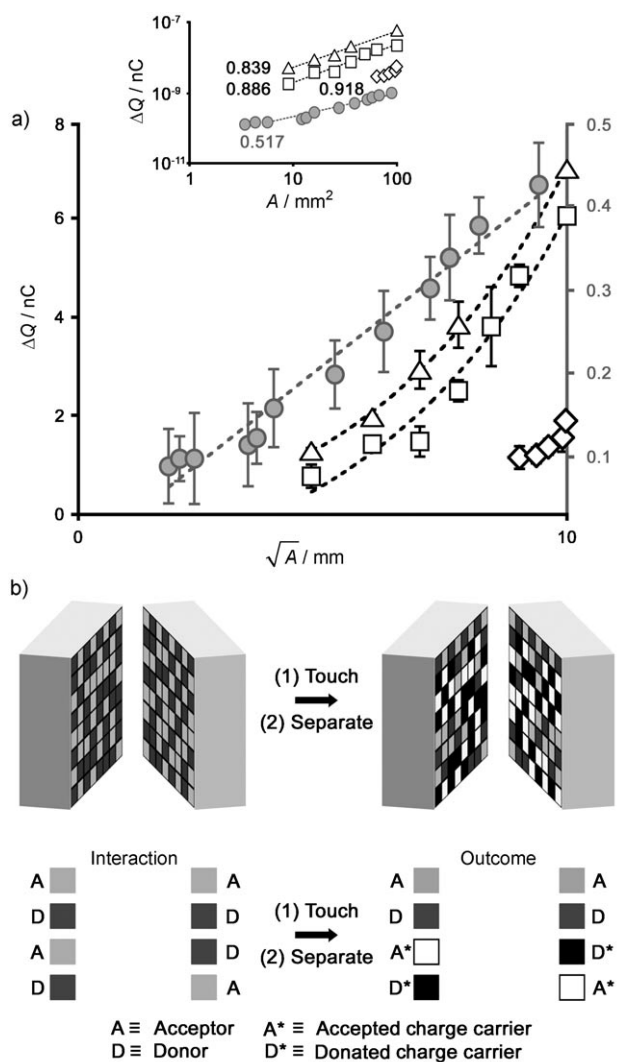


Figure 2. a) Charge difference $\Delta Q(1)$ separated during the first contact between a piece of PDMS and a piece of PDMS (\bullet and right y axis); and (left y axis) between PDMS and PVC (Δ), stainless steel (\square), or copper foil (\diamond). The dependencies are plotted as a function of the square root of the area of contact \sqrt{A} . For the PDMS–PDMS contacts, Q scales linearly with \sqrt{A} , whereas for all other pairs of materials, Q scales linearly with A (i.e., quadratically with \sqrt{A}). Inset: log–log plot of the same data. The slopes of the lines correspond to the exponents of experimental dependencies: ca. 0.5 for PDMS–PDMS contacts and $Q \propto \sqrt{A}$ scaling, and ca. 1 for other material pairs and $Q \propto A$ scaling. Error bars are based on at least 25 experiments for each condition. b) The theoretical model, with charge transfer occurring between contacting donors (dark gray) and acceptors (light gray). Donors that have donated their charges: black; acceptors that have accepted charge: white.

developed on the PDMS blocks during peeling off the wafer was thoroughly discharged using an ionic gun (Terra Universal, 2005-55), and complete discharging was confirmed by charge measurements in a Faraday cup connected to a high-precision electrometer (Keithley 6517).

To study CE, the PDMS pieces were held between a pair of micromanipulators and were brought into conformal contact along their atomically flat surfaces. When the pieces were subsequently separated, the charges on each piece were

measured individually using the Faraday cup. The charges developed on the contacting surfaces were of equal magnitudes but opposite polarities: $+Q$ and $-Q$ (Figure 1b). Importantly, these charges did not depend on 1) the time of contact (for times 2 s to 1.5 h); 2) the pressure applied during contact (0.01–4.5 MPa); 3) the elastic properties of the PDMS (varied by changing the curing times from 24 to 96 h, range of Young's moduli 360–2000 kPa); 4) the perimeter of the contacting surfaces (for a given surface area); and 5) the way in which the surfaces were separated (i.e., rapidly or slowly peeled off one another).

