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Electrostatics and Electrochemistry: Mechanism and Scope of Charge-Transfer Reactions on the Surface of Tribocharged Insulators

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ABSTRACT: The phenomenon of surface electrification upon contact is a long-standing scientific puzzle, with for instance written accounts of charged samples of amber attracting feathers dating back to the 600 B.C. The electrostatic hazards associated with electrical insulators subject to mechanical friction are well documented, and the design of commercial products, such as copiers and laser printers, is based on the static charging of electrical insulators. Nonetheless, the physical-chemical origin of this phenomenon remains debated. This perspective outlines both recent advances in our understanding of the mechanism behind contact electrification, as well as the emerging research area of electrochemistry on insulators. Research is beginning to demonstrate how to harness static charges, present on insulating surfaces, with the purpose of driving redox reactivity. These studies have helped to clarify the triboelectrification mechanism, and have defined new platforms for electrochemiluminescence, metal nucleation, and mask-free lithography. This article will help researchers working within electrochemistry, physics, green energy, sensing and materials, to gain an understanding of the implications of contact electrification to their respective fields. Special attention is given to the chemical, electronic and mechanical factors influencing triboelectrochemical reactions, concluding with the perceived challenges facing the further development of this field.

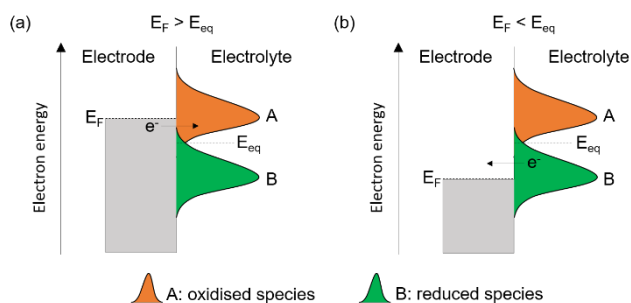
1. INTRODUCTION

When two materials are brought into contact and then separated, with or without deliberate rubbing, they often become charged. One surface develops a net positive charge, while the other acquires a net negative charge of comparable magnitude. This phenomenon, referred to as contact- or tribo-electrification,³ has widespread practical consequences and applications. For example, it underpins seemingly unrelated phenomena and technologies, such as a car static zip, the failure of automotive bearings,⁸ and the transfer of inks in xerography.⁹ The first written account on the static charging of an insulator is generally attributed to Thales of Miletus, who lived around 600 B.C.¹⁰ The topic of electrostatics became popular in the 18th century after Franklin's iconic "Philadelphia kite" experiment,¹¹ but its systematic study started only with the 1844 ice pail experiment by Michael Faraday. Several versions of this experiment are still performed today, and not only for demonstration purposes.¹² The majority of current research on tribo-electrification is aimed at solving engineering problems, with limited research devoted at clarifying its mechanism and harnessing its potential in chemistry. For example engineers, and to a lesser degree material scientists,¹³⁻¹⁴ are familiar with the triboelectric series,¹⁵ which are empirical tables that rank materials based on their propensity to develop

statics. When two different materials are contacted against each other, the material higher in the series is likely to gain a positive charge, while the material lower down the series will likely gain a negative charge. Charges on insulators cannot easily move, and are often long-lived. Thus, insulators charge more strongly than metals and semiconductors, and occupy top and bottom positions of the series. Moreover, both positive and negative charges can coexist at different locations of the same surface.³ Importantly, the empirical information on surface charging and reactivity contained in these ordered series has yet to be harvested by chemists.

While the study of triboelectricity remains an engineering-dominated field, several of the recent conceptual advances towards a correct and complete understanding of the mechanism by which two non-conductors gain a net electrical charge are largely due to chemical research.⁴⁻⁵ Studies of the chemical aspects of static electricity are rapidly expanding, but still in their infancy.¹⁶⁻¹⁹ For example evidence of thermodynamic²⁰ and kinetic^{16-17, 21-22} effects on chemical bonding by directional static electric fields have only been published in the last ten years. Static electricity affects the kinetics of non-redox and non-polar reactions performed on single molecule, around droplets,^{19, 23-26} or in monolayer systems,^{16, 21} but scaling up of this concept towards a practical scale still faces several major technical

Figure 1. Electronic states at the interface between a metal electrode and a redox couple A/B in solution at equal concentrations of the electroactive species. The applied potential lifting or lowering E_F above or below E_{eq} corresponds to electro-reduction (a) and electro-oxidation (b) reactions.



lenges.¹⁶ On the contrary, as we will outline in this article, there are relatively fewer hurdles to using surface charges of insulating objects to assist heterogeneous redox reactivity.^{2, 4-5}

Liu and Bard were the first to demonstrate electrochemistry at statically charged insulators.² In 2008 they showed that contact electrification produces highly energetic electrons on tribocharged PTFE (polytetrafluoroethylene), capable, for example, of prompting hydrogen evolution and electrochemiluminescent reactions.² The authors suggested that the charge carriers were free electrons. More recently, a link between the magnitude of redox work delivered by a statically charged insulator and the stability of its charged plastic fragments was established.⁴ This work indicated that instead the transfer of charged polymer fragments between surfaces occurs during the triboelectrification process. This marked the beginning of a constructive debate over the nature of the charge carriers involved in contact electrification, which led to several groups entering this blossoming area of chemical research.

Despite the contact charging phenomenon being very common, those who have spent time experimenting on it will appreciate its complexity. For instance mechanical factors cannot be taken lightly; surface deformations,¹ material transfer^{5, 27} and generation of heat, all play a role. Further, the exact chemical details of the surfaces involved are important,²⁸ and so are the participation of ions derived from water²⁹⁻³⁰ and from gas dissolution.³¹ The material's shape will affect the coulomb readings measured by a Faraday cup. This change is reversible, and it was used to point out the likelihood of charged plastics ionising surrounding air molecules.¹² This is in line with published data indicating

that the magnitude of tribocharging under inert atmosphere can be significantly diminished or augmented.³² For example, in 2018, Grzybowski and co-workers observed the magnitude of charging developed on polymers by contact-electrification to be dependent not only on the tribocharged material, but also on the substrate that was used to support the polymer.³³ Charges measured on a polymer are dependent on the conductivity of doped silicon that supported the polymer backside but in fact never directly contacted the charge-separating interface. It was suggested that a conductive support could decrease charges on the polymers by arc discharge through the surrounding gas. Similarly, recent experiments have revealed the influence of atmosphere on contact charging, as well as on charge dissipation, when solid CO_2 was rubbed against dielectrics.³² Faraday cup data showed that tribocharging is diminished under argon (by a factor of 1.6), and that for PDMS, PTFE, and PVC samples handled in argon only 34, 52, and 90 % (respectively) of their statics has dissipated 20 s after their separation from the CO_2 surface. For the same systems (plastic- CO_2) a faster decay is observed in air, where 85, 91, and 96 % of the negative charges are lost over the same period of time. The dielectric strength of air (3 kV mm^{-1}) is six times larger than that of argon (0.5 kV mm^{-1}), and therefore these data are consistent with an atmosphere of high dielectric strength destabilising the charged systems.

Surface water is known to play a role in the electrification of dielectrics. It is a source of H^+ and OH^- and it is involved in both the charge generation as well as charge dissipation processes.³⁰ As a notable example, contact charging experiments in a water-free environment under a highly non-polar liquid (paraffin oil), showed that even though water is not essential for charge separation to occur, the magnitude of charging is smaller than that observed in air with water traces present.³⁴ Regarding the effect of water on the charge dissipation process, this is highly debated. Some reports indicate that a higher ambient humidity speeds-up charge decay,³⁰ other groups put forward data indicating that water can help stabilizing surface charges.³⁴ The second view is underlined by the known ability of polymers to harbor surface water layers, in which charges can be stabilized/solvated on dielectrics.

All in all, it remains difficult to obtain a coherent and complete picture of the charging part of the phenomenon. It is precisely in this context that triboelectrochemistry has become extremely valuable. The purpose of this perspective is to outline the current understanding and challenges towards harnessing the electrochemical reactivity of tribocharged insulators.

