Contact Electrification

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Patterns of Electrostatic Charge and Discharge in Contact Electrification**

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Here we describe a study of the charging and discharging of solids in a system comprising a metal sphere that rolls across an electrically insulating plate.[1–4] There are two kinetically distinct processes: 1) charging at a constant rate; 2) abrupt discharging, when the potential difference between sphere and surface reaches a critical value determined by the dielectric strength of air. This work has two objectives: 1) to develop a procedure for examining the rate of charging and discharging as a function of a range of relevant variables; 2) to use this information to test the hypotheses that charge separation involved ions and that discharge of the potential produced involved a breakdown of air. In published work, we have described this system;[2] this study demonstrates the wealth of quantitative information it can provide as a tool for studying the atomic/molecular mechanisms of contact electrification. These mechanisms are relevant to processes ranging from lightning[5] to xerography, and are a subject of active controversy.[6–10]

Three mechanisms appear to contribute to contact electrification:[1] 1) ion transfer between surfaces having mobile ions, 2) partitioning of ions from adsorbed water onto the surfaces of non-ionic insulators,[11] and 3) electron transfer between conductors and semiconductors (materials with mobile electrons and well-defined Fermi surfaces). We have concluded[1]—in agreement with a hypothesis by Diaz[12,13]—that the transfer of ions between the contacting surfaces is the most common mechanism for charge separation when organic materials are involved. The data we present here are consistent with contact charging by the slow transfer of ions, interrupted by episodic, rapid discharge events involving ionized plasmas when the difference in electrical potential between the surfaces exceeds the breakdown limit of air.

These experiments used the rolling sphere tool (RST, Figure 1) developed by Grzybowski et al.[2–4] We investigated contact electrification between stainless steel spheres ($d = 3.2$ mm) and three different surfaces (relative humidity, RH = 20–25 %, $T \approx 22\,^{\circ}\mathrm{C}$, $\omega = 80$ rpm). The Supporting Information contains the experimental procedures we followed for preparing the insulating surfaces: 1) glass (a 1.0 mm thick, 76 mm diameter wafer of low-alkali glass); 2) glass silanized with *N*-trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride; 3) glass silanized with 3-(trihydroxysilyl)-1-propane-sulfonic acid.

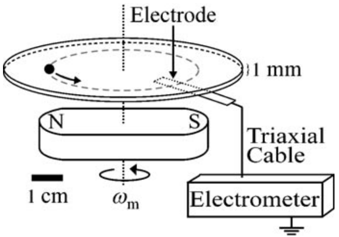

Figure 1. Illustration of the "rolling sphere tool" to measure the kinetics of contact electrification between rolling stainless steel spheres and insulating surfaces. The Supporting Information contains additional graphical representations.

When the sphere was far (more than ca. 2.5 cm) from the electrode (width 5 mm, 0.2 radians), the electrometer reported only the charge on the portion of the insulator (the glass plate) to which the electrode coupled (Q_w). When the sphere passed over the electrode, the electrometer registered a peak in the charge, the height of which was the sum (Q_{s+w}) of the charges that the electrode sensed on the sphere (Q_s) and Q_w. Figure 2a shows the charge the electrometer recorded for one revolution of the sphere. The full-width at half-maximum of the peak was about 0.63 radians.

Figure 2b shows a representative plot of the complex pattern of charge (Q, in picocoulomb, pC: 1 pC = 6.2×10^6 elementary charges) the electrometer reported as the sphere rolled on a glass wafer. When the sphere was directly over the electrode, the electrometer measured a fraction of the charge on the sphere (80–90 %; see the Supporting Information).[2] Q_w (grey dot-dash guidelines) and Q_{s+w} (black dashed guidelines) increased linearly with time. Sharp discontinuities—discharge events through air—interrupted the charging. Subtracting Q_w from Q_{s+w} gave Q_s—the charge that the electrometer sensed on the rolling sphere alone—as a function of time (Figure 2c). We have observed qualitatively similar behavior on a variety of materials, including organic polymers; we will detail these experiments in a full paper.

