

Electrostatic electrochemistry at insulators

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The identity of charges generated by contact electrification on dielectrics has remained unknown for centuries and the precise determination of the charge density is also a long-standing challenge. Here, electrostatic charges on Teflon (polytetrafluoroethylene) produced by rubbing with Lucite (polymethylmethacrylate) were directly identified as electrons rather than ions by electrochemical (redox) experiments with charged Teflon used as a single electrode in solution causing various chemical reactions: pH increases; hydrogen formation; metal deposition; $\text{Fe}(\text{CN})_6^{3-}$ reduction; and chemiluminescence in the system of Teflon(-)/ $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ (analogous to electrogenerated chemiluminescence). Moreover, copper deposition could be amplified by depositing Pd first in a predetermined pattern, followed by electroless deposition to produce Cu lines. This process could be potentially important for microelectronic and other applications because Teflon has desirable properties including a low dielectric constant and good thermal stability. Charge density was determined using Faraday's law and the significance of electron transfer processes on charged polymers and potentially other insulators have been demonstrated.

Although both contact electrification of insulating materials (dielectrics), such as Teflon and glass¹, and electrochemistry at electronic conductors, such as metals and semiconductors², deal with charged interfaces, they have largely remained distinct fields. The possible chemical effects of electrostatic charge have not been widely studied. Despite its long history³, the charge identity (electron or ion) on rubbed insulators is still poorly understood. Whereas Harper recognized the role of an electron transfer mechanism for metals and semiconductors^{4,5}, on the basis of their relative Fermi level energies, he favoured an ion transfer mechanism for insulators^{5,6}. He emphasized that 'if insulators take part, then electrons do not'⁵. Although others proposed an electron transfer mechanism for insulators, such as polymers⁷⁻¹⁰, Diaz and co-workers developed a detailed ion transfer model^{11,12} and pointed out that 'for both the ion and electron transfer model, similar expressions are derived... those general expressions are not proof of the mechanism, nor do they allow one to distinguish between ion and electron transfer models'¹¹. Experiments designed to test if ion transfer occurred during contact electrification were not successful¹³. Whitesides and co-workers stated that an 'exclusive ion- or electron-transfer mechanism cannot explain contact electrification'¹⁴, but favoured an ion transfer (hydroxide adsorption) model in a recent paper¹⁵. Comparison of the two models has been reviewed¹⁶ and a triboelectric series for polymer materials reported¹⁷.

We are interested in chemical measurements of charged insulators. The presence of faradaic (redox) reactions produced by those electrostatic charges, as typically found in electrochemical systems², would provide strong evidence of an electronic component in the contact electrification and a unique tool for measuring the charge density, energy and spatial distribution through analysis of reaction products. Here, we demonstrate that faradaic reactions can be identified on charged surfaces at Teflon (polytetrafluoroethylene) and Lucite (polymethylmethacrylate).

Experiments were carried out by immersion of charged Teflon into an acidic solution to note any change in pH and formation of hydrogen gas. After 37 pieces of Teflon septa were rubbed with

Lucite discs and then briefly immersed in 3 ml of a 0.1 mM HCl solution one after another, the solution pH increased from 4 to 6.2. In another experiment, the pH of 3 ml of an HCl solution changed from 3.1 to 4.1, 5.2 and 7.3 after consecutive contact with charged Teflon tapes. However, this result alone does not prove that the negative charges on Teflon were electrons instead of ions, because H^+ could also adsorb on charged Teflon or an adsorbed anion, such as hydroxide, transferred to the surface during charging¹⁵ could leach into the solution and cause a pH change. However, if hydrogen gas was produced, the charge carriers on Teflon must be electrons because there is no known way for adsorbed ions to generate hydrogen. Indeed, hydrogen was detected by ultrahigh vacuum (UHV) mass spectrometry. In this case, D_2O was used and samples were prepared inside a glove box. Charged Teflon tape was introduced through a Teflon tube into a glass reactor with 50 ml D_2O solution containing 1.5 ml DCl (35%). The reactor, which was equipped with a metal joint, was then connected to a stainless-steel tube sealed with a valve. Note that some tape stayed above the DCl solution; careful shaking and tilting of the reactor were necessary for them to fully contact the solution. The reactor was then taken out and connected to a UHV system (1.5×10^{-9} torr). Liquid nitrogen was used to freeze the reactor solution and the gas was first introduced into a sample transfer chamber before it reached the main UHV chamber. A clear D_2 peak appeared in the mass spectrum, whereas a control experiment carried out under the same conditions without contact to charged Teflon showed only a flat baseline.