2. STATIC ELECTRICITY: CHARGE AND ELECTROSTATIC POTENTIAL MEASUREMENTS

The movement, or transfer, of electrons is central to our understanding and steering of chemical reactivity. As shown in Figure 1, electrons will move spontaneously from high to low energy levels. Changes to the potential applied to a metallic electrode induces changes to the average electrochemical potential of electrons (Fermi level, E_F) in the solid. The

position of E_F relative to the energy levels of donors and acceptors found on the solution side of the interface, as characterized by an equilibrium potential (E_{eq}), will define the net direction of the charge transfer reaction at the solid-liquid interface. For example, raising E_F will favour the reduction of the species A into B, as result from electrons transferring from an occupied state on the electrode to an empty state on the species A (Figure 1a). The opposite, that is the transfer from an occupied level on B, to an empty state on the electrode, represents the oxidation of B (Figure 1b). For metals and semiconductors, E_F is raised or lowered at will by changing the voltage between the electrode and a suitable reference.³⁵ In insulators, E_F falls within a forbidden gap, and therefore no longer represents a real energy level accessible to electrons. Furthermore, in an electrical insulator E_F cannot be lifted or lowered to alter at will the oxidizing or reducing power of the material. That is, bulk electrical properties, such as E_F are of little use to describe redox reactivity of insulators. More relevant are two surface properties: the net number of elementary charges localized by the surface, and its work function (for insulators a “working” definition of work function is probably better phrased as the first ionization energy of the material).

2.1 Faraday Cup Measurements of Static Charges

The Faraday cup, also known as the Faraday pail, is the most widely used instrument for the measurement of static charges,^{4, 32} and it is the pillar of any laboratory interested in electrostatics. It has the advantages of simplicity, accuracy, precision, low-cost, and it is suitable for both solid and liquid samples. The Faraday cup is named after its inventor, Michael Faraday, and is routinely used as an aerosol analyzer,³⁶ and for the analysis of tribocharged powders and pharmaceutical granules.³⁷ A common version consists of two metal cups isolated from each other. One cup is accessible to an electrometer and houses the sample, while the other acts as an outer shield. The precision of commercial Faraday cup units is as good as 1 pC, the equivalent of only 10^6 – 10^7 elementary charges. This is a remarkable figure, when for example compared against the detection limit of an XPS measurement, which is around 10^{13} – 10^{14} atoms/cm². One of the successes brought about by simple Faraday cup readings is the establishment of the triboelectric series, which is used to predict the sign and extent of the static electrification likely to develop upon contact and separation of different dielectrics.

The measurement is simple, but not free from limitations. A first cautionary note is that the charge measured by a Faraday cup is the net sample’s charge (sum of its negative and positive charges), meaning for example that a small net charge reading does not exclude the simultaneous presence of much larger amounts of negative and positive charges of similar magnitude. A direct implication of this aspect has only emerged recently, when surface probe measurements proved that charge densities in any microscopic charged domain could be up to 100 times greater than the net charge measured on the entire surface.³ That is, while each contact electrified piece develops a net charge of either positive or

negative polarity, the surface can support a random “mosaic” of oppositely charged regions of nanoscopic dimensions. The discovery of this mosaic effect suggests that much more material is transferred during the contact electrification process than was previously thought.³⁸ A second aspect of this seemingly simple measurement warrants attention. Based on the concept of a triboelectric series, one would not expect any net charge to develop by rubbing two chemically identical materials. However, this is not the case. Rubbing two pieces of the same material leads to static electricity.^{39–40} This observation is mirrored by a related fact, that is, different formulations of a given polymer, such as polyethylene terephthalate in the form of either Mylar or Ertalyte,^{8, 15} take up different positions in the triboelectric series. This indicates that mechanochemical aspects underlie contact electrification,^{41–42} including substrate softness, adhesion and roughness.⁵

Finally, to further complicate this deceptively simple charge measurement, Soh and co-workers recently showed that changing the shape of a statically charged object, while it is kept inside the pail, affects the net coulomb reading.^{12, 43} Bending a charged plastic sample causes a charge drop in the range of 0.05–0.1 nC (ca. 10% of the total charge). This change is reversible, and when the bent sample is returned to its extended shape the charge reading picks up again. The mechanism the author proposed involves ionization of surrounding air molecules, which immediately indicates that strict environmental controls are necessary when measuring small charge levels, and highlights the challenges in ensuring the lab-to-lab reproducibility of Faraday cup measurements.

2.2 Potential Difference: Kelvin Probe Methods

Arguably, developments in the Kelvin probe force microscopy (KPFM) technique have been a major factor in advancing our understanding of contact charging.^{3, 38} KPFM, first reported in 1991, is a non-contact AFM implementation of the technique proposed in the nineteenth century by Lord Kelvin.⁴⁴ KPFM measures the surface potential difference between materials, with lateral resolution below 50 nm and potential resolution below 10 mV, all without contact. KPFM uses a vibrating tip to sense the surface potential difference between the sample and the probe, but unlike its macroscopic counterpart, in KPFM a conductive AFM tip is moved at a constant topographic distance over the sample. The tip-sample system can then be seen as a capacitor, and the electrical force between tip and sample is the capacitor gradient of potential energy. The voltage between tip and sample is modulated, and the corresponding electric force is measured. Using the lock-in technique, and by recording the voltage that nulls the modulated component of the force signal, the work function difference is measured with high spatial resolution.

KPFM measurements make it possible to map the electrostatic potential on the surface of insulators.³⁸ As mentioned in the previous section, evidence for the existence of positive and negative domains, within a sample of an overall net polarity, were first obtained by KPFM. Through KPFM analysis of PDMS (polydimethylsiloxane) surfaces, in 2011

Grzybowski and co-workers demonstrated that when two polymers are pressed together, and then separated (Figure 2a), at the nanoscopic level material transfer accompanies charge exchange.³ The authors demonstrated that a tribocharged sample is best described as an irregular “mosaic” of nanoscopic regions of opposite charge polarity. The net charge of a macroscopic sample is the arithmetic sum of these positive and negative domains mapped by KPFM (Figure 2b). Figure 2c shows a typical linear potential scan, which fits well to the potential calculated for two oppositely charged surface “patches”, each containing ca. 500 elementary charges of the same polarity. The authors suggest that the surface charge density is approximately one elementary charge per $\sim 10 \text{ nm}^2$; that is, or of the order of mC/cm^2 . In essence, the mosaic model by Grzybowski, depicted in Figure 2a, has revealed that charging is not a rare event, affecting for example as few surface groups as one in 10000,³ but

it is likely to be as extensive as one charge for every hundred surface groups.

3. WHAT ARE THE CHARGE-CARRYING SPECIES ACCOUNTING FOR THE CHARGING AND REDOX REACTIVITY OF INSULATORS?

What are the charge-carrying species that allow insulators to become charged? And to what extent do charged surface entities drive redox reactivity? Conclusive answers to these questions are still lacking, but arguably finding answers to the second question will help to address the first.¹⁻² Between 2008 and 2020, a series of reports begun to show that negatively charged plastics could promote redox reactions, including reduction of