The polarity of charge separation was invariant when a steel sphere (positive) rolled on a clean glass wafer (negative) (Figure 3a). When the sphere rolled on a surface with bound

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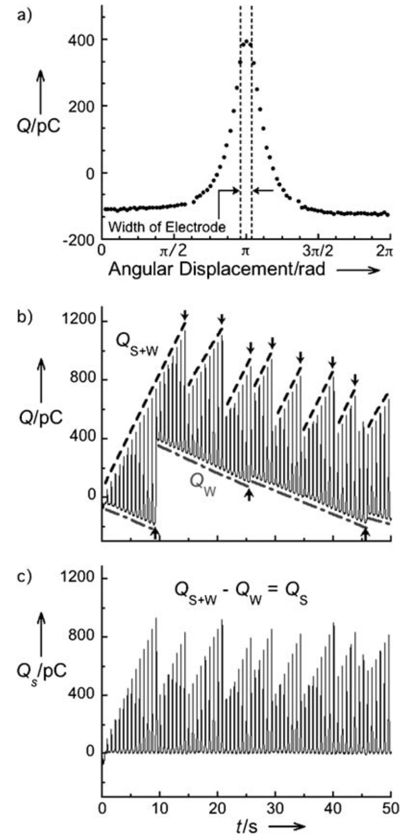

Figure 2. Contact electrification of a stainless steel sphere ($d = 3.2$ mm) rolling on a glass wafer. a) Electrometer response (charge transferred to/from the electrode) as a function of angular displacement of the sphere around its circular path. b) Unprocessed data: charge sensed by the electrometer versus time. The width of the electrode was 5 mm (0.2 radians); the circumference of the path of the sphere was ca. 150 mm. Sharp discontinuities (black arrows) interrupted the accumulation of Q_w, the charge the electrode sensed on the wafer (grey dot-dash guidelines) and of Q_{s+w}, the sum of the charge that the electrode sensed on the sphere and the wafer (black dashed guidelines). c) $Q_{s+w} - Q_w$: the charge that the electrometer sensed only on the sphere (Q_s).

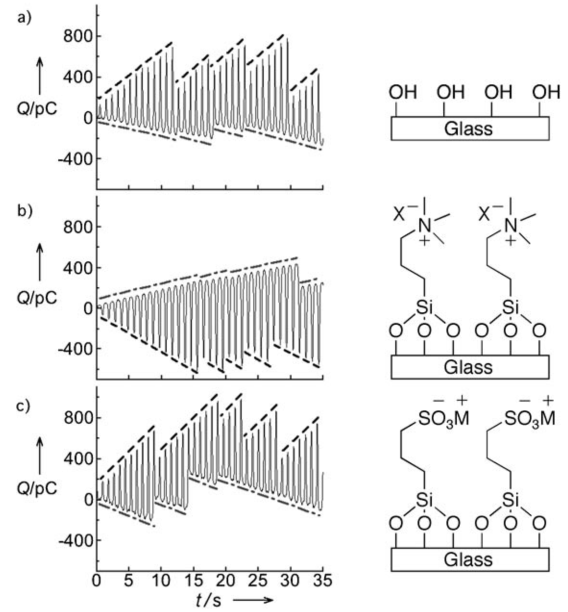

Figure 3. Traces of the dynamics of contact electrification between a stainless steel sphere and (a) plain glass, and glass wafers silanized with (b) *N*-trimethoxysilylpropyl-*N*,-*N*,-*N*-trimethylammonium chloride or with (c) 3-(trihydroxysilyl)-1-propane-sulfonic acid.

ammonium ions and mobile anions (Figure 3b), the wafer charged positively, while the sphere charged negatively. Conversely, when a steel sphere rolled on a surface with bound sulfonate anions and mobile cations (Figure 3c), the wafer charged negatively, while the sphere charged positively. The polarity of charging in our experiments is consistent with the ion-transfer model of contact electrification.[6,12] We have so far identified only the sign and magnitude—not the chemical structure—of the ion that transfers during contact electrification.

The simplest accepted mechanism of electrical discharge has several steps:[14] An adventitious ion/electron pair in a region of high electric field initiates the discharge. The proposed sources of these charged species are ionized gaseous molecules from either cosmic rays or background radioactivity.[15] These oppositely charged particles accelerate and initiate avalanches of collisions that produce enough gaseous ions and electrons to lower the resistivity of the gas by 10^9–10^{10} (dielectric breakdown).[14] Breakdown of air at atmospheric pressure between insulators causes a number of microdischarges to form between the materials.[16] The magnitude of electric field at which dielectric breakdown of air occurs is ca. 30 kV cm^{-1}.