Hydrogen generation clearly shows that energetic electrons were present on the Teflon surface and caused a reduction process that should be faradaic as in conventional electrochemistry ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$). In this process, as opposed to that of a typical two-electrode electrochemical cell, the solution becomes negatively charged with an excess of anions. If all of the pH change can be ascribed to the proton reduction, the observed pH change could be used as an accurate way to measure the electrostatic charge density on an insulator. Indeed, when the total number of H^+ ions removed from the solution is divided by the geometric

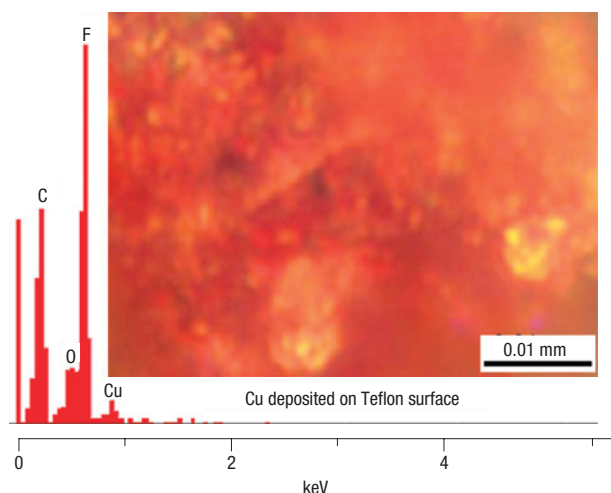


Figure 1 Cu deposited on charged Teflon. EDS of a Cu film on Teflon that was rubbed with Lucite and then briefly immersed in a 1 mM CuSO_4 solution, causing the reaction $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}$ (and leaving the solution negatively charged with excess SO_4^{2-} ions). Inset: Image of the film taken with an optical microscope. Cu films were formed on only a few isolated spots probably through surface diffusion and aggregation of Cu atoms instead of consecutive electron transfer to attain the nucleation of multiple Cu ions on the same point.

Teflon surface area involved in the treatment, an average electron density of the order of 10^{15} cm^{-2} was found. This was obviously an overestimation because the actual surface area of the rubbed Teflon must be significantly larger than the apparent one. Nevertheless, it still seems to be a higher charge density by contact electrification than that usually reported on a polymer surface. It is not clear if electrons at such a high density have some mobility, even in an insulator such as Teflon, considering that charges distributed more than $10 \mu\text{m}$ deep into the bulk on some polymers, including Teflon, have been found after electron beam deposition¹⁸.

Note that the determination of the true charge density is a long-standing problem in contact electrification, because it is very difficult to access all areas on a surface that is rough or porous. Soft rubber¹⁹ and mercury²⁰ have been used to increase the contact area for more accurate measurements. Indeed, mercury contact achieved elementary charge densities on some polymers up to $\sim 10^{12} \text{ cm}^{-2}$, significantly higher than that produced with a conventional rigid solid contact²⁰. This density, however, was still over ten times smaller than that obtained on an atomically smooth mica surface where a good contact could be made²¹.

We also considered the possibility of faradaic metal electrodeposition with charged insulators. When a charged Teflon rod was briefly immersed in an aqueous solution containing 1 mM CuSO_4 , small amounts of Cu^{2+} were reduced and deposited as Cu metal on the surface (Fig. 1, inset). The Teflon surface was carefully examined before and after the deposition so that Cu spots could be correctly identified as confirmed by energy dispersive X-ray spectroscopy (EDS) (Fig. 1). A Cu peak in EDS was seen on each spot examined and no Cu was noted on uncharged Teflon. The F and C peaks in Fig. 1 originate from the area beneath the Cu spot that was thin enough for the electron beam to penetrate, because the scanned area for the EDS was smaller than the Cu spot. The peak height of F relative to C was much larger in EDS scans obtained on bare Teflon compared with the Cu-deposited one, suggesting that F was possibly deficient beneath the Cu spot. The O peak shown in Fig. 1 suggests that Cu in the spot might be partially

