FRONTIERS ARTICLE

Electrons on dielectrics and contact electrification

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ARTICLE INFO

ABSTRACT

Surfaces of dielectrics (insulators) often become charged following contact with metals, semiconductors, and dielectrics with or without rubbing. The mechanism and participants in the charge transfer (electrons or ions), although widely investigated, are still controversial. Whereas the identity of the charge carrier cannot be distinguished by electrostatic measurements, we have recently found that charges on a dielectric surface, e.g. for polymers like Teflon (polytetrafluoroethylene or PTFE) and Lucite [poly(methylmethacrylate) or (PMMA)], can carry out different chemical redox reactions, e.g. metal deposition, ion reduction, and chemiluminescence. This suggests that *electron* transfer occurs in electrification. This chemical approach allows determination of the surface density of electronic charge as well as processes involved in charging and discharging the dielectrics. An overview of this work is presented.

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1. Introduction

This perspective deals with the nature of the charges that reside on dielectric materials (insulators) and the charge transfer that occurs on contacting dielectrics with various materials. Two types of charged species are generally dealt with in chemistry: electronic charge: electrons and the absence of electrons (holes), and ionic charge: an excess (anions) or deficiency (cations) of electrons localized on atoms or molecules. Generally, free electrons and holes are discussed in connection with solids, but, except in rather rare circumstances, e.g. solvated electrons in liquid ammonia and transiently in water, charge in liquids is usually ionic. (Both free electrons and ions can be present in the gas phase, but this is not discussed further in this perspective.) The presence or absence of excess charge of both types, e.g. on solid surfaces, and the interconversion of electronic and ionic charge are important in many chemical processes and play a central role in the field of electrochemistry.

Electrons are spatially localized within atoms and molecules, occupying specific atomic or molecular orbitals. When one considers larger assemblies, like nanoparticles of metals and semiconductors, interatomic and intermolecular delocalization of the electrons becomes more important and in the bulk materials, like semiconductors, one conventionally talks about valence and conduction bands, separated by a band gap, E_g, where electrons are largely delocalized in the lattice. In these materials, additional electronic states are possible. For example, the interfaces (surfaces and grain boundaries) of materials, at both the bulk and nanoparticle (NP)

level, are characterized by *surface states*, characteristic of the terminated lattice and with unique electronic energies. Within the lattice, vacancies or other defects, as well as the presence of impurities or dopants, either at interstitial or lattice sites can also produce unique electronic states. Such surface or bulk states are sometimes described as *traps* or *impurity states*. While the band theory is often applied to small band gap materials, like Si ($E_g = 1.1$ eV), these descriptions have been adopted and also work well for rather large band gap materials, like TiO$_2$ (anatase) ($E_g = 3.2$ eV) and ZnS ($E_g = 3.6$ eV) that are insulating in the intrinsic or undoped state.

When one deals with larger E_g materials, i.e. dielectrics or insulators, for example polymers like Teflon (PTFE) or Lucite [poly(methylmethacrylate) or PMMA], crystals like NaCl, or ceramics like SiO$_2$, MgO, or Al$_2$O$_3$, these are often described with the same band language as semiconductors, but with very large E_g-values; e.g. for Al$_2$O$_3$, $E_g \geqslant 7$ eV, and with very narrow 'bands,' so that charge is largely localized within the structures and conductivity is very small. However, these materials can also contain other electronic states, e.g. interface states, impurity states, and defect sites. For example, MgO exposed to hydrogen atoms has *excess electrons* at trapping sites on the surface [1]. The formation of color or F-centers, e.g. under gamma irradiation, with the generation of electron paramagnetic resonance (EPR) signals in polymers and ceramics is well known. Similarly, mechanical action on polymers like PMMA, e.g. by slicing or ball milling, produces ESR signals [2]. In all of these cases, these states or traps can be described as localized electrons on 2D (at interfaces) or 3D (in bulk) sites or cavities that have been compared to those for electrons in liquids like ammonia. We have some evidence, described later, that these can behave as reducing sites.

