Controlling the Kinetics of Contact Electrification with Patterned Surfaces

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This communication describes a new strategy for preventing contact electrification (tribocharging) and unwanted electrical discharges, based on our understanding of the ion-transfer mechanism.[1,2] The objective of this work is to use surfaces patterned with oppositely charged functional groups to control the rate of contact electrification. Contact electrification can generate electric fields sufficiently large to cause electrical discharges.[3,4] Developing strategies for eliminating these discharges is an important element in preventing (for example) (i) damage to microelectronics, (ii) explosions during transfer of flammable liquids (e.g., during fueling of vehicles), (iii) damage caused by discharges of ungrounded helicopters, and (iv) explosions of dust in silos.[5−7] The prevention of contact electrification and "static discharge" is a problem that requires a combination of chemistry and electrostatics to create materials with new capabilities. Current strategies for limiting the accumulation of net charge on surfaces fall into two categories: (i) decreasing the resistivity of a material, such that excess charge conducts to ground (examples include carpets made of mixtures of fibers of nylon and conducting carbon)[8] or distributes evenly on the surface (such as with topical antistatic additives);[9] and ii) using ionizing devices, such as a Zerostat gun, to reduce charge.[10]

Several research groups,[1,2] including ours,[3,4] have noted that materials that contain ionic functional groups consistently develop, by contact electrification, the same sign of charge as that of the less mobile ion. This observation, and others,[1] is consistent with an ion-transfer mechanism for contact electrification. Here, we used patterns of oppositely charged functional groups to *suppress* the net contact electrification of surfaces and electrical discharges between them. To our knowledge, this example is the first of a surface rationally designed to *resist* charging based on an application of the ion-transfer mechanism of contact electrification.

We measured contact electrification using the "rolling sphere tool" (RST) described by Grzybowski et al.,[11] in which a rotating bar magnet causes a ferromagnetic steel sphere ($d = 3.2$ mm) to roll along a circular path (circumference $\approx$ 13 cm, $\omega = 80$ rpm) on an insulating surface. We briefly describe its operation here; complete descriptions are published elsewhere.[3,11] An electrode (connected to an electrometer) capacitively measures the charge on the planar surface and the sphere as the sphere rolls. When the sphere is far from the electrode, the electrometer reports only the charge on the portion of the glass wafer to which the electrode is coupled. When the sphere is directly above the electrode, the electrometer reports the sum of the charges that the electrode senses on the sphere and the wafer. We controlled the relative humidity (RH = 15−20%) around the sphere and surface.[12]

The sphere rolled on glass patterned with areas of self-assembled monolayers of positively charging, ammonium-terminated siloxanes (*N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride, **1**) and the negatively charging glass surface (Figure 1). These surfaces are convenient for the present demonstration of surfaces that resist
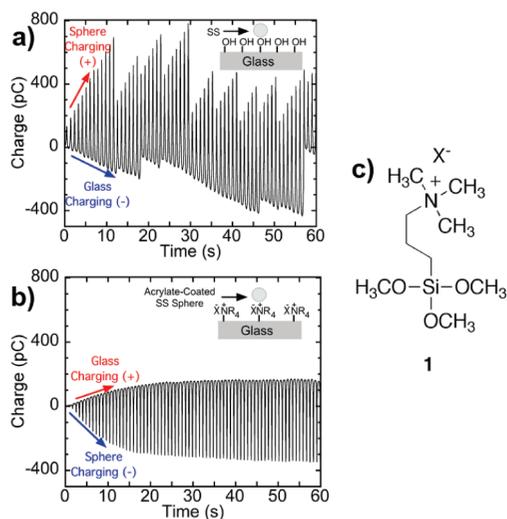

Figure 1. Representative charge vs time due to contact electrification from (a) a steel sphere rolling on clean glass or (b) an acrylate-coated steel sphere rolling on glass silanized with **1**. (c) Structure of cationic siloxane **1**.

contact electrification. We used both bare steel spheres and spheres coated with an insulator (commercial acrylic waterproofing spray). When a stainless steel sphere rolled on a uniform surface (0% or 100% silanized), the rate of charging of the sphere was 60−80 pC/s; the chemical functionality of the surface controlled the direction of charge separation. The consistent increase in electrical potential caused the bare steel sphere and surface to discharge by the dielectric breakdown of air (sharp discontinuities in charge as a function of time, as seen in Figure 1a) approximately once every 7 s.[3]

We hypothesized that a surface patterned in a mosaic of positively and negatively charging regions would suppress the charging of a sphere rolling on it. To test this hypothesis, we used the RST to measure contact electrification of a steel sphere ($d = 6.4$ mm) rolling on a glass wafer, one-half of which was silanized with **1**; we performed the experiment with the electrode underneath either one of the two halves (Supporting Information). Each half of the wafer developed a sign of net charge expected for the fixed ion: negative for the bare glass and positive for the cationic siloxane. Because the sphere acquired both positive and negative charges, it accumulated net charge more slowly than it did on either homogeneous surface: the net charge on the sphere was 100−150 pC after 75 s, less than 10% of the charge required for dielectric breakdown.