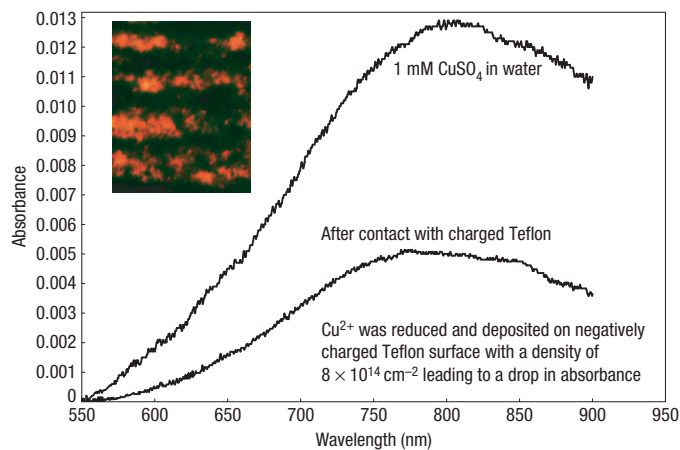


Figure 2 Cu plated on charged Teflon. Optical absorbance of 1 mM CuSO_4 solution before and after contact with charged Teflon. Inset: Optical image ($167 \times 225 \mu\text{m}^2$) of Cu lines formed by electroless deposition on Teflon in a designed pattern in a separate experiment. (Plating of Pd, followed by deposition of Cu in a catalysed chemical reaction.)

oxidized. However, a small O peak in EDS was also seen with a bare Teflon surface. When a small drop of 1 mM CuSO_4 was purposely placed on Teflon and dried, the EDS obtained from that spot showed strong S and O peaks in addition to Cu, F and C, confirming that the Cu film described above was the result of Cu^{2+} reduction by electrons on Teflon. A hydroxide adsorption mechanism¹⁵ could also be excluded here because the expected product of $\text{Cu}(\text{OH})_2$ would dissolve into solution, whereas the Cu deposited on Teflon could not be washed away with water. In addition, the colour of $\text{Cu}(\text{OH})_2$ could not be confused with that shown in Fig. 1. Moreover, the optical absorbance of Cu^{2+} in the solution decreased on immersion and removal of the Teflon as shown in Fig. 2. The concentration change after Teflon contact corresponded to an average charge density of about $8 \times 10^{14} \text{ cm}^{-2}$ (geometric area), slightly smaller than, but of the same order of magnitude of, the charge density calculated from the pH change. Some H^+ reduction might also occur in this experiment and consume a fraction of the available electrons. When the deposited Cu on Teflon was dissolved in nitric acid, analysis of the Cu concentration by absorbance yielded a charge density of $7.6 \times 10^{14} \text{ cm}^{-2}$.

The Cu deposition effect could be amplified by using the available charge on Teflon in an electroless deposition mode. After a Teflon surface was rubbed with the edge of a Lucite rod or machined with a cutting tool in a lathe in a pattern of lines, it was briefly dipped in a saturated PdCl_2 solution. This produced Pd metal particles that appeared dark and could act as catalysts for Cu deposition. It was then washed and immersed in a Cu plating bath containing CuSO_4 , $\text{KNaC}_4\text{H}_4\text{O}_6$, NaOH and HCHO (ref. 22). Cu was deposited on Teflon in the same pattern as shown in the inset of Fig. 2. Although we did not explore this approach in any detail, it suggests that the Teflon surface can be charged in a designed pattern and then metallized to form a desired structure. Teflon has a low dielectric constant and good thermal stability, which are desirable properties for microelectronic and other applications²³.

To further verify if charges on Teflon were indeed electrons instead of ions, charged Teflon was immersed in a solution containing $\text{Fe}(\text{CN})_6^{3-}$ to be reduced. The formation of $\text{Fe}(\text{CN})_6^{4-}$ in the bulk solution would provide strong evidence of a redox reaction. As shown in Fig. 3, a single steady-state current plateau corresponding to $\text{Fe}(\text{CN})_6^{3-}$ appeared in the cyclic voltammogram