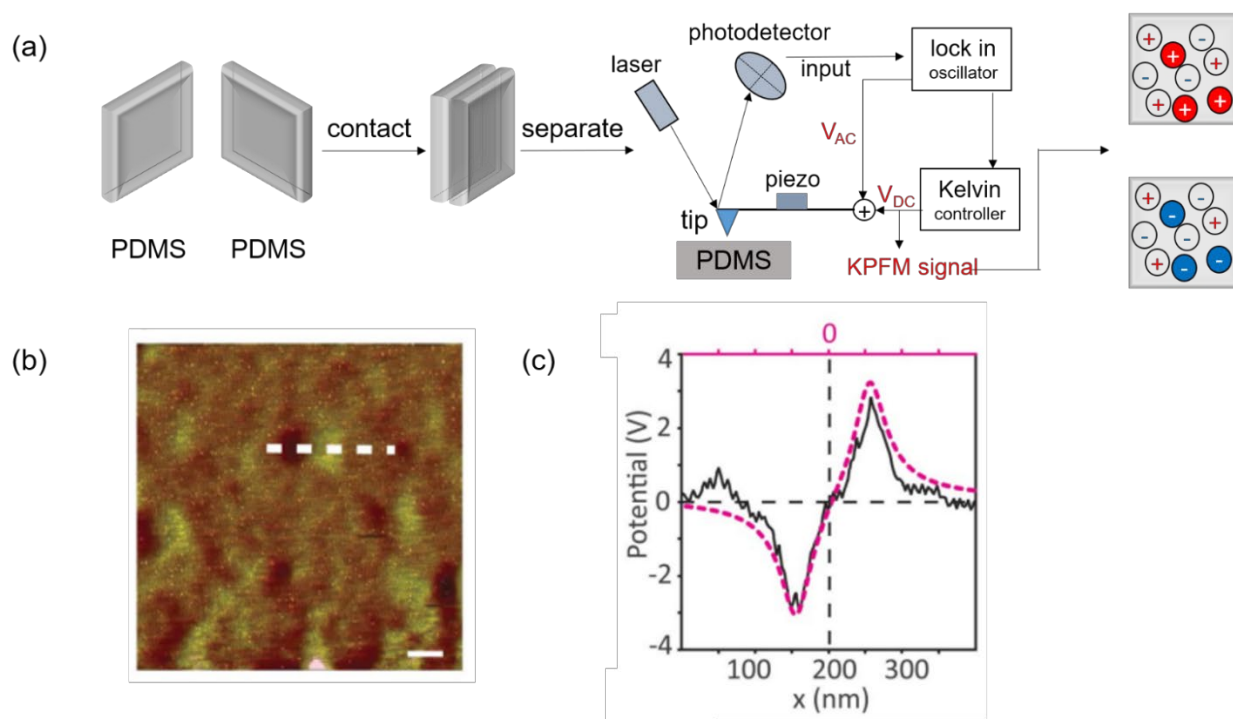


Figure 2. (a) Contact charging, and KPFM mapping, of PDMS samples. The two samples develop a mosaic-like pattern of nanoscopic charged-domains that carry a roughly equal net charge of opposite sign.³ (b) A representative KPFM potential. Scale bar is 100 nm. The white dashed line corresponds indicate the sampling geometry corresponding to the potential profile shown in (c) (black trace). The red, dotted curve in (c) is a calculated potential profile, sampled at $\sim 100 \text{ nm}$ above the surface at a location presenting two oppositely charged, nearby “islands.” Theoretical potential fits the experimental profile assuming that each of the nanoscopic islands comprises ~ 500 elementary charges (corresponding to surface charge $\sim \text{mC}/\text{cm}^2$). (b-c) Adapted with permission from ref 3. Copyright 2011 American Association for the Advancement of Science.

organic and inorganic molecules, hydrogen evolution, and electrochemiluminescent reactions.² The reductive entities were initially very cautiously defined as “cryptoelectrons”,² that is, electrons residing in high-energy states on, or near, the polymer surface. A series of options was left open regarding the nature of these putative high-energy states, which, in the words of the authors, could include “impurities or additives in the polymer, reactive end groups of the

polymers, unique states of polymer chains or surface states induced by the mechanical breakage of the bonds”.¹

At present there is growing evidence against the transfer of free electrons being the sole mechanism responsible for statics. For instance, after their tribocharging, not only can negatively charged samples, such as PTFE, reduce Ag^+ and Au^+ ions, but the same outcome can be achieved with a net-positive nylon sample.⁴ Further, the extent of redox work

delivered by a statically charged surface scales in proportion to the amount of plastic material that is exchanged upon charging.⁵ Several authors have recently demonstrated this.^{1, 27, 45}

In the following sections we seek to establish what is known unambiguously about the nature of the charge carriers, and in the case of contrasting views, we will try to define which assumptions underlie them.

3.1 Electrochemical Reactions on Electrical Insulators: Charged Surface States on Insulators

For metal–metal, metal–semiconductor and semiconductor–semiconductor contacts, the electrification mechanism is relatively well understood: electrons transfer from one material to another to bring Fermi levels into alignment. However, when an insulator contacts another insulator, a semiconductor or a metal, the electrification mechanism becomes very complicated, and often controversial. The interfacial electron transfer (if there is any) is believed to be facilitated by surface states (electronic states at the surface) on the insulator.²¹ To complicate things further, surface states are highly sensitive to the environment, sample preparation and sample history. Additionally, quantitative measurements of electronic charges on the surface of an insulator can be easily masked, partially or fully, by physically adsorbed ions. To specifically minimise adventitious adsorption effects, early studies of contact electrification were carried out under high vacuum, on plastic samples that were broken, so to expose a fresh surface in a clean and controlled environment. In these studies a sharp metal probe was then gently brought in contact with the freshly cleaved surface, with normal and lateral contact forces minimized so as to avoid as much as possible material transfer.⁴⁶ These vacuum studies of metal–insulator contacts revealed a linear relationship between the charge developed on an insulating polymer and the metal’s work function, proving the involvement of electron transfer in contact electrification.²¹

Electron transfer is therefore the prevalent mode of charge transfer when a metal is touching an insulator, and the direction of the electron movement is defined by differences in work functions. However, for insulators the usual definition of workfunction, that is the energy difference between an unbound electron and one on the surface (with surface energy generally being that of an electron at the top of the conduction band), loses physical meaning, and cannot be directly applied to predict directions of charge transfer in contact electrification involving two insulators. As mentioned above, for insulators a “working” definition of work function is probably better phrased as the first ionization energy of the material (vide infra). When two identical insulators come into contact, electron transfer may also occur given that the two surfaces may be different in terms of occupancy of their surface states. Significantly, reductive species are produced in contact electrification, as demonstrated by a range of redox reactions carried out on triboelectrically charged plastic surfaces.^{2, 7, 47}

One such example is the reduction of Cu^{2+} ions to metallic copper by PTFE surfaces charged against Lucite (polymethylmethacrylate).² After immersion and removal

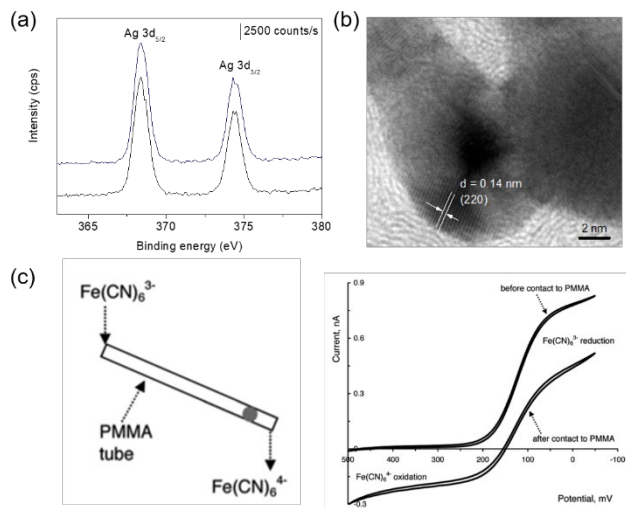


Figure 3. (a) XPS analysis of the PDMS (840-5541, RS Components Australia®) sample indicates a Ag 3d spin–orbit-split emissions consistent with literature values for metallic silver (Ag 3d_{3/2} and Ag3d_{5/2} at 374.4 eV and 368.4 eV, respectively) at the beginning of the measurement (black trace), and after a 5 min of exposure to the X-ray source (blue trace), showing no links between silver reduction and XPS analysis times. Prior to XPS analysis the tribocharged sample was immersed, and then withdrawn, from an aqueous 50 mM AgNO₃ solution. (b) HRTEM image indicating a lattice spacing of 0.14 nm, corresponding to fcc Ag particles formed upon redox reactions guided by tribocharged plastic. Diffraction data indicate the spacing of (220) lattice planes.⁴ (c) Tribocharged poly(methyl methacrylate) (PMMA) can reduce soluble Fe(CN)₆³⁻ into Fe(CN)₆⁴⁻. Cyclic voltammograms (10 mV/s) acquired with platinum ultramicroelectrodes in an aqueous solution of 0.2 mM K₃[Fe(CN)₆] before and after the solution was passed through a PMMA tube, as illustrated by the diagram on the left.⁷ (b) Adapted with permission from ref. 4. Copyright 2019 American Chemical Society. (c) Adapted with permission from ref. 7. Copyright 2009 American Chemical Society.

of the charged PTFE from a copper sulphate solution, based on the drop in the solution optical absorbance (following the peak maxima at about 810 nm), Liu and Bard concluded in favour of the insulator being redox active. From the change in the concentration of Cu^{2+} ions after the PTFE immersion, the authors estimated that an average charge density of about $8 \times 10^{14} \text{ cm}^{-2}$ (geometric area) was present on the PTFE rod before its discharge in solution.

