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Contact Electrification

# Strain-Induced Reversal of Charge Transfer in Contact Electrification**

*Mamadou Sow, Ross Widenor, Ajay Kumar, Seung Whan Lee, Daniel J. Lacks,* and R. Mohan Sankaran**

The electrostatic charging of material surfaces as a result of contact, referred to as contact electrification, is ubiquitous. Despite the widespread importance of contact electrification in many technological and natural areas, a mechanistic understanding remains elusive.[1–3] The most fundamental questions are still being debated, such as what type of species is transferred during contact to cause the charging (electrons, ions, or bits of material),[4–8] and why charge transfer occurs between surfaces of identical material.[9–11] Prior experiments have suggested that material strain can play a role in contact charging.[12–17] However, no clear link has been established between strain and contact electrification. Herein, we show that material strain can have a dominating effect on contact electrification and reverse the direction of charge transfer in contact electrification.

Our study is based on the classic demonstration of contact electrification in which a balloon is rubbed against another material. Balloons are composed primarily of latex rubber, an elastomeric material that can be reversibly strained by simply inflating and deflating. The novelty of our approach is that we compare the contact electrification from inflated (strained) or deflated (relaxed) balloons. We contact either the strained or relaxed balloons with a teflon surface and analyze the charge that develops on the teflon surface (rather than the balloon surface) to circumvent issues associated with changes in the surface area of the balloon. We show that the strain induced in the latex rubber controls the direction of charge transfer.

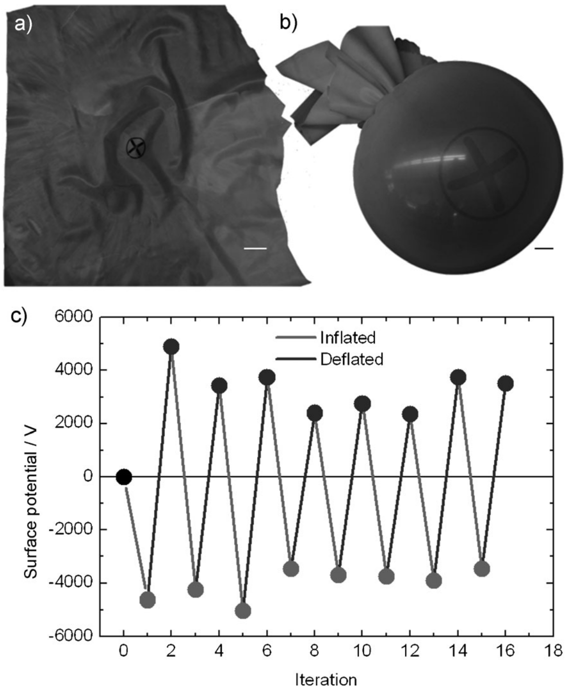

***Figure 1.*** Contact electrification with strained material. Images of a) original relaxed rubber sheet and b) inflated strained rubber balloon (scale bars correspond to 1 cm). The change in the size of the ink mark indicates a strain $\varepsilon$ of 500%. c) Surface potentials measured on a teflon surface alternately contacted with the relaxed and strained rubber.

Typical results are shown in Figure 1 for the following sequence of steps: 1) a neutralized teflon surface was contacted with an inflated balloon and separated, and the voltage of the teflon surface was measured to be −4000 V; 2) this charged teflon surface was then contacted with a deflated balloon, and the voltage of the teflon surface was +4000 V; 3) the teflon surface was then contacted again with the inflated balloon, and the voltage of the teflon surface was −4000 V; 4) this process can be repeated a number of times, with the charge polarity being reversed by alternating contacts with an inflated and deflated balloon. Eventually the buildup of material transferred between surfaces disrupts the reproducibility; for this reason, we carried out more careful tests with freshly cleaned samples.

To confirm the effect shown in Figure 1, we performed a statistically significant number of trials under controlled conditions. Freshly cleaned samples were used for each trial (see Experimental Section for cleaning details), in which each trial consisted of 10 soft touches with either the deflated or inflated balloon, followed by measurement of the surface voltage (on the teflon surface). These trials were carried out in a glove box purged with $N_2$ gas. Of 112 trials carried out on multiple days (half with the deflated balloon, and half with the inflated balloon), all but one trial led to the teflon charging positive when contacted with the deflated balloon, and negative when contacted with the inflated balloon.