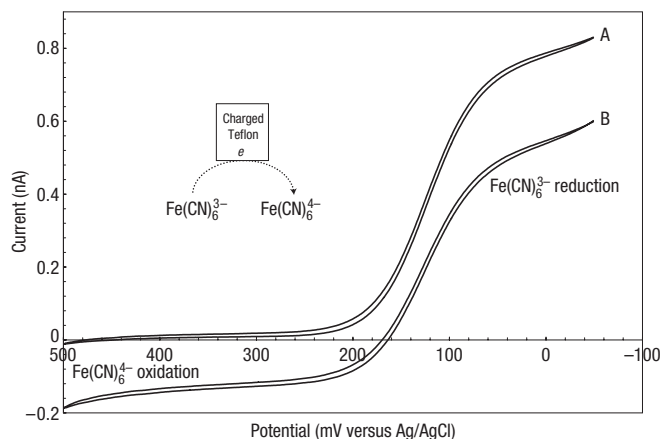


Figure 3 $\text{Fe}(\text{CN})_6^{3-}$ was reduced by charged Teflon to $\text{Fe}(\text{CN})_6^{4-}$. Cyclic voltammograms (10 mV s^{-1}) at a $23 \mu\text{m}$ glass-encased Pt ultramicroelectrode in water containing $0.2 \text{ mM Fe}(\text{CN})_6^{3-}$ and 0.1 M KCl before (A) and after (B) the immersion of Teflon tapes charged with Lucite by rubbing.

for the initial solution. However, the height of the plateau decreased and an anodic one appeared after the solution had contacted charged Teflon tape. This new plateau corresponded to $\text{Fe}(\text{CN})_6^{4-}$ in the solution and clearly indicated that the reduction reaction of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ took place on charged Teflon. Note that some $\text{Fe}(\text{CN})_6^{4-}$ might also adsorb on the Teflon because the current for $\text{Fe}(\text{CN})_6^{4-}$ oxidation seems smaller than the current decrease in $\text{Fe}(\text{CN})_6^{3-}$ reduction (Fig. 3). In a well-controlled experiment, 16 pieces of Teflon septa, the same as those used for the pH experiment, were charged with Lucite and then immersed briefly one after another in 1 ml of an aqueous solution containing $0.2 \text{ mM Fe}(\text{CN})_6^{3-}$ and 0.1 M KCl . The current plateau for $\text{Fe}(\text{CN})_6^{3-}$ reduction dropped by 23%, corresponding to an electron density of $7.7 \times 10^{14} \text{ cm}^{-2}$ (geometric area) on charged Teflon septa assuming 100% reaction efficiency. Such a density is essentially the same as the one obtained from Cu deposition. Note that contacting the solution with uncharged Teflon never showed production of $\text{Fe}(\text{CN})_6^{4-}$. In all of the experiments, more $\text{Fe}(\text{CN})_6^{3-}$ molecules were reduced to $\text{Fe}(\text{CN})_6^{4-}$ with more charged Teflon immersion, independent of the shape, size and brand of the Teflon, indicating again that electrons were involved in the charging/discharging process. The reduction potentials of Cu^{2+} and $\text{Fe}(\text{CN})_6^{3+}$ are $+0.34 \text{ V}$ and $+0.36 \text{ V}$, respectively, so the potential of the charges on Teflon are at least that negative. Experiments to determine the energy level (or distribution of levels) using different redox couples are in progress. Some of the electrons on Teflon following rubbing might attract counter ions that, although not reducible, can effectively shield the electrons from being sensed by a physical probe. On immersion into a solution, however, reducible species such as Cu^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ are able to be reduced by these shielded electrons, so that a much higher charge density could be determined with chemical measurement compared with conventional physical methods.

Electrogenerated chemiluminescence (ECL) is a method of generating light by using electrochemical (faradaic) reactions to produce highly reactive species at the surface of an electrode that can produce excited states in energetic electron transfer reactions²⁴. They are highly sensitive methods of determining very low levels of species in solution (for example, at the picomole level) and hence of detecting small amounts of charge and are thus well suited to studying electronic charges on insulator surfaces. Indeed,

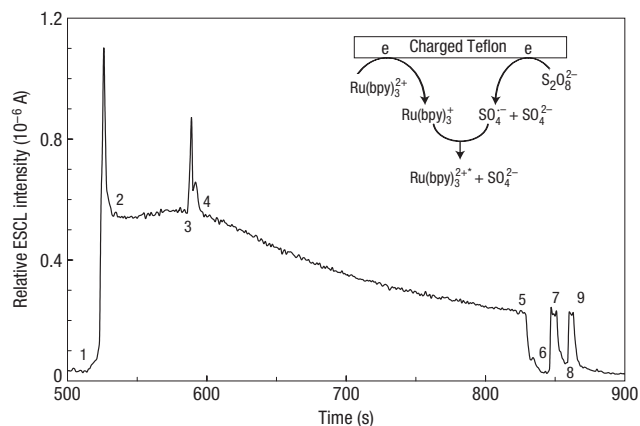


Figure 4 Charged-Teflon-generated chemiluminescence. Relative ESCL intensity as a function of time when a charged Teflon disc at the bottom of a rod was gradually introduced, portion by portion, into a $\text{MeCN}/\text{H}_2\text{O}$ (1:1, v/v) mixture containing $2.5 \text{ mM S}_2\text{O}_8^{2-}$ and $0.25 \text{ mM Ru}(\text{bpy})_3^{2+}$. See text for details.

as shown by the experiments described below, use of charged insulators for generating ECL provides a new and completely different approach to this type of analysis, which we have called electrostatic chemiluminescence (or ESCL).

