TRIBOELECTRIFICATION BETWEEN DISSIMILAR SMOOTH METAL SURFACES WITH SELF-ASSEMBLED MONOLAYERS

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ABSTRACT
We have simultaneously measured the friction and triboelectrification between two adhering SAM-coated molecularly smooth dissimilar metal surfaces using a modified surface forces apparatus. As the pressure is increased, triboelectrification increases drastically with large fluctuations about the mean. When the surfaces are in static contact, none of these effects is observed. Triboelectrification strongly depends on the friction type and force, sliding distance, contact area and sliding history. We also show that both SAMs and metal substrates contribute to the charge transfer mechanism.

INTRODUCTION
The existence of shear-induced charge transfer, triboelectrification, has been known for a long time, but the basic mechanism for triboelectrification is still not fully understood, especially at insulator-insulator junctions. It is known that when two different surfaces are brought into static contact, there is already some charge transfer due to the difference in the surfaces’ work functions (1). If we consider the shearing of ‘ideal’ surfaces, i.e. surfaces that are mathematically flat and where there are no surface deformations or damage during sliding, it is believed that the charge transfer should be the same as during static contact. In fact, triboelectrification has been observed even between two nominally symmetrical surfaces (2). Understanding achieved by past studies is limited because none of these studies has systematically investigated the dynamics of triboelectrification and used molecularly smooth surfaces.

Understanding triboelectrification is both of fundamental and practical importance since (i) Charge transfer and exchange interactions can determine tribological properties including the friction force itself (3); (ii) When the reverse process occurs, i.e., when shearing causes the charge transfer, it can result in sparking and stimulate chemical reactions which can cause corrosion and damage (4); (iii) Triboelectric effects can be particularly important in small dynamic devices where the surface to volume ratio is high such as in micro-electromechanical systems (MEMS), microfluidic devices, micro- and nano-switches, and hard disks.

The chief purpose of this work is to investigate dynamics of triboelectrification, and thereby provide some fundamental insight on its mechanism.

METHOD AND MATERIALS
We have modified a surface forces apparatus (SFA) to measure the triboelectrification between two shearing molecularly smooth surfaces while simultaneously visualizing the contact junction using multiple beam interferometry, and measuring the normal and friction forces. Using this apparatus, we have investigated triboelectrification between dissimilar metals, Au and Ag or Ti, each coated with a self-assembled monolayer (SAM) of the surfactant, hexadecanethiol.

The surfaces used were back-silvered atomically smooth muscovite mica sheets, glued onto cylindrical silica discs with a UV curing glue. The deposited films on mica were Ag or Ti, 80Å thick, or a 16-18Å thick precursor film of chromium overcoated by 80Å of gold. The Cr layer was deposited to improve the adhesion and smoothness of the Au layer. All depositions were carried out at 1 Å/sec using an e-beam evaporator at ~2x10-6 Torr. After the metal layer depositions, thin shielded flexible wires were glued to the metal layer of each surface using conducting-epoxy glue. Next, the wired surfaces were coated with SAMs by placing them, metal sides up, in a 0.9 mM solution of 1-hexadecanethiol in ethanol for 10 minutes. The surfaces were then slowly pulled out of the solution, dipped in ethanol to remove any excess hexadecanethiol, and placed in a laminar flow hood to dry. After the surfaces were dry, cyanoacrylate glue was carefully painted over the conducting epoxy to reinforce the bond and serve as an insulator.