On the other hand, the magnitudes of the separated charges Q depended on the number of consecutive touches n and on the area A of the contacting surfaces. Specifically, $Q(n)$ increased monotonically with n ; however, each subsequent contact resulted in a smaller degree of charge separation (see Figure 1b and Figure 3). The charging

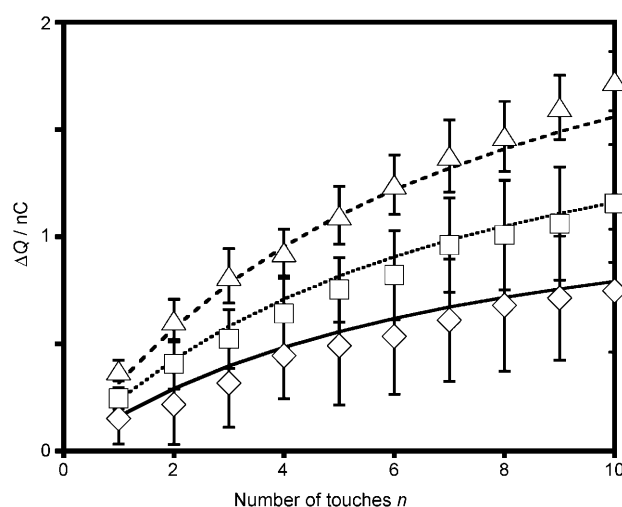


Figure 3. Experimental (symbols) and theoretical data (curves) for contact charging between pairs of PDMS pieces of the same areas. Each curve corresponds to a different area of contact: 16.00 (\diamond), 34.22 (\square), and 61.62 mm² (Δ). Standard deviations are based on the averages of at least six independent experiments for each number of touches.

curves ultimately leveled out at most at 3.0 nC cm⁻² in air and 0.5 nC cm⁻² in argon (these values correspond to electric fields of 3.4 kV mm⁻¹ and 0.6 kV mm⁻¹ between the separated pieces and are close to the dielectric strengths of air and argon, respectively). When the area of contact was systematically varied, the amount of charge developed during single contact $Q(1)$ scaled, to good approximation, as the square root of A , $Q(1) \propto \sqrt{A}$ (Figure 2a). This scaling was in contrast to the linear dependence, $Q \propto \sqrt{A}$, observed when PDMS was contacted against other materials, such as copper foil, stainless steel, and flexible poly(vinyl chloride) (Figure 2a).

The challenge in rationalizing these observations lies in the fact that apparently no thermodynamic driving force exists that could promote continued (i.e., increasing with n) contact charging between pieces of the same material. However, the experimental evidence is congruent with a model in which CE is due to small but inherent fluctuations in

the compositions of the contacting surfaces. To show this, let us represent these surfaces (denoted by the superscripts $i = 1, 2$) as composed of N groups/centers of which N_D^i can donate and N_A^i can accept charge during CE (Figure 2b). Although the surfaces are macroscopically identical and the averages are equal ($\langle N_D^1 \rangle = \langle N_D^2 \rangle$ and $\langle N_A^1 \rangle = \langle N_A^2 \rangle$), the exact numbers N_D^i and N_A^i can deviate slightly from these average values, and the probability densities of having exactly N_D^i donor or N_A^i acceptor groups can be approximated as a binomial distribution with mean values $\langle N_D^i \rangle = p_D N$ and $\langle N_A^i \rangle = p_A N = (1 - p_D)N$, respectively (see also the Supporting Information, Section 1, for an alternative, multinomial formulation). For donors on surface i , we have:

$$p(N_D^i, p_D) = \frac{N!}{N_D^i!(N - N_D^i)!} p_D^{N_D^i} (1 - p_D)^{N - N_D^i} \quad (1)$$

which for large N may be approximated as a normal distribution with a mean $\langle N_D^i \rangle = p_D N$ and variance $p_D(1 - p_D)N$:

$$p(N_D^i) \approx \frac{1}{\sqrt{2\pi p_D(1 - p_D)N}} \exp\left(\frac{-(N_D^i - p_D N)^2}{2p_D(1 - p_D)N}\right) \quad (2)$$

With these preliminaries, we first consider the net amount of charge ΔQ transferred in a single touch between macroscopically identical, uncharged PDMS pieces (note that for the first touch, $Q(1) = \Delta Q$). When the two pieces are brought into contact, charge transfer will occur when a donor group overlaps (see Figure 2b) with an acceptor group. For the N_D^1 donors on surface 1, the chance that each of them will contact an acceptor on surface 2 is N_A^2/N ; the corresponding probability for the N_D^2 donors on surface 2 is N_A^1/N . The net result of these processes can be written in the form of the kinetic equation:

$$\Delta Q = \alpha N_D^1 \frac{N_A^2}{N} - \alpha N_D^2 \frac{N_A^1}{N} \quad (3)$$

where the constant α denotes probability of charge transfer for contacting donors/acceptors. (see Ref. [21]). Noting that $N_D^1 + N_A^1 = N_D^2 + N_A^2 = N$, Equation (3) simplifies to:

$$\Delta Q = \alpha(N_D^1 - N_D^2) = \alpha\Delta N \quad (4)$$

Because both N_D^1 and N_D^2 are normally distributed, so is their difference (with zero mean and twice the variance of the individual distributions). Thus,

$$p(\Delta N, p_D) \approx \frac{1}{\sqrt{4\pi p_D(1 - p_D)N}} \exp\left(\frac{-\Delta N^2}{4p_D(1 - p_D)N}\right) \quad (5)$$