When a charged Teflon rod was immersed in an acetonitrile (MeCN)/water (1:1, v/v) mixture, a transient luminescence at the few nanoampere level was detected with a photomultiplier tube operated under a bias of -750 V (compared with a background level of 0.2 nA). This represents a very low-level discharge or chemiluminescent background process. When a mixture of typical ECL reagents, that is, $0.25 \text{ mM tris}(2,2'\text{-bipyridine})\text{ruthenium (II) perchlorate}$ [$\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$] and $2.5 \text{ mM tetra-}n\text{-butylammonium peroxydisulphate}$, $(\text{TBA})_2\text{S}_2\text{O}_8$ in MeCN/water was used, and the charged Teflon rod was introduced, a strong ESCL emission was detected, at about the milliampere level ($\sim 10^6$ times higher than background) that saturated the detection system. We ascribe this emission to the well-known ECL process where available electrons on Teflon reduce $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ to generate the light-producing species, as described in more detail below. Note that when either of these reagents alone was present in the solution, the luminescence was not above the background level on charged Teflon introduction.

To monitor the process of ESCL, the charged Teflon rod was slowly introduced manually into the mixture section by section, so that the luminescence could be measured at a lower level over a longer period of time as shown in Fig. 4. In this case, a fraction of the charged Teflon rod was first immersed in the mixture and held there for a moment (point 1 in Fig. 4); the ESCL quickly increased to over $1 \mu\text{A}$ and then dropped rapidly as electrons were consumed. Before the ESCL decayed to the baseline, fresh Teflon was gradually introduced into the solution (point 2) and a near-steady-state ESCL was seen for about 1 min. At point 3, the Teflon rod was moved more rapidly into the solution leading to an ESCL spike followed by a slow movement (point 4) and decay. When the rod was moved out of the solution at point 5 in Fig. 4, the ESCL dropped to the baseline, confirming that the detected luminescence was indeed produced by the charges on Teflon. The ESCL reappeared when a fresh portion of the charged Teflon was immersed in the solution again (point 6). Such a process could be repeated at points 7 and 8. ESCL was always observed as long as the electrons on the Teflon were not fully depleted. Finally, Teflon was removed from

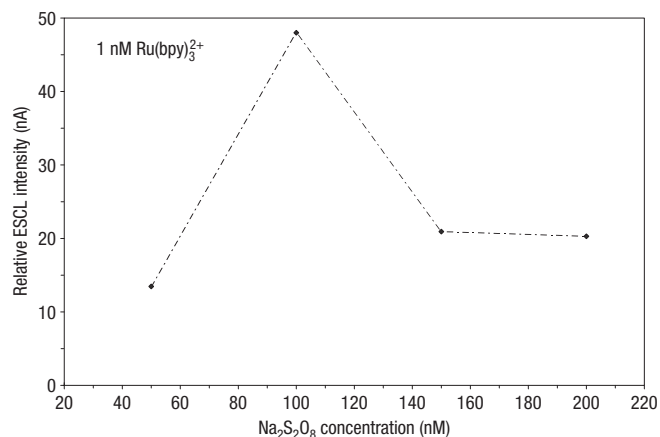


Figure 5 Charged-Teflon-produced chemiluminescence. Relative ESCL intensity generated by charged Teflon as a function of Na₂S₂O₈ concentration in MeCN/H₂O solution (1:1 by volume) with 1 nM Ru(bpy)₃²⁺.

the solution (point 9) and the ESCL disappeared. Because this experiment was carried out by hand in a dark room, it is difficult to quantify the area of Teflon rod immersed in recording each of the above points. Note that it was the charges on Teflon rather than simply Teflon itself that triggered the luminescence, because no ESCL was detected when uncharged or fully discharged Teflon was immersed in the same solution. Interestingly, similar results had been obtained when Mg powder was introduced into the same system²⁵. The identical effect generated from both charged Teflon and a strong reductant, such as Mg powder, in the same system is clear evidence that the luminescence observed was indeed a result of an electron transfer reaction, rather than a spark from an electrostatic discharge. Such a conclusion was also supported by the fact that both Ru(bpy)₃²⁺ and S₂O₈²⁻ must coexist in the MeCN/H₂O mixture to produce strong luminescence.