A simplified representation of the discharge events that occurred when a steel sphere rolled on clean glass (Figure 4a) shows the total charge on the sphere immediately before ($Q_{\max}$) and immediately after ($Q_{\min}$) discharges. The discontinuities consistently showed a decrease in the magnitude of charge on the sphere ($\Delta Q_s = (-440 \pm 120)$ pC; that is, ca. 2.7×10^9 (4.5 fmol) elementary charges). Three lines of evidence indicate that the discontinuities in the charging data are due to electrical discharges through air between the sphere and the insulating surface: 1) The value of $Q_{\max}$ was (940 ± 60) pC (ca. 5.9×10^9 elementary charges, or 1 charge for every 5000 nm^2 of surface area of the sphere). The electric field at the surface of an isolated sphere ($d = 3.2$ mm) in vacuum with this magnitude of charge is 33 kV cm^{-1}.[17] Although our experimental system is electrostatically more complicated than an isolated sphere (the sphere rests on an oppositely charged insulating plate, and there is a continuum of distances between these two charged bodies), the electric field we calculate is (perhaps partly by coincidence) within 10% of the electric field at which breakdown occurs in air under standard conditions (conducting, parallel-plate electrodes spaced 2.5 mm apart). 2) This maximal magnitude of charge on the sphere was independent of the chemical structure of the three insulating surfaces we examined (see the Supporting Information). 3) The values of $Q_{\max}$ in other gases correlated with the reported dielectric strengths[18] of those gases: $Q_{\max}$ was 3–4 times smaller in noble gases (helium and argon) and 1.5 times larger in sulfur hexafluoride than in air (RH ca. 20%).

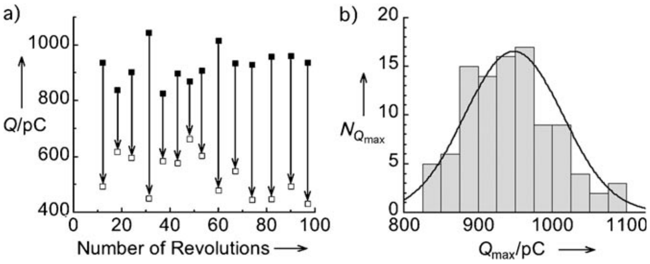

Figure 4. (a) A simplified representation of contact electrification between a stainless steel sphere and glass, in which we show Q_{max} (filled squares) and Q_{min}(open squares) for each abrupt discharge. (b) Histogram of 100 measured values of Q_{max} (with 11 bins with a width of 25 pC). The y-axis, N_{Qmax} is the number of times we recorded a value of Q_{max} in each bin. The overlaid curve is the best-fit normal distribution (R = 0.96), with mean $\mu = 940$ pC and standard deviation $\sigma = 60$ pC.

It is likely that adventitious photoionizations of gaseous molecules initiated the discharges that we observed. The other known mechanism for initiation of electrical discharge—field emission—requires electric fields greater than 500 kV cm^{-1}.[19] The normal distribution of $Q_{\max}$ (Figure 4 b) is consistent with the initiating events of the discharges being independent and random.[15]

The detail and ease of analysis of the type of data shown in Figure 2 and 3 provide a flexible and convenient approach to the kinetics of contact electrification and discharge, and will make it possible to study correlations between these processes and the structures of materials participating in these processes. We conclude that charging involves the physical transfer, by contact, of ions between the sphere and the surface of the wafer.[1,20] Although we can correlate the polarity of charge transfer with the formal charge of the siloxane layer, we have not yet directly observed or identified the ion that transferred. The electrochemical details of the plasma-mediated discharge remain speculative. The potential at which discharge begins seems to be set by dielectric breakdown, and initiated by advantageous ionization. We do not understand what processes extinguish the plasma. We infer that the dielectric breakdown of the surrounding medium (here air or another gas) sets an upper limit on the amount of net charge *any* material can hold; this limit is an important constraint in any study or proposed use of contact electrification.

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