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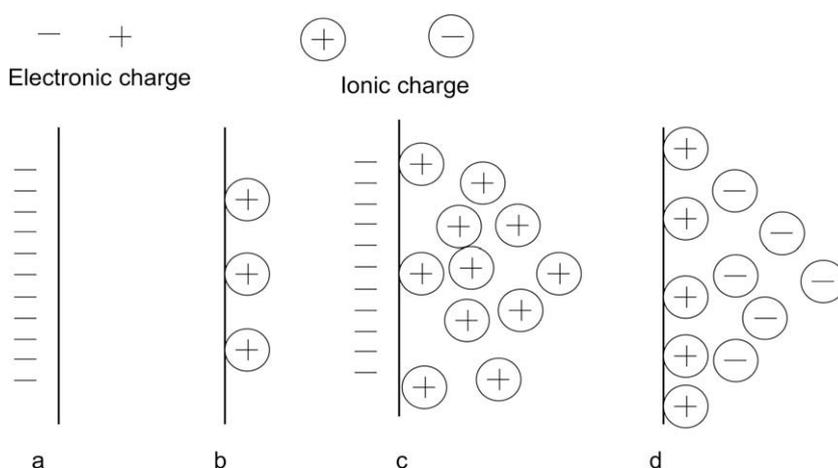
Scheme 1. Schematic representation of different types of charged interfaces. (a) Electronically charged surface; (b) ionically charged surface; (c) electronically charged surface compensated by specifically adsorbed ions and a diffuse layer of ions; and (d) ionically charged surface compensated by a diffuse layer of ions. The diffuse layer is often described by the Gouy–Chapman–Stern model.

Surfaces of solids can become charged in different ways (Scheme 1). For example metal or carbon electrodes immersed in a liquid electrolyte in an electrochemical cell are charged by applying a potential between them (e.g. they can behave as an electrolytic capacitor). In this case, the charge on the metal surfaces is usually described as due to electrons or holes. This charge is largely compensated by ions in the solution that are attracted or repelled from the surface and form a 'double layer.' Alternatively a solid may adsorb ions, e.g. an SiO_2 surface in alkaline solution adsorbs OH^-, and again a double layer forms in solution by attraction of cations and repulsion of anions. The net charge on a surface is the sum of the electronic and the ionic charge and the nature of the charge cannot be distinguished by simply measuring the total surface charge or surface potential.

2. Background

Of particular interest here is the nature of charge transfer when two phases are brought into contact. For example when carbon or an inert metal like Au contacts an electrolyte solution containing a redox pair, e.g. $Ru(NH_3)_6^{3+/2+}$, electron transfer between the phases alters the potential of the metal electrode (with respect to a stable reference electrode), as a double layer forms. The current model is that the redox couple establishes a Fermi level in solution, which then equilibrates with the metal via electron transfer (ET). However, equilibration of the two phases does not necessarily occur rapidly, e.g. if the kinetics of ET is sluggish. For example, it is unlikely that lightly doped TiO_2 equilibrates with an electrolyte, although it is generally represented as doing so.

We consider here the case of two solids (e.g. a metal and a dielectric, or two dielectrics) placed in contact, with or without rubbing, and then separated. This phenomenon, known as contact electrification, frequently causes the two solids to become charged, one positive and the other negative. Contact electrification is a widely studied phenomenon that has been known for over 2000 years and is the basis of applications like xerography [3,4]. Despite the long history and extensive studies, the mechanism of contact electrification of dielectrics is still poorly understood [5,6]. Since the two contacted objects are always charged oppositely after separation, it is natural to assume that an electron transfer occurred. However, for insulators in which electrons are considered immobile, the transfer of an electron from one insulator to another appears less likely, in contrast to widely accepted models for metal/metal [7] and metal/semiconductor [8] contacts that are based on electron flow from the low work function material to that with a higher work function until the two Fermi levels coincide [9]. Thus, extension of the well-developed electron transfer theory to insulators raises theoretical concerns [10–12]. For example, electrons are localized and not accessible in the bulk of the dielectric, in contrast to metals and semiconductors, where electrons are delocalized throughout the entire volume. Moreover, surface states are accessible to any electron with a proper energy from a metal but not from an insulator, where empty and filled states on the two insulators must be physically very close to each other to communicate. One can raise the possibility of electron transfer from surface states, but the nature, or even the existence, of intrinsic surface states for ionic or molecular solids is unclear, due to the poor overlap among orbitals of their constituent ions or molecules [12–15]. Indeed, many organic solids are treated as 'molecular gases,' since the identity of the individual molecules in the lattice is largely preserved as a result of weak intermolecular interactions [16,17]. On the other hand, a large amount of experimental work has been done for metal/dielectric contacts, including polymers, over the last few decades that demonstrate charge transfer occurring during contact electrification [5].