On the basis of earlier studies in ECL from this system at metal electrodes^{25,26}, we propose a reaction mechanism as shown in the inset in Fig. 4. The electronic excited state of Ru(bpy)₃^{2+*}, responsible for luminescence, was produced through an electron transfer reaction from Ru(bpy)₃⁺ to SO₄^{•-} radical, generated by reduction of Ru(bpy)₃²⁺ and S₂O₈²⁻ on the charged Teflon surface. The SO₄^{•-} radical could also be made by the reaction²⁷



Another path leading to the excited state involves generation of Ru(bpy)₃³⁺ by reaction of SO₄^{•-} with Ru(bpy)₃²⁺ followed by reaction with Ru(bpy)₃⁺. Note that the first steps for the luminescence generation in this system involve the reduction of both reactant Ru(bpy)₃²⁺ and co-reactant S₂O₈²⁻ to trigger the series of reactions. Therefore, ESCL obtained here, again, is consistent with the idea that the charges on Teflon were electrons.

To study possible analytical applications, the ESCL dependence on the concentrations of Ru(bpy)₃²⁺ and S₂O₈²⁻ was studied, similar to previous ECL studies²⁸. For 1 nM Ru(bpy)₃²⁺, the ESCL increased with S₂O₈²⁻ concentration up to roughly 100 nM (Fig. 5), and then the emission dropped off sharply, probably because of quenching of Ru(bpy)₃^{2+*} by S₂O₈²⁻ as reported earlier²⁹. Similar results were obtained for different concentrations of Ru(bpy)₃²⁺ over a range of 5 orders of magnitude. Table 1 shows the maximum ESCL response at a given Ru(bpy)₃²⁺ concentration from separate measurements for each mixed with 4 or 5 different concentrations of S₂O₈²⁻.

Table 1 Emission intensity as a function of [Ru(bpy)₃²⁺] and [S₂O₈²⁻] in CH₃CN:H₂O (1:1 v/v) averaged from 10 measurements.

[Ru(bpy) ₃ ²⁺]	[S ₂ O ₈ ²⁻]	Relative ESCL intensity (nA)
0 M	0.5 mM	9.1
1 nM	0 M	2.4
0.1 nM	10 nM	23
1 nM	100 nM	48
10 nM	1,500 nM	93
100 nM	10 μM	176
1 μM	180 μM	594

At 0.1 nM Ru(bpy)₃²⁺, a clear ESCL signal was seen that was well above the background level. As the electrostatic charges on the Teflon surface were generated through rubbing with Lucite, reproducibility of these measurements was a concern. A series of measurements showed that the ESCL intensities did not vary significantly over 10 separate experiments (2 different solutions with the same composition and Teflon rods of the same size and shape, 5 new rubbings for each) with 1 nM Ru(bpy)₃²⁺ and 100 nM S₂O₈²⁻ and yielded an averaged signal of 49 nA with a standard deviation of 5.8 nA (see Supplementary Information, Fig. S1).

Some questions remain about the molecular nature of the charges, their energies and distributions. The electrochemical approach used here, by studying the effects with different redox couples that span a range of potentials, has the possibility of addressing these questions. A table based on reducing/oxidizing power of electrostatic charges on different insulators could then be constructed. Such a study may also find applications to single-electrode electrochemistry³⁰ without a counter electrode and power supply and, as ESCL, in analytical applications, for example, for clinical analysis of species labelled with a luminescent molecular tag, different than, but complementing, the widely used ECL techniques³¹.