Therefore, whilst it is equally probable that either surface 1 or surface 2 will have more donor groups than the other, the characteristic magnitude of this difference is non-zero:

$$\begin{aligned} \langle |\Delta N| \rangle &= 2 \int_0^\infty \frac{\Delta N}{\sqrt{4\pi p_D(1 - p_D)N}} \exp\left(\frac{-\Delta N^2}{4p_D(1 - p_D)N}\right) d\Delta N \\ &= 2\sqrt{\frac{p_D(1 - p_D)N}{\pi}} \end{aligned} \quad (6)$$

Finally, as $N \propto A$, we arrive at the result that the magnitude of the separated charge is proportional to the square root of the area of contact, which is in agreement with experiments.

Two remarks should be made when considering this result. First, for a given pair of pieces, the relative asymmetry in their surface compositions is assumed to be permanent (unless their material properties were in some way altered). To test this assumption, we performed a series of experiments in which we contact-charged two given pieces, discharged them using ionic gun, and then contact-charged again. In all cases, the polarities of the individual pieces were the same on the first charging and on the second charging (even after several months). This trend rules out a possibility that CE occurs by some accidental exchange of charge between the contacting pieces. If this were the case, the polarities of contacting pieces on the second charging should not correlate with the polarities developed during first charging; colloquially put, the system should have no memory. The second observation is that the model does not assume any specific chemical nature of the donors, acceptors, or the charge carriers:^[13–15, 21–23] in other words, we do not attempt to resolve this issue, and leave the controversy between the electron-transport^[21–23] versus ion-transport^[14, 15, 24, 25] pictures open for future research. Whilst for the case of PDMS it might reasonably be speculated that the donors are oxygen sites, the acceptors are silicon, and CE results in the transfer of electrons; the model works without these assumptions and predicts CE to occur for all materials presenting heterogeneous donor/acceptor surfaces. This supposition is in line with our observation that CE occurs in several other polymeric systems that we tested. In this context it is important to emphasize that the model does not apply to conductors whose surfaces cannot be represented as a union of distinct donor and acceptor sites; indeed, in experiments where pieces of the same metal were contacted, no charge separation was observed.

The model, as described in Equation (3), can be extended to explain the increase of Q with the number of consecutive contacts n between the surfaces (Figure 1b and Figure 3). The key assumption to make is that if a successful charge transfer had taken place between a given donor and acceptor during a contact n , these sites cannot participate in CE during the $n + 1$ and subsequent contacts. Thus, the numbers of donors and acceptors change between consecutive contacts according to the following difference equations:

$$N_D^1(n + 1) - N_D^1(n) = N_A^2(n + 1) - N_A^2(n) = -\frac{\alpha}{N} N_D^1(n) N_A^2(n) \quad (7)$$

$$N_D^2(n + 1) - N_D^2(n) = N_A^1(n + 1) - N_A^1(n) = -\frac{\alpha}{N} N_D^2(n) N_A^1(n) \quad (8)$$

The net charge difference between two pieces after multiple touches may then be written as

$$Q(n) = \sum_{i=0}^n \Delta Q(i) \quad (9)$$

with initial conditions before CE being $N_D^1(0) - N_A^1(0) = N_D^2(0) - N_A^2(0) = N$ and $\Delta Q(0) = 0$. The charging equations can be iterated numerically for different realizations of $\rho = N/A$, $p_D = N_D^1/N$, and parameter α by using a Monte Carlo method, where N_D^1 and N_D^2 are randomly distributed according to equation (2); this procedure then yields the average magnitudes of separated charge, namely $\langle Q(n) \rangle$. The curves in Figure 3 give theoretical fits (all with the same model parameters: $p_D = 0.5$, $\rho = 2.90 \times 10^{18} \text{ mm}^{-2}$, and $\alpha = 0.132$) to several typical experimental series. (For further comments on the model, see the Supporting Information.)

In summary, we have shown that contact electrification can occur between two identical materials. This behavior appears to be generic to non-elemental insulators. The notable fundamental finding of this work is that random, microscopic-level fluctuations—here in surface composition—can translate into macroscopic effects, such as the predictable accumulation of charge. In the context of the effort to control static electricity in many industrial applications, it becomes evident that charging of contacting surfaces/components cannot be eliminated simply by coating them with the same material. Design of true antistatic coatings will thus require careful engineering not only of charge-transfer parameters of the bulk materials but also of their surface compositions.

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