We repeated the experiments many different ways and consistently found that the strain-induced charge reversal described above is independent of experimental details (see

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[*] Dr. M. Sow, R. Widenor, Dr. A. Kumar, S. W. Lee, Prof. D. J. Lacks, Prof. R. M. Sankaran
Department of Chemical Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, OH 44106-7217 (USA)
E-mail: daniel.lacks@case.edu
mohan@case.edu

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the Supporting Information), with the following caveats: 1) The charge reversal occurs reproducibly for latex rubber purchased from some manufacturers, but not others; this result is not surprising as latex rubber refers to a rather broad class of materials, with significant chemical variations depending on how it is processed. This issue is discussed further in the Supporting Information. 2) To obtain high reproducibility, the materials must be carefully cleaned before each trial (see the Experimental Section); the cleaning is necessary to remove contaminants that result from material transfer during contact, as described in detail below.

We address the issue of material transfer during the contacts in regard to its possible role in either causing the charge transfer or more simply contaminating the surfaces and limiting reproducibility in repeated experiments. Micro-Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were employed to characterize the teflon surface before and after contact with latex rubber. Figure 2a shows a series of Raman spectra collected from the teflon before and after contact (contact with deflated latex rubber). A spectrum collected from latex rubber (before contact) is also included for comparison. The spectrum of the clean teflon is consistent with the previously reported spectrum of polytetrafluoroethylene (PTFE).[18] After contact, new peaks appear in the spectra (indicated by *), presumably due to material transfer; we could not identify these peaks by comparing with the spectrum of latex rubber, and these peaks remain even after sonication of the teflon in acetone, suggesting newly formed covalent bonds. XPS analysis of the teflon surface before and after contact (with deflated latex rubber) is shown in Figure 2b. A spectrum for latex rubber (no contact) is again included for comparison. The XPS spectrum of the teflon before contact is consistent with PTFE, but after contact new peaks appear that can be attributed to material transfer from the latex rubber, including Mg, Si, and O. Although material transfer certainly occurs during contact, we cannot conclude whether this represents the mechanism by which charge transfer occurs (i.e., electron or ion transfer can also occur). However, the presence of material transfer does imply that the surfaces must be cleaned between trials to obtain reproducible results. Our initial observations suggest that material transfer is more prominent when the teflon is contacted with relaxed latex rubber rather than strained latex rubber (see the Supporting Information), but further work is needed to confirm the generality of these observations.

Our results introduce a new phenomenon, whereby material strain controls the direction of charge transfer in contact electrification. This phenomenon arises because strain alters the driving force for the relevant (yet unknown) species to be transferred (these species are either electrons, ions, or bits of material[4–7]). For example, the strain-induced distortion of chemical bonds could increase the energies of electrons in these bonds, or change the binding strength of ions adsorbed on the surface. Strain-induced structural changes at the surface could also alter the extent of material transfer. These ideas are supported by recent studies of “mechanochemistry”,[19] whereby mechanical strain activates chemical reactions.

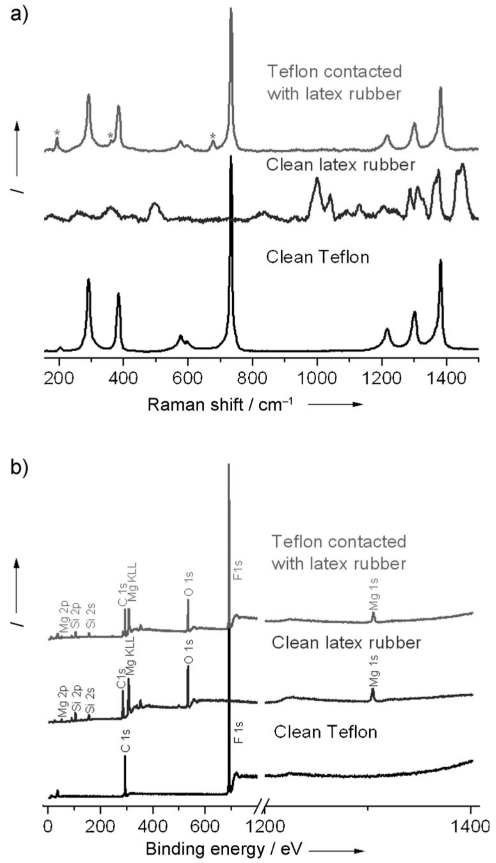

*Figure 2.* Characterization of teflon surface before and after contacting with latex rubber. a) Micro-Raman spectra of clean (black) and contacted (light gray) teflon surfaces, respectively. The micro-Raman spectrum of the latex rubber (dark gray) is included for comparison. Three new peaks at 193, 359, and 676 $\text{cm}^{-1}$ (indicated by *) were identified on the teflon surface after contacting with the latex rubber. b) X-ray photoelectron spectra (XPS) of clean (black) and contacted (light gray) teflon surfaces, respectively. The XPS spectrum of latex rubber (dark gray) is included for comparison. Lines corresponding to Mg, Si, and O were identified on the teflon surface after contacting with latex rubber. Although these elements are not principal components of latex rubber, they may have been incorporated during processing.