METHODS

Teflon and Lucite (rods, discs and plates) were the primary materials in the study. Different kinds of Teflon were used, including septa with a diameter of 12 mm (Alltech Associates, Applied Science Labs), tapes, discs, rods and plates of different sizes and shapes. They all showed similar results. Metallic impurities were below 0.1 p.p.m. for all of the materials used here as determined with a Varian UltraMass inductively coupled plasma mass spectrometer. The Teflon surface was rubbed by hand with another substance such as metal, glass, Nylon or Lucite, and in all cases became negatively charged as determined with an electrometer (Model 6517, Keithley Instruments). After rubbing with Teflon, the Lucite surface became positively charged and could be measured in the same way. Contact without rubbing generated less charge. Generally, rubbing was discontinued when discharge sounds were heard, accompanied by sparks that appeared on the rubbed Lucite surface and edges and were clearly seen with the naked eye in a dark room. Experiments were always carried out by rubbing the Teflon and Lucite by hand and separating these for use in the experiments (rather than rubbing them while immersed in the test solutions). This was designed to avoid the possible occurrence of 'tribochemistry' (that deals with the relation between mechanical work and mass transformation³², such as can be found during milling of insulators. All other chemicals used were reagent grade. MilliQ deionized water was used to prepare all solutions. For the pH experiment, Teflon septa (12 mm in diameter) or tapes were placed on Lucite plates (18 cm × 18 cm) and rubbed by hand for about 10 s with Lucite discs (2.5 cm in diameter and 1.2 cm in height) and then briefly immersed in solution for a few seconds. A pH meter (Orion Research, model 701A) was used. For hydrogen generation, the sample was prepared in a glove box (Terra Universal) with continuous N₂ flow. D₂O (D, 99 at.%, Aldrich) and DCl (35 wt% in D₂O, Aldrich) were used to avoid any H₂ background. For Cu deposition, Teflon rods (9.5 mm in diameter) were charged by rubbing with a Lucite plate by hand for about 10 s and the deposited Cu spots were inspected with an optical

microscope (Olympus). To examine a particular spot with a scanning electron microscope (LEO 1530), orienting marks were placed on the area under an optical microscope before the sample was mounted in the scanning electron microscopy chamber. For reduction of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$, Teflon septa or tapes were charged in the same way as described above. Cyclic voltammetry was carried out with a 23 μm Pt ultramicroelectrode. A Model 100a electrochemical analyser (Bioanalytical Systems) was used to analyse the solution composition change following the treatment with charged Teflon. All ESCL measurements were carried out in a black box located inside a double-door dark room to minimize effects of stray background radiation. Teflon rods (2.1 cm in diameter) were rubbed at one end by hand with a piece of Lucite plate and ESCL was determined with a photomultiplier tube (Hamamatsu R4220P).

We attempted to use a Faraday cup approach to measure the charge on the end of a Teflon rod rubbed with Lucite. When the rod was perpendicularly introduced through a hole into a Faraday cup with about half of its (uncharged) length outside, the charge measured clearly increased with firm contact to the cup by pushing the Teflon rod by hand from the outside. However, when the pressure was removed, and the rod was just lightly resting under its own weight on the bottom of the cup, the measured charge decreased by over 10%. Teflon is soft and easily deformable; thus, the charged area is much larger than the apparent one as opposed to a hard surface, where the contact-charged area might be only a fraction of the geometric area. Although the studies described here have concentrated on Teflon, which is negatively charged, oxidation reactions at the charged Lucite were also obtained and will be reported separately.