These initial studies, supporting the notion of electron transfer reactions occurring on the surface of statically charged insulators, were however not received without scientific scepticism. For example, the metal deposition on tribocharged PTFE surfaces was criticised by Piperno *et al.*,⁴⁸ who suggested that XPS photoelectrons caused the reduction of metal ions to metal. Nonetheless, there are several data, published and unpublished, indicating that charged plastics undoubtedly are the carrier of reducing equivalents (Figure 3a–c).^{4, 49} For example, the time-resolved XPS data, that is, data acquired at the beginning of the measurement and after exposure to the X-ray, in Figure 3a shows the same

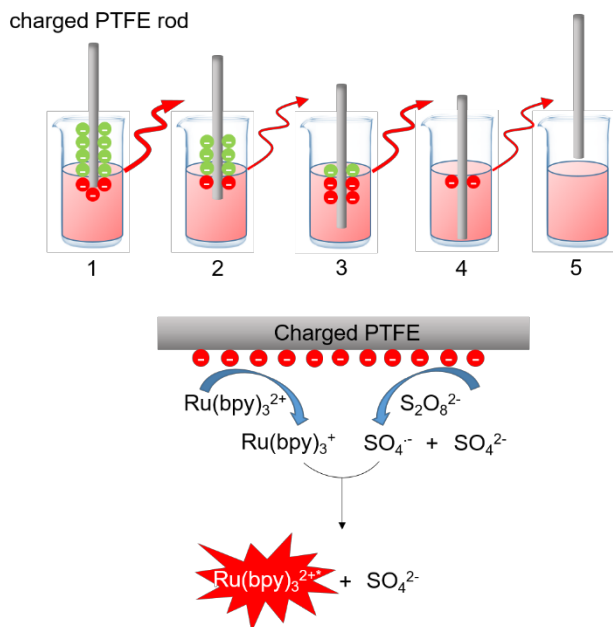


Figure 4. Electrostatic electrochemiluminescence. The surface of a negatively charged PTFE rod triggers a transient electrochemiluminescence output when gradually immersed into an acetonitrile/water (1:1) solution containing 2.5 mM $S_2O_8^{2-}$ and 0.25 mM $Ru(bpy)_3^{2+}$.² The intensity of the 620 nm emission results from the decay of excited-state $Ru(bpy)_3^{2+*}$ and tracks the immersion and withdrawal sequence depicted in figure.

position and similar intensity of Ag signal (two Ag 3d spin-orbit-split XPS emissions of spectral position consistent with literature values for metallic silver). These data were obtained by reducing Ag^+ ions on tribocharged poly(vinyl chloride) (PVC). If the XPS electrons are causing reductions, more exposure time will lead to more reduction, but this is not observed. But even more importantly, the conclusion that plastics can mediate redox work is supported by other types of experiments. The key ones are high-resolution transmission electron microscopy (HRTEM), electrochemical measurements, and the detection of electrochemiluminescent bursts around tribocharged plastics. Firstly, reduced metallic nanoparticles are detected by HRTEM⁴ upon discharge of plastics in metallic silver solutions (Figure 3b). Secondly, cyclic voltammograms at ultramicroelectrodes, such as those in Figure 3c, reveal a drop in the bulk concentration of $Fe(CN)_6^{3-}$ ions when the solution is repetitively flowed on a tribocharged surface.⁷ Nonetheless, several practical questions remain open concerning the effect of material type, temperature, environment, roughness, adhesion and contact force effects on charge densities and surface potentials.^{5,27}

The early experiments by Liu and Bard opened a new platform for “single electrode” electrochemistry, that is,

electrochemistry with only the working electrode, and without counter and reference.² To demonstrate the scope of this new concept in which a statically charged surface can act as a solid-state reductant, the authors expanded beyond the deposition of inorganic ions, and reported examples of heterogeneous redox chemistry with conventional soluble couples (e.g. $Fe(CN)_6^{3-}$, Figure 3d), as well as one example of an electrochemiluminescent (ECL) reaction. Figure 4. depicts how the light-emitting redox path of the $Ru(bpy)_3^{2+}/S_2O_8^{2-}$ system,² normally triggered by an external bias on metallic electrodes, can be achieved by harnessing the Faradaic reactivity of charged PTFE samples. Using charged insulators to produce light-emitting excited states represents a completely new path to ECL, termed electrostatic chemiluminescence.² As depicted schematically in Figure 4, at first only the extremity of a charged PTFE rod is immersed in the $Ru(bpy)_3^{2+}$ and $S_2O_8^{2-}$ solution (point 1 in Figure 4). A transient red luminescent emission rises quickly when the PTFE rod is first wetted. The remaining dry portion of the PTFE surface is then gradually immersed (point 2) and a near steady-state ECL is measured for about 1 min. At point 3, the PTFE rod is moved more rapidly into the solution, leading to a second luminescent spike followed by a light-emission decay (point 4). When the rod was removed from the solution at point 5, the ECL output dropped to baseline, confirming that the luminescent output was indeed mediated by the charges initially present on the PTFE surface.

“Redox discharge” experiments with non-ionic polymer insulators prove the existence of electrons in contact electrification and support the reductive nature of statically charged plastics. However, contact electrification is a physical process and material transfer undoubtedly occurs. When an ionic polymer contacts a metal, and then is separated from it, polymer-derived ions are transferred to the metal surface. Since the two surfaces in contact are not atomically flat, the material transferred is randomly distributed over the metal surface.³⁹ This scenario is for example in line with the experimental charge distribution across a metal surface after this has been contacted with dielectrics stamps with protruding features. As measured by KPFM, gold surfaces after contact and separation from a poly(dimethylsiloxane) (PDMS) stamp of a specific 2D pattern, develop similarly arranged 2D charge patterns.⁶ If electrons were transferred, instead of polymeric material, these electrons would arguably spread homogeneously over the gold substrate, instead of orderly congregating in patterns. Moreover, as mentioned earlier, contact between chemically identical materials generates a degree of static charges.^{39, 50} Identical materials have identical (macroscopic) work function, and therefore no electronic driving force exists for the electron transfer. On the other hand, a mechanical contact cannot be completely symmetrical at the

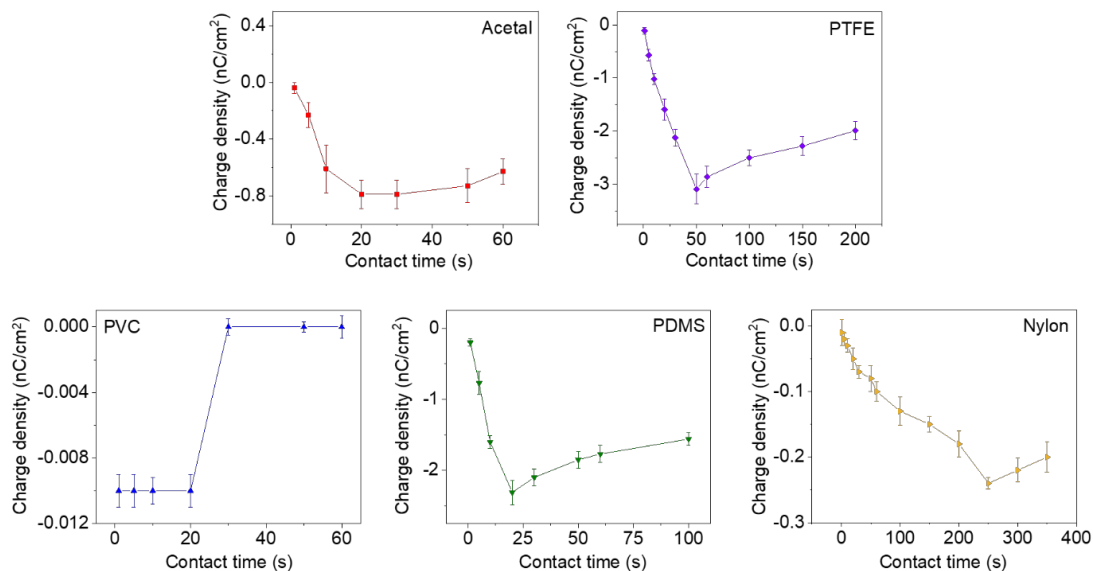


Figure 5. Triboelectrification of non-ionic plastics: evolution of charge density with contact time. For several polymers (acetal, PTFE, PVC, PDMS, nylon), charging magnitude initially increased, reached a maximum value, and then dropped.⁴⁰ Adapted with permission from ref. 40. Copyright 2020 Royal Society of Chemistry.