2.1. Electron vs. ion transfer

Another possibility that has been raised is that charge transfer to dielectrics uniquely involves ions. The two mechanisms of *ion* vs. *electron* transfer explain contact electrification equally well since 'the overall electrical effect of a positive ion being transferred from a surface cannot be distinguished from an electron transferred to that surface to neutralize the ion' [5]. A comparison and analysis of the *ion* vs. *electron* transfer debate has been extensive, e.g. in review papers [5,18]. Harper, for example, in his authoritative text states: 'when insulators take part [in contact electrification], then electrons do not' [12]. He proposed an ion transfer process from an insulator surface covered with loosely bound ions that have some mobility on the surfaces and could diffuse across to another surface or redistribute themselves on two surfaces in contact [12,19]. For surfaces with largely different binding, 'a double layer will form and bring the relevant [ionic] energy levels [the Gibbs free energies] to the same height. When the surfaces separate, the double layer will be split into its component sheets of charge almost at once' [12]. Harper failed to identify these ions or where they originate, e.g. in non-ionic insulating polymers like

PTFE. Kornfeld [20,21] assumed that insulators are not electrically neutral because of structural defects and local charges compensated by ions adsorbed from air (where the ion density is typically of the order of 10^9 m^{-3}). When two ion-coated surfaces are rubbed against each other, he suggests that the compensation is disturbed and thus the surfaces become electrified. Although the nature of the inherent charge (electronic or ionic) is not specified, it would appear that environmental conditions or random surface contamination would be a significant contributor to the behavior. However, such an assumption was not consistent with results obtained under different conditions, including vacuum. Diaz and Fenzel-Alexander developed a more detailed *ion* transfer model for ion-containing polymers (ionomers or polyelectrolytes) [22,23]. The effects of ion content, mobility, and stability on the electrification were considered. They concluded that 'for both the *ion* and *electron* transfer model, similar expressions [concerning electrostatic charge] are derived… those general expressions are not proof of the mechanism, nor do they allow one to distinguish between *ion* and *electron* transfer model' [22]. Recently, McCarty and Whitesides also proposed an ion transfer model based largely on experiments with ionomers. For non-ionic polymers, like PTFE and PE, hydroxide ion adsorption was proposed [24]. This model assumes a water layer existing on both polymer surfaces and, upon contact, hydroxide and hydronium ions in the water bridge are redistributed with OH$^-$ preferentially accumulated on one polymer and H$^+$ on another. After separation, the polymer with more OH$^-$ acquires a net negative charge, and the one with more H$^+$, a positive one [24]. The nature of the water film, e.g. on a hydrophobic surface like PTFE, and the reason why hydroxide segregates at such interfaces were not spelled out. Water films on these polymers were noted at 80% relative humidity, but these are not good conditions for contact electrification of these materials. Note also that contact electrification can also take place in vacuum, even with freshly cleaved polymer surfaces that were never exposed to atmosphere [10,25–27]. Contact electrification is also favored by dry environments, e.g. the familiar charging of clothes coming from a dryer.

There have also been numerous studies that favor the electron transfer model. The strongest evidence for an electron transfer mechanism, however, probably comes from studies of the metal/insulator contact in vacuum where charge on the insulating polymer was shown to depend linearly on the metal work function [5,25,28]. It is, perhaps, such a linear relationship that helps the well accepted electron transfer theory for metal/metal and metal/semiconductor contacts be extended to insulators that are assumed to have some energy levels that are related to the Fermi level of the metal [5,18]. Electron transfer at a metal/polymer contact has also been treated theoretically [25,29–33]. A fundamental concern is whether or not thermodynamic equilibrium between electrons in insulators and metals can be established, or even be approached, during contact [34], considering that electronic states in insulators are strongly spatially localized. Such equilibrium is achieved very rapidly for two metals and often at metal/liquid electrolyte interfaces. Moreover, a Fermi level cannot be defined for insulators in which electrons may only persist in non-equilibrium states; for example, as in long lasting electron trapping in organic molecular crystals (that has been proposed for data storage) [35–40]. In addition, an energy level mismatch is also a concern; for example, calculations show that for polyethylene the lowest vacant orbital level, equivalent to the bottom of a conduction band, is located above the vacuum level, while the highest filled level, equivalent to the top of the valence band, is over 8 eV below the vacuum level [41–46], as confirmed by photoemission and photoconduction measurements [47–49], compared to work functions of metals, 4 or 5 eV. Therefore, electron transfer between the inherent polymer orbitals and the Fermi level in the metals does not appear likely. However this does not rule out the presence of other states that can participate in electron transfer.

3. Recent developments

We thought it would be possible to probe the question of electron transfer to dielectrics by seeing if one could detect chemical consequences of any electronic charges, as is conventionally done in electrochemistry. Such a chemical approach to study the mechanism of dielectric contact electrification involves immersion of a polymer that has been charged negative in air into a solution containing a reducible chemical species. Observation of a reduction reaction provides evidence for available electrons on the polymer surface and allows quantitative determination of their surface density (independent of any ions that may have also transferred) [50]. For a good insulator like PTFE, the electrostatic charge can persist on the surface in air for a long time, allowing one to characterize systematically the charge under different conditions and perform a variety