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References

- Jonassen, N. *Electrostatics* 2nd edn (Kluwer Academic, Norwell, 2002).
- Bard, A. J. & Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications* 2nd edn (Wiley, New York, 2001).
- Gilbert, W. *De Magnete* (Chiswick, London, 1600).
- Harper, W. R. The Volta effect as a cause of static electrification. *Proc. R. Soc. A* **205**, 83–103 (1951).
- Harper, W. R. *Static Electrification* 3–10 (Inst. Phys. Conf. Ser., Vol. 4, Adlard & Son, Dorking, 1967).
- Henry, P. S. H. Survey of generation and dissipation of static electricity. *Br. J. Appl. Phys.* **4** (suppl. 2), S6–S11 (1953).
- Davies, D. K. *Static Electrification* 29–36 (Inst. Phys. Conf. Ser., Vol. 4, Adlard & Son, Dorking, 1967).
- Davies, D. K. Charge generation on dielectric surfaces. *Br. J. Appl. Phys.* **2**, 1533–1537 (1969).
- Duke, C. B. & Fabish, T. J. Contact electrification of polymers: A quantitative model. *J. Appl. Phys.* **49**, 315–321 (1978).
- Lowell, J. & Rose-Innes, A. C. Contact electrification. *Adv. Phys.* **29**, 947–1023 (1980).
- Diaz, A. F. & Fenzel-Alexander, D. An ion transfer model for contact charging. *Langmuir* **9**, 1009–1015 (1993).
- Diaz, A. F., Fenzel-Alexander, D., Wollmann, D. & Barker, J. A. Importance of dissociated ions in contact charging. *Langmuir* **8**, 2698–2706 (1992).
- Folan, L. M. *et al.* Electrometer for repeated charge exchange measurements between a microparticle and a surface: Effect of water adsorption. *J. Electrostat.* **25**, 155–163 (1990).
- Wiles, J. A. *et al.* A tool for studying contact electrification in systems comprising metals and insulating polymers. *Anal. Chem.* **75**, 4859–4867 (2003).
- McCarty, L. S. & Whitesides, G. M. Electrostatic charging due to separation of ions at interfaces: Contact electrification of ionic electrets. *Angew. Chem. Int. Ed.* **47**, 2188–2207 (2008).
- Diaz, A. F. & Guay, J. Contact charging of organic materials: Ion vs. electron transfer. *IBM J. Res. Dev.* **37**, 249–259 (1993).
- Diaz, A. F. & Felix-Navarro, R. M. A semi-quantitative tribo-electric series for polymeric materials: The influence of chemical structure and properties. *J. Electrostat.* **62**, 277–290 (2004).
- Sessler, G. M., Figueiredo, M. T. & Ferreira, G. F. L. Models of charge transport in electron-beam irradiated insulators. *IEEE Trans. Dielectr. Electr. Insulat.* **11**, 192–202 (2004).
- Cottrell, G. A. The measurement of true contact charge density using soft rubber. *J. Phys. D* **11**, 681–687 (1978).
- Medley, J. A. The electrostatic charging of some polymers by mercury. *Br. J. Appl. Phys.* **4** (suppl. 2), S28–S30 (1953).
- Horn, R. G. & Smith, D. T. Contact electrification and adhesion between dissimilar materials. *Science* **256**, 362–364 (1992).
- Mance, A. M., Waldo, R. A. & Dow, A. A. Interactions of electroless catalysts with plasma-oxidized surface of polystyrene-based resins. *J. Electrochem. Soc.* **136**, 1667–1671 (1989).
- The National Technology Roadmap for Semiconductors: Technology Needs*, SIA, Semiconductor Industry Association, 101–105 (1997).
- Bard, A. J. (ed.) *Electrogenerated Chemiluminescence* (Marcel Dekker, New York, 2004).
- White, H. S. & Bard, A. J. Electrogenerated chemiluminescence. 41. Electrogenerated chemiluminescence and chemiluminescence of the tris(2,2'-bipyridine)ruthenium(2⁺)-peroxydisulfate(2⁻) system in acetonitrile-water solutions. *J. Am. Chem. Soc.* **25**, 6891–6895 (1982).
- Bolletta, F., Ciano, M., Balzani, V. & Serpone, N. Polypyridine transition-metal complexes as light-emission sensitizers in the electrochemical reduction of the persulfate ion. *Inorg. Chim. Acta* **62**, 207–213 (1982).
- Miao, W. & Choi, J.-P. in *Electrogenerated Chemiluminescence* (ed. Bard, A. J.) Ch. 5 (Marcel Dekker, New York, 2004).
- Ege, D., Becker, W. G. & Bard, A. J. Electrogenerated chemiluminescent determination of tris(2,2'-bipyridine)ruthenium ion ($\text{Ru}(\text{bpy})_3^{2+}$) at low levels. *Anal. Chem.* **56**, 2413–2417 (1984).
- Bolletta, F., Juris, A., Maestri, M. & Sandrini, D. Quantum yield of formation of the lowest excited state of tris(bipyridine)ruthenium(II) $\text{Ru}(\text{bpy})_3^{2+}$ and tris(phenanthroline)ruthenium(II) $\text{Ru}(\text{phen})_3^{2+}$. *Inorg. Chim. Acta* **44**, L175–L176 (1980).
- Liu, C.-Y. & Bard, A. J. Electrochemistry and electrogenerated chemiluminescence with a single faradaic electrode. *Anal. Chem.* **77**, 5339–5343 (2005).
- Debad, J. D., Glezer, E. N., Wohlstader, J., Sigal, G. B. & Leland, J. K. in *Electrogenerated Chemiluminescence* (ed. Bard, A. J.) 359–396 (Marcel Dekker, New York, 2004).
- Heinicke, G. *Tribochemistry* (Akademie-Verlag, Berlin, 1984).

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