Our results have the following general implications in regard to contact electrification:

1) The triboelectric series has an inherently limited applicability. Contact electrification can be modeled phenomenologically by defining a generic “charge transfer potential” $\phi$, such that negative charge is transferred from the surface with higher $\phi$ to the surface with lower $\phi$ value. The “triboelectric series” is an empirical ordering of materials in terms of $\phi$ value, and this ordering is known to have variations from experiment to experiment.[12,20] We show herein that strain can shift the value of $\phi$ and change the tendency of a material to charge positively or negatively. When the value of $\phi$ is similar for two unstrained surfaces, strain-induced shifts reverse the direction of charge transfer. This result may help explain experimental differences and suggests that even small

changes to a material surface as a result of strain can have important consequences on triboelectric charging.

2) Contact electrification may never be quantitatively predictable. Even for materials not explicitly strained, localized strains exist on small (e.g., nano) spatial scales.[21,22] Since strain can change the magnitude and even direction of charge transfer between surfaces, unless these localized strains are fully characterized, their contribution to contact electrification cannot be known. In support of this argument, relaxation of strain in a polymer glass by thermal annealing has been found to alter contact electrification.[16]
3) The non-uniform charge distributions found on contact-electrified surfaces, wherein nominally negative (or positive) charged surfaces have “mosaics” of both positive and negative regions on the surface,[7,23,24] may be due to localized strains inherent on the surface.[21,22] This link between strain and the magnitude and even the direction of charge transfer has now been demonstrated.
4) The contact electrification between surfaces of identical materials may be due in part to random statistical differences in the localized strains inherent on a surface. Apodaca et al. showed that the charge generated by contact between surfaces of identical surfaces scales as the square root of the surface area, which is consistent with the charge transfer being driven by a difference between Gaussian-distributed variables.[10] While the previous investigation addressed the random distribution of sites for donating/accepting single charges, fits of this model to experimental results led to a site density of $2.9 \times 10^{18}\,\text{mm}^{-2}$, which appears to be too high to be physically possible (equivalent to $>10^4$ sites per $\text{Å}^2$). In contrast, if there were a statistical distribution of localized strain on length scales of nanometers or larger, where the contact between regions of different strain systematically transferred multiple charges, then the experimental results could be fit using physically relevant parameters (see the Supporting Information).

## Experimental Section

Natural latex rubber sheets were purchased from McMaster–Carr. The sheets ranged in thickness from 0.15 to 0.25 mm. The rubber sheets were cleaned by sonicating in an acetone bath for 15 min to remove any organic contaminants followed by drying with an ion gun (Model 7901, Exair Corp.) to eliminate any remnant surface charge. The rubber sheets were strained by shaping into balloons and inflating with air; the magnitude of strain was determined from the change in diameter of a circular ink pattern stamped on the balloon. Teflon rods were purchased from McMaster–Carr and cut into multiple disks for repeated tests with fresh surfaces. Before contact charging experiments, the teflon surfaces were cleaned by mechanically polishing with silicon carbide sand paper (grit size = 500), sonicating in acetone for 15 min, and finally rinsing with methanol and drying with the ion gun. After contacting, the surface potential of the teflon surface was measured by a noncontacting electrostatic voltmeter (Model 370, Trek, Inc.). The contacting, either by rubbing or repeated touches, was carried out past the point of charge saturation. Glove box experiments were performed inside a Labconco 50350 glove box. The latex rubber and teflon samples were placed inside the glove box, sealed, and evacuated with dry nitrogen gas to reduce the humidity to less than 10% before contacting and measuring the surface charge.

Micro-Raman spectra were obtained with an inVia Renishaw spectrometer at a laser excitation wavelength of 633 nm. Raman spectra were collected from approximately 10 different spots on the teflon surface and averaged. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI VersaProbe XPS Microprobe. A monochromatic $\text{Al}_{\text{K}\alpha}$ X-ray (1486.6 eV) source was used with a spot size of 300 μm. XPS spectra were collected from three spots and averaged.

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