To control the rate and sign of contact electrification, we patterned **1** on glass:[13] a hexagonal array of circular posts on a PDMS stamp protected those areas of a homogeneously silanized glass slide that it contacted, while an air plasma oxidized the
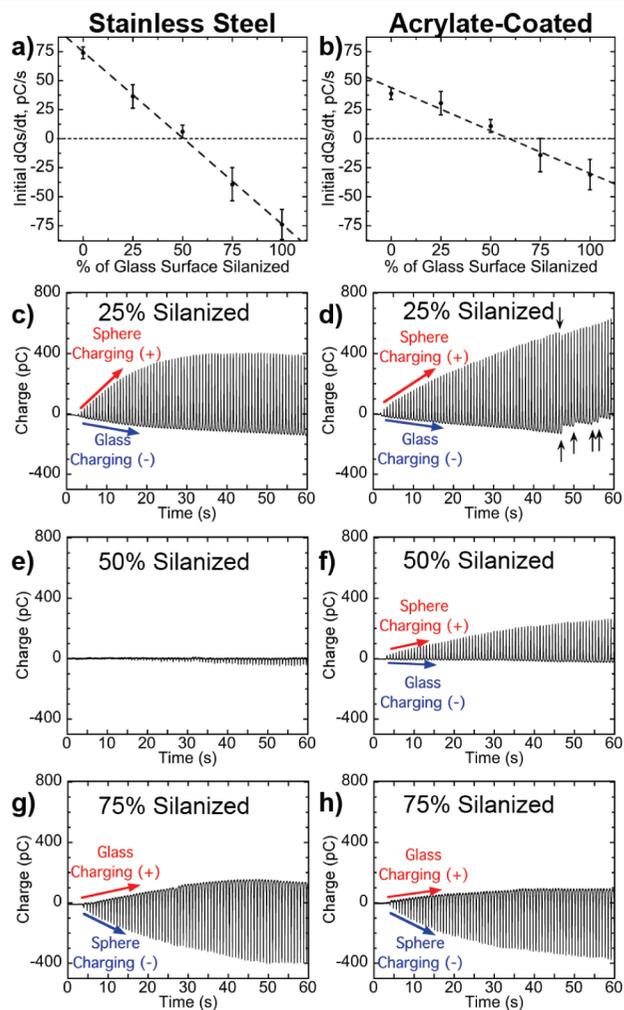
Figure 2. (a, b) Rate of charging of a rolling steel sphere (a) or an acrylate-coated sphere (b) as a function of the percentage of the glass surface that was silanized with **1**. Each data point is the mean of 7−8 measurements at RH = 15−20%; the lengths of the error bars represent the standard deviations of these means. (c−h) Representative traces of contact electrification between a sphere and a glass slide silanized on 25%, 50%, or 75% or its surface area. Vertical arrows indicate electrical discharges.

exposed areas of silanized glass and regenerated silanol groups. The hexagonal pattern of posts on the stamp presented many pathways for the plasma to access the glass. The center-to-center distance between posts (with diameters 100 μm, 1 mm, or 10 mm) determined the percentage of the surface that PDMS protected. We used this procedure to pattern wafers with siloxane **1** that covered 25%, 50%, or 75% of the surface area (See Supporting Information).

The initial rate of charge separation correlated with the percentage of the surface treated with cationic siloxane **1** (Figure 2). This trend held whether the diameter of the circular features on the planar insulator was 100 μm, 1 mm, or 1 cm (Figure S4). The charge on plain steel spheres that rolled on samples silanized on 50% of their surface stopped accumulating at 100−200 pC (4−5× less than the minimal charge required to cause discharge).[3] Surfaces with tailored ratios of positively and negatively charging functionalities therefore suppressed contact electrification and prevented electrical discharges.

This strategy also controls charge separation between two insulating surfaces, which can be particularly challenging with conventional techniques. Spheres coated with an insulating acrylic waterproofing spray discharged when they rolled on a clean glass surface; the average amount of charge that these spheres lost upon discharge was ~10% ($\Delta Q_{acryl} = 40 \pm 20$ pC) of the charge bare stainless steel spheres lost ($\Delta Q_{ss} = 440 \pm 120$ pC). We believe this result reflects the restricted conductivity of the insulator: only the area on the sphere close to the substrate participates in the transfer of charge. Although the rates of charging of the acrylate-coated spheres that rolled on the homogeneous surfaces were slower than the rates for the plain steel spheres, their rates of charging correlated linearly with the percentage of the glass silanized with **1** (Figure 2b).

This approach uses chemically patterned surfaces to determine the rate and sign of the separation of charge between two contacting materials with four unique characteristics: (i) it does not require any of the materials to be conductive; (ii) it relies on functional groups that are covalently bound to one of the contacting materials and should therefore be less resistant to wear than topical antistatic coatings; (iii) it relies only on surface chemistry; the bulk properties of the contacting materials remain unchanged; (iv) the process to pattern the surface is simple and easy to perform on large surface areas. It has the disadvantages that the percentages of positively and negatively charging materials on one surface will be different for contact with different materials and that one surface must be amenable to area-selective functionalization. More generally, it demonstrates that the ion-transfer mechanism of contact electrification enables the rational chemical design of electrets with new capabilities.

Supporting Information Available: Experimental details and additional time-dependent charging data. This material is available free of charge via the Internet at http://pubs.acs.org.

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