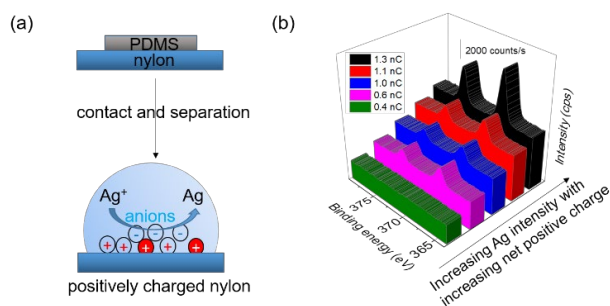


Figure 6. (a) Schematic depiction of the discharge of aqueous silver ions, leading to metallic silver, on the surface of positively charged nylon. Due to a “mosaic” nature of charged domains on a tribocharged dielectric, even a net-positive sample has negatively charged surface domains.⁴ (b) Narrow scans of the Ag 3d region for tribocharged nylon samples that were discharged by means of immersion into a 5.0×10^{-2} M aqueous solution of silver nitrate.

microscopic level, and therefore asymmetric material exchange is reasonably expected, even between chemically identical materials. For example, recent experiments have shown that in homo-systems (such as PTFE contacted against with PTFE), charge densities reach the maximum value after a material-specific contact time. Attempts to charge a sample beyond its peak value leads to a progressive drop in charge (Figure 5). The authors propose that this drop results both from the electrostatically driven segregation of polymer ionic fragments, as well as from the discharge of unstable fragments by dielectric breakdown when a sufficiently high surface charge density is reached.⁴⁰

The last paragraph clearly illustrates how difficult it is to reproduce a given charge density on an insulator. The conditioning and history of the sample, such as, washing methods or adsorption of contaminants from air, can have a severe impact on the charging of insulators.⁵¹ Interface states, which are often appear inside the energy gap and are commonly used to characterize the surface electronic properties, are very sensitive to the environment. Interface states on one surface can donate or accept electrons to or from other interface states existed on another surface when the two surfaces contact with each other. Interface states, which are extensively studied in semiconductors, occur on insulators as well. When insulators are involved in contact electrification, charge transfer occurs between the two surfaces and surface states are unavoidably involved, while E_f is pretty much irrelevant. Low-lying empty states readily accept electrons, while high energy filled surface states would be eager to give electrons away. In essence, while the discharge of a statically charged insulator can fall under the umbrella of electrochemistry, the charging side of the phenomena falls definitely under the domain of mechanochemistry.^{41-42, 52} Transfer of charged material upon contact, as well as energetic considerations of the redox reactivity of these charged plastic fragments, are discussed in the next section.

3.2 The Redox Work delivered by a Statically Charged Object is a Material-Specific Property

When two polymer surfaces are brought into intimate contact, and then macroscopically separated from one another, a degree of chemical bond rupture is expected to occur, resulting in the formation of ions and radicals. It is proposed that contact charging originates from the transfer of weakly bound ions (or radicals), leaving behind strongly bound ions (radicals).^{4, 53} A mobile ion has freedom to transfer

from one surface to another, because it has a counter ion of opposite electrification.³⁴ Baytekin and co-workers showed that charge exchange takes place between two non-ionic polymers in the total absence of water. However, while these results cannot exclude hydroxide adsorption when water is present, they undoubtedly highlight that different tribocharging mechanisms are operational under different environmental conditions.

One recent study has revealed a relationship between the net negative charge of a plastic sample and the amount of solution metal ions reduced to metallic particles, with the coefficient of proportionality (redox work vs plastic's charge) reflecting the balance between the plastic electron affinity (stability of its anionic fragments) and ionization energy (stability of its cationic fragments).⁴ These data are an additional piece of evidence in support of ionic plastic fragments being a charge-carrying species in triboelectricity. Further, they show that unless electron affinities and ionization energies are accounted for, the total Coulombs measured for a statically charged sample are a poor indicator of the heterogeneous electrochemical work that can be harvested.⁴ The coefficient of proportionality between metal ions being discharged on the surface and charging magnitude is therefore a material-specific property. Moreover, the same study showed that surfaces bearing a net positive charge can also promote reduction reactions.^{1, 4} Silver deposition proceeds over nylon samples that bear a net-positive charge after contact with PDMS (Figure 6a). XPS data in Figure 6b show that the discharge of aqueous silver ions on the charged polyamide surface occurs in proportion to the sample's net positive charge. This observation further reinforces on the simultaneous presence, on the surface of a tribocharged insulator, of both positive and negative surface domains.

3.3 Radicals on the Surface of Charged Insulators

With some notable exceptions, such as nitroxides⁵⁴⁻⁵⁵ and Blatter radicals,⁵⁶ unpaired electrons generally result in large chemical reactivity. Recent results have shown that when two insulators undergo contact and separation, not only are ions formed but also radicals.¹ Also, quantum mechanical calculations predict that charges on organic polymers can be stabilized by radicals on nearby polymer chains and it is because of the formation of intermolecular odd-electron, two-center bonds with possible concomitant spin density redistribution. Therefore, when radicals are generated upon contact charging, both the radicals and static charges are stabilized.⁵⁷ These reports indicate that electrochemical reactions driven by electrified dielectric surfaces involve mechanoradicals.

One such example is experiments in which Baytekin and co-workers used contact-electrified surfaces to bleach solutions of redox-active dyes.¹ Both positively and negatively charged samples were immersed in aqueous solutions of Neutral Red (NR, 3-amino-6-dimethylamino-2-methylphenazine hydrochloride) resulting in the bleaching of the organic dye (Figure 7a). The authors used their findings to argue against the transfer of free electrons. If the ob-

served bleaching was due to an electron-mediated reduction, the extent of this reduction would increase with decreasing pH (based on the dependency of the dye standard redox potential on pH). On the contrary, for all dielectrics tested, and regardless of the sample's polarity, the extent of bleaching increased with increasing pH (Figure 7b). Further, the authors tested dyes of different redox potentials,

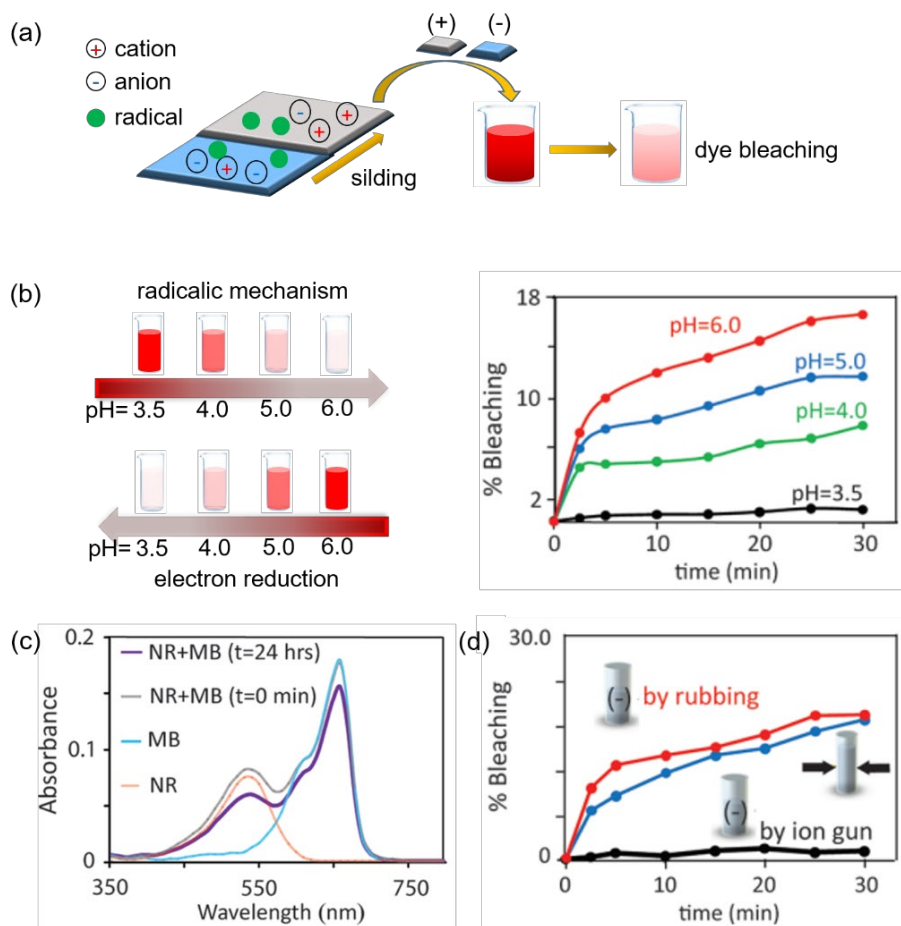


Figure 7. (a) Polymer samples, first charged by sliding or pressure, where then immersed into aqueous solutions of Neutral Red.¹ Both the negatively charged (-) and the positively charged (+) samples bleached the dye solution. (b) Depiction of the bleaching trends expected for either the radical or the redox bleaching of Neutral Red (left). Under redox considerations, the colouring of the Neutral Red solution would decrease with decreasing pH. The experimental trend indicates colour decreasing with increasing pH. (c) UV-vis spectral evidence of bleaching of an equimolar mixture of Neutral Red and Methylene Blue after contact with negatively charged PTFE samples at different times (0 min and 24 h). (d) % Bleaching of aqueous Neutral Red poured into hollow dielectric tubes: (red curve) the inner surface of the tube was charged to a net-negative Coulombs value by rubbing it against a polystyrene (PS) rod; (blue curve) the tube was compressed from the outside, but its inner surface was not contacted by any material and was therefore uncharged; and (black curve) the inner surface of the tube was charged by an ion gun and not touched by another dielectric.¹ (b-d) Adapted with permission from ref. 1. Copyright 2012 American Chemical Society.