The disks were installed into the SFA chamber in a crossed-cylinder configuration and some P2O5 was placed in the sealed chamber to maintain dryness. The wires were then connected to the picoammeter using low noise shielded BNC cables. To decrease external noise, low noise cables were used whenever possible, and special care was taken to prevent any ground loops for all the connections. The SFA chamber conveniently acts as a Faraday Cage, which further helps minimize external noise. The top SAM coated Ag or Ti surface was sheared against the stationary bottom SAM coated Au surface at various loads and sliding conditions by an electrically driven motor, during which the friction forces and current were simultaneously recorded using a digital data acquisition system. In these experiments we measured, and distinguish between current fluctuations about the mean, and the net charge transferred after a certain time.
RESULTS AND DISCUSSIONS

Atomic force microscopy (AFM) and FECO images indicate that the RMS roughness of our hexadecanethiol coated metal surfaces is less than 2 nm which enabled us to eliminate the variable of microscopic roughness in our study.

The charge transferred during shearing was a strong function of the normal pressure applied. At low pressures, as shown in Fig. 1a, the average current density was zero before, during, and after shearing, but the fluctuations drastically increased during shearing. Generally, during shearing, these fluctuations were on the order of a few mA/m² peak-to-peak, or equivalently an average of 1-2×10⁻² e/s per hexadecanethiol molecule. The magnitude of these fluctuations depended on the specific type of friction observed where stick-slip motion generated the largest fluctuations.

At high pressures, the charge transfer behavior during shearing changes significantly: the charge transferred during shearing is about three orders of magnitude larger than at low pressures (cf. Fig. 1b) i.e. 5-15 A/m² peak-to-peak, or 6-19 e/s per hexadecanethiol-metal complex. In addition, the electron charge transfer during shearing is now always non-zero and unidirectional, i.e., the charge is always transferred from the silver to the gold surface, which is as expected from their work functions. Sometimes, the damage occurred to the SAMs and underlying metal surface. This was readily observed in the FECO and in the current density. Damage to the surfaces was accompanied by very large increases in the current, presumably due to direct metal-metal contact. Surprisingly, however, the friction forces did not change in any dramatic way either during or after the damage.

If we consider the details of the results, it is interesting to note several characteristics in the behavior of the current density: First, on the commencement of sliding the mean current grows quickly (within a few seconds), but on stopping it decays more gradually (over 10-20 seconds). Second, the magnitude of the current fluctuations depends on the shearing direction, especially at high loads. Third, during each cycle the amplitude of the current fluctuations often changed in a complex but systematic way, for example, exhibiting phase shifts (in time) with respect to the change in the sliding direction. Fourth, the magnitude of the fluctuations increases as the friction forces increase. All of these effects are likely to be related to the different and continually changing molecular configurations in the upper and lower monolayers within the contact area during sliding and reversing.

As shown in Fig. 1, the behavior and the magnitude of the current density were very different at high loads than at low loads. At low pressures the monolayers’ contribution to the charge transfer mechanism seems to dominate while at high pressures the difference in the work functions of the metal substrates seems to dominate, although there is still a contribution from the monolayer. At high loads, the electrons were always transferred from the lower work function shearing surface to the higher work function surface. Moreover, the current density was higher for the Ti/Au system than it was for the Ag/Au system which is consistent with the work function dependence. Conversely at low loads the average current density was generally nearly zero with a very low net charge transfer that did not always go in a particular direction indicating that the contribution from nearly identical monolayers to the charge transfer was more important than that of the substrate metal layers. It is expected that the charge transport between metal substrates through ~ 2 nm thick alkanethiol SAMs is via tunneling (5), which is known to decay exponentially with the metal-metal separation. Therefore it is expected that the effect of tunneling is stronger at higher pressure (due to chain compression, tilting or interdigitation).

CONCLUSIONS

In conclusion, we show that when two asymmetric SAM deposited metal surfaces are sheared, there is a net charge transfer between surfaces accompanied by current fluctuations, both of which increase with the applied load or pressure. The load, sliding distance, contact area and history also have a significant influence on both the triboelectrification and friction forces. Interestingly, triboelectrification is much more sensitive to some of these parameters than the friction force. We propose that nano-scale perturbations of the SAM structures during sliding as well as the work function differences of the metal substrates are the cause of the charge transfer, and that these are related to the friction forces.

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REFERENCES