immersing charged plastics into mixtures of NR and Methylene Blue (MB). According to differences in their standard electrode potentials (for MB, 0.108 V at pH 5; for NR, -0.198 V at pH 5), if bleaching involved a redox process, the two dyes would be reduced according to their standard electrode potentials. However, the authors observed that both dyes were bleached with comparable speed, hence triboelectricity appears not to follow normal trends of redox reactivity (Figure 7c). We note however that Nernst equation describes the equilibrium position of a redox reaction, while the speed of charge transfer involves kinetic considerations. There is, perhaps, not yet sufficient understanding of the appropriate kinetic model for redox reactions involving plastics to enable definitive conclusions from these types of experiments. This is definitely an open question, and one that warrants immediate attention. The experimental challenge

here is that one would have to find a systematic method for changing the redox potential of the plastic electrode and then measure changes in redox rates. Furthermore, the authors' consideration of pH effects – that is, the observation of bleaching increasing with increasing pH – did not account for any plausible difference in the availability of hydroxide ions at the hydrophobic-water interface, relative to bulk values.⁵⁸ In essence, at this stage, we believe that the principal merit of these bleaching experiments is to show that charged plastics are redox-active.

Further, a control experiment in which polymers were charged by an ion gun (Figure 7d), showed that dielectrics charged in this fashion are unable to drive any of the redox reactions tested (Figure 7d, black curve). In another experiment, the charged dielectrics were immersed into degassed acetonitrile solutions containing the radical scavenger

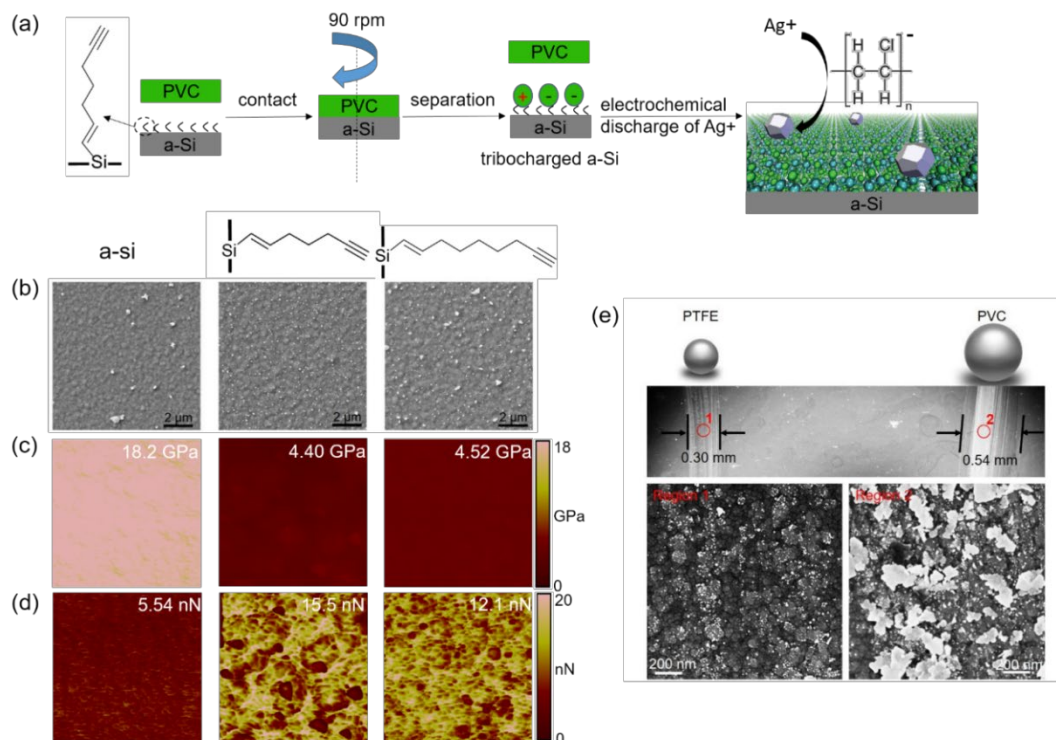


Figure 8. (a) Schematics for the electrodeposition of silver nanoparticles on tribocharged undoped amorphous silicon (a-Si) samples. (b) SEM images of Ag nanoparticles reduced on charged a-Si, a-Si modified with 1,6-heptadiyne and a-Si modified with 1,8-nonadiyne. (c) Atomic force microscopy PeakForce™ QNM™ measurements of surface hardness (DMT modulus) and (d) adhesion for a-Si, a-Si modified with 1,6-heptadiyne and a-Si modified with 1,8-nonadiyne samples. (e) SEM images of silver particles patterns generated by reducing silver ions on a-Si samples tribocharged by rolling PVC and PTFE spheres. The pattern is developed by immersing tribocharged samples in AgNO₃ aqueous solutions. Changes to particle densities and sizes are shown in the SEM images marked as region 1 (small particles of width of 20 nm) and region 2 (larger particles of up to 200 nm).⁵ Adapted with permission from ref. 5. Copyright 2019 American Chemical Society.

DPPH (2,2-diphenyl-1-picrylhydrazyl), and the numbers of mechanoradicals created per unit of area were estimated by monitoring the decrease in the solution absorbance. The number of these mechanoradicals (10^{14} cm^{-2}) was close to the previously estimated numbers of cryptoelectrons.² These findings indicate that radicals generated upon contact and friction are probably involved in the reactivity of charged dielectrics.

4. TRIBOELECTROCHEMISTRY OF DYNAMIC DIELECTRIC-SEMICONDUCTOR CONTACTS

Research on contact electrification between plastics and semiconductors is limited. One recent work on the topic has shown that charged material transferred from a polymer to a semiconductor is the effector of the redox reactivity observed on the charged semiconductor. This effect implies localised tribocharging, which could be used in a new form of redox lithography. An example of such surface redox reactivity, induced by contact electrification between organic monolayer-modified silicon wafers and PVC (polyvinyl chloride), is shown in Figure 8.⁵ The schematics of the process that leads to the reductive nucleation of silver nanoparticles on chemically modified, and then tribocharged, amor-

phous silicon is shown in Figure 8a. Using established covalent Si-C monolayer chemistries, Zhang and co-workers systematically varied surface hardness and adhesion of silicon surfaces. This type of surface chemistry/triboelectricity experiment reveals a link between surface adhesion, hardness, and the amount of static charges that build up on an insulator. The subsequent magnitude of redox work delivered by the tribocharged silicon surface, as a function of both its adhesion and its hardness, is shown in Figure 8b-d. This surface chemistry approach opens doors to mask-free and bias-free patterning of metal nanoparticles on tribocharged photoconductors (Figure 8e). For example, the sample region marked as “region 1” was tribocharged by rolling on it a PTFE sphere, while “region 2” was tribocharged using a PVC sphere (Figure 8e). SEM images show metallic line-shaped patterns matching the trajectory along which the plastic PVC or PTFE spheres had moved. Notable is the difference in particle density and size between the two regions: region 1 had small particles of widths around 20 nm, while region 2 showed larger particles of about 200 nm. An explanation for the difference in the deposit size, between the a-Si/PTFE and a-Si/PVC systems, is that contact-charging with PVC, a material softer and of higher adhesion than PTFE, leads to a more substantial material transfer to

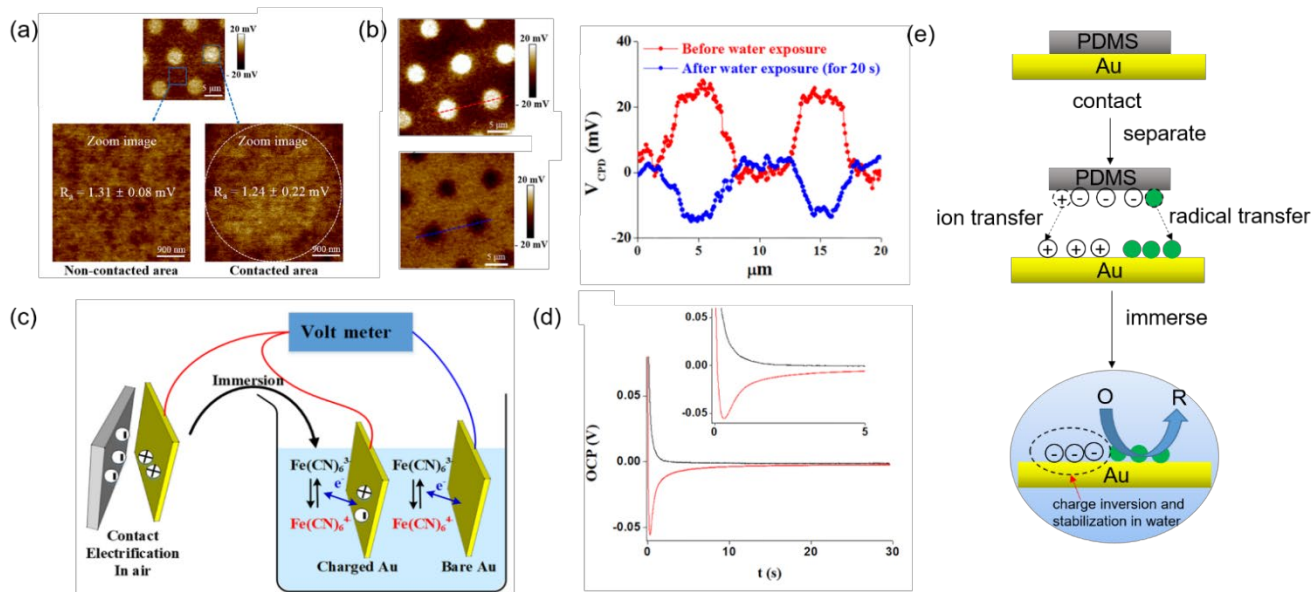


Figure 9. (a) Contact potential difference (VCPD) images of gold surfaces after their contact and separation with PDMS sheets bearing dot-shaped protruding patterns. Larger magnification images with of the KPFM data for the contacted and non-contacted areas, marked by rectangular blue dotted lines. (b) VCPD images (left) of a tribocharged gold surface (charged by contact against PDMS stamps) before (upper) and after water exposure (lower) for 20 s, and line profiles of the VCPD are adapted from red and blue dotted lines (right). (c) Illustration of the experiment aimed at measuring the potential difference between charged and un-charged (bare) gold samples. (d) Plot of the open circuit potential (OCP versus bare Au) vs time for gold samples charged by contact against PDMS (red curve) and for bare Au (black curve). (e) Illustration of the proposed mechanism accounting for the electrification and redox reactivity of charged gold.⁶ (a-d) Adapted with permission from ref. 6. Copyright 2018 American Chemical Society.

a-Si. Furthermore, the observation that metallic particles grow preferentially over surfaces that are relatively soft (low DMT modulus) and highly adhesive, indirectly proves that the triboelectrification of a dielectric-semiconductor dynamic contact is caused by the transfer of ionic fragments from a dielectric to a semiconductor, rather than by the movement of free electrons. This work also points to a surface-chemistry method to maximise tribocharges, with relevance in single-electrode electrochemistry, and outlines a concept suitable for the mask-free and bias-free patterning of metal nanoparticles on insulators and photoconductors. A technically important note is that when replacing highly resistive intrinsic amorphous silicon with crystalline silicon of extremely low doping, for example n-type Si (100) of 0.007–0.013 Ω cm in resistivity, the tribocharged material was unable to mediate redox work. This observation points to the importance of selecting sufficiently resistive semiconductors, or alternatively resorting to photoconductors shielded from light.

5. TRIBOELECTROCHEMISTRY OF DYNAMIC INSULATOR–METAL CONTACTS

For dynamic insulator–metal contacts there is a linear relationship between the charge density created on the polymer and the metal work function. This observation argues strongly in favour of an electron transfer mechanism.⁵⁹ However, this relationship does not always hold, indicating

that more than one mechanism may be operative in the charge generation process.⁶⁰ Triboelectrochemistry driven by contact electrification between metals and dielectrics has been investigated, and a notable example is the work of Yun and co-workers on contacts between gold and polydimethylsiloxane (PDMS) stamps.⁶ The authors charged gold surfaces by contact (and then separation) against PDMS sheets bearing a protruding dot-shaped pattern. The localised charging of the gold surface tracks the geometrical features of the PDMS stamp, as revealed by charging maps obtained by KPFM (Figure 9a). Positive charging localised in regions where the PDMS dots touched the gold, suggesting transfer of ionic plastic fragments from the stamp to the metal. When the positively charged gold surface was then subsequently immersed in water, the polarity of these rounded features was inverted to a negative value (Figure 9b). The mechanism behind this charge inversion is not yet conclusively established, but it is interesting to note that PDMS is in fact located toward the negative end of the triboelectric series, hence the initial positive charge is equally puzzling.

This observation raises the question of whether reduction or oxidation reactions occur on the gold sample upon its immersion into a redox-active solution. The gold open circuit potential (OCP) in $\text{Fe}(\text{CN})_6^{3-}$ solution was used to estimate whether the charged gold could drive mainly oxidations or

reductions (Figure 9c). If the sample was to drive a net oxidation, its OCP would increase to a positive value, while for a reduction, OCP would decrease. As shown in Figure 9d, when the charged gold

is not fully clear at present. This is highly significant, because charges and potentials measured by researchers (by Faraday cup and KPFM) generally refer to a "prior to immersion" dry scenario.

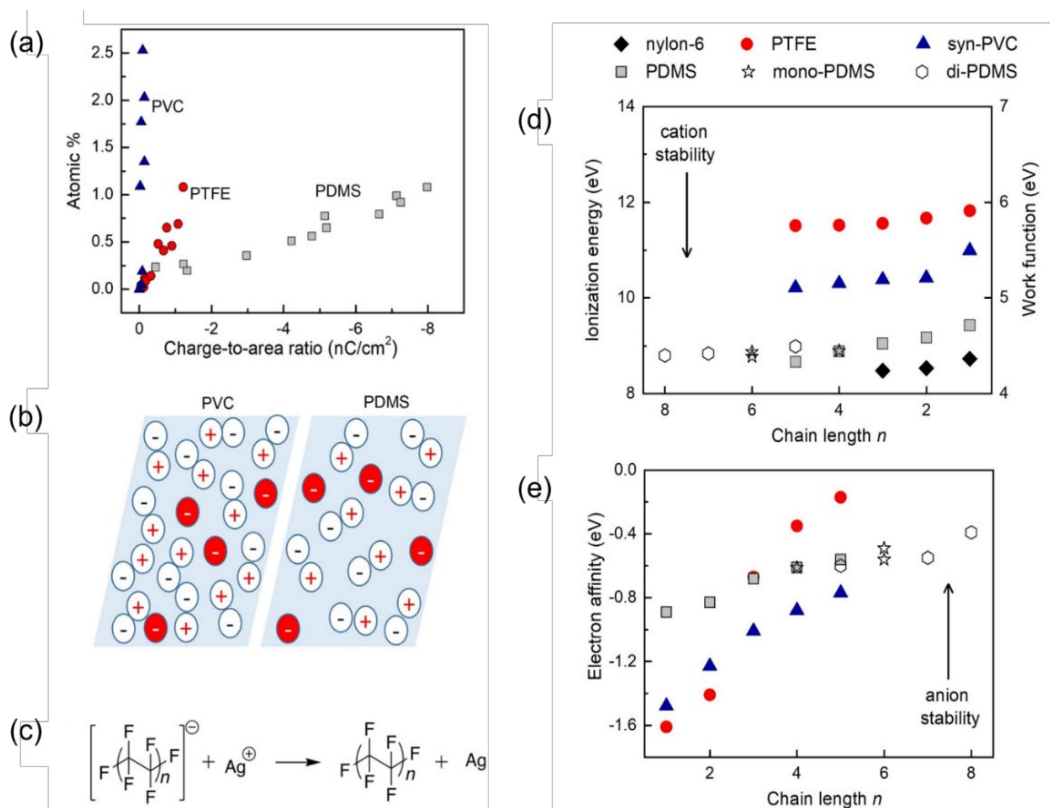


Figure 10. (a) XPS measurements tracking the amount of metallic silver, deposited on plastic samples charged by contact against a glass surface, as function of the plastic sample's initial charge-to-area ratios. (b) Schematic of a "mosaic" ensemble of triboelectric charges on two samples carrying the same net charge. Due to differences in ionization energies, two samples with the same net charge density may have significantly different amounts of negatively charge domains. (c) Depiction of the outer-sphere electron transfer reaction for the reduction of Ag⁺ ions by anionic fragments present on tribocharged PTFE. (d) Computed 298 K ionization energies (IE), and (e) electron affinities (EA) for selected polymers as function of chain lengths.⁴ Adapted with permission from ref 4. Copyright 2019 American Chemical Society.

was immersed in the redox solution, its OCP dramatically decreased, which is ascribed to the reduction of Fe(CN)₆³⁻ to Fe(CN)₆⁴⁻. For gold samples that were immersed in the redox solution, but not charged against PDMS, the OCP moved towards the zero. These OCP results show that charged gold has a more negative potential compared with un-charged gold, indicating that the reduction on its surface is triggered by the charge transfer between surface charged species and Fe(CN)₆³⁻. This demonstrates that the charged gold induces reductions rather than oxidations. Upon separation with PDMS, the adsorbates, including cations and neutral radicals are transferred to the gold surface, yielding a net-positive charge on the sample. When this is immersed in water of aqueous solutions of Fe(CN)₆³⁻, the sample positive charge is inverted to negative. At the same time, radicals with sufficiently high energy drive the reduction reaction. An important observation from these elegant experiments is that net-surface polarity can be inverted by a simple wetting process, although the mechanism of this event

6. MECHANICAL, CHEMICAL, AND AMBIENT FACTORS AFFECTING TRIBOCHARGING AND TRIBOELECTROCHEMICAL RATES

6.1 Mechanical Properties (Softness and Adhesion)

Contact charging of polymers cannot be explained only on the basis of their electronic properties, it requires one to consider the transfer rate of material between the contacting surfaces. The exchange of ions between two contacting polymers,^{4, 32, 53} and the rate of charge generation, relate to mechanical properties of the contacting dielectrics, such as their softness and adhesion.⁵ Recent results from Grzybowski and co-workers have revealed that contact charging involves a spatially inhomogeneous material transfer process.²⁷ With the help of surface characterization techniques, including AFM (to study surface mechanical properties such

as elastic moduli and surface adhesion), XPS (to analyze surface composition), and confocal Raman spectroscopy (to detect changes in the surface composition), the authors have highlighted a relationship between surface hardness and material transfer rates. That is, a relatively soft material will transfer more fragments to a contacting surface.²⁷ Related studies have studied quantitatively the reduction of silver ions on intrinsic amorphous silicon surfaces that are statically charged by contact against plastic polymers (Figure 8),⁵ and shown that softness and adhesion influence the size and densities of nanoparticles generated electrochemically by statics.

6.2 Stability of Cationic and Anionic Polymeric Fragments

Ion transfer is involved in the contact charging and the redox reactivity of ionic fragments present on the surface of charged dielectrics. The energetics of cations and anions derived from the polymer influence both the charge generation as well as its decay over time. Reports on the influence of stability of cations and anions on both contact charging and triboelectrochemistry have been recently published.⁴ An almost linear relationship exists between a plastic sample's net negative charge and the amount of solution metal ions discharged to metallic particles on its surface. The coefficient of proportionality between charge and redox work is linked to the electron affinity (stability of anionic fragments) of the material (Figure 10).⁴ In essence, the maximum magnitude of reductive redox work is not only dependent on the achievable charge density, but is also material-dependent: metallic particles grow to a larger extent over charged dielectrics that yield stable cationic fragments and unstable anionic fragments. For example, for equally stable anions, a lower ionization energy – more stable cations – would account for losing its net negative charge rapidly in air. Therefore, in PVC both the stability of its cations and the instability of its anions – low positive ionization energy and large negative electron affinity – are in line with the faster discharge observed, which leads to PVC mediating larger redox work despite having the smaller net charge (Figure 10a, d, e). This is further evidence in support of triboelectricity being a mosaic of positive and negative tribocharges (Figure 10b).

7. CONCLUSIONS AND OUTLOOK

Our chemical understanding of contact charging has improved significantly over the last two decades. In this perspective we have outlined what is unambiguously known on the electrification of dielectrics, and what is still debated. When contrasting views are presented, we have tried to clarify what these views are based upon. Particular attention has been given to the controversy over the nature of the charge carriers (ions versus electrons) and over what drives the charge transfer. The process of contact charging involving insulators is complex, leading to challenges in the further development of triboelectrochemistry. One of the factors that hampered the initial experimental scrutiny of electrochemistry at insulators was the assumption of a lim-

ited ability of plastic to store surface charges. This was addressed by the seminal 2011 “mosaic” article,³ which succeeded in demonstrating that at the microscopic level charge density can be as high as one elementary charge per ~ 10 nm², or on the order of mC/cm². This value is significantly higher than the net surface charge density measured for a macroscopic electrified polymer in a Faraday cup (generally in the nC/cm² range).

Future improvements in our understanding of the electrostatic charging mechanisms will lead to a range of applications in electroanalytical chemistry, lithography nanotechnology and catalysis. Several proof-of-principle studies of each have been presented in this article. Nonetheless, the following important questions still need to be addressed. Why, in contrast to reduction, have only a limited number of oxidative processes on charged plastics been reported, despite clear evidence that reactive cationic fragments are present on the surface of charged insulators? To what degree does the charge inversion, observed when statically charged objects are wetted, be predictably harnessed, and what are the reaction rates and rate constants for redox reactions on charged dielectrics? This last point has been to date completely overlooked.

One can envision that an improved understanding of the redox reactivity of insulators will help solving the debate over the electronic component (if any) of friction,⁶¹ which is especially timely since a link between friction coefficients and materials electron affinities has recently been demonstrated.⁶² Analogously, there is the expectation that “electrostatic electrochemiluminescence” experiments, such as those reported in 2008 by Bard,² will lead to new analytical/physical chemistry capabilities. For example, electrochemically generated luminescence, triggered transiently at the interface between plastics and water solutions, could be a way of detecting optically the existence of a vacuum layer at the interface between water and a hydrophobic solid.⁶³ A region of decreased solvent density exists at the interface between water and a hydrophobic surface, and is frequently referred to as the hydrophobic gap. However, the presence of a hydrophobic gap has been so far only demonstrated reproducibly by x-ray and neutron reflectivity data of atomically flat silicon and gold substrates. A basic missing piece of information is whether this gap is present on microscopically rough substrates, on substrates with poorly defined chemistries, and whether there is a relationship between nanoscopic water depletion and macroscopic contact angle. Information on the structure of water at interfaces is essential to the understanding of interfacial phenomena,⁶⁴ from charge transfer to self-assembly, but method currently available to probe the buried water–hydrophobic interface requires strict sample preparation. Methods applicable to microscopically rough polymer surfaces, that could be used to link macroscopic water contact angles to the presence or absence of a nanoscopic water gap, are still lacking. In this context, electrochemistry on insulators could provide a solution.

A recent proof-of-concept study used electroluminescence on insulators, charged by falling water droplets, to convert mechanical energy into light energy.⁶⁵ We anticipate a burst of studies focusing on transient light-emitting

reactions driven by the static charges found on the surface of electrical insulators, both for energy harvesting⁶⁶ as well as for fundamental chemical research. For instance, by using light-emitting compounds with an appreciable charge-transfer (CT) character, one could test the spectral tuning by electrostatic forces of widespread, and biologically relevant luciferins (e.g. firefly luciferin⁶⁷). On transparent substrates the presence of a near-surface electrified gap at the solid–liquid interface would open similar possibilities both with biological CT vision pigments such retinal,⁶⁸ as well as with technologically relevant smaller organics such as azulene. These are but of a few of the developing applications of tribocharging in chemistry that are taking us one step further to the Holy Grail^{69,70} of harnessing the electric fields of electrified surfaces and interfaces.

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Notes

The authors declare no competing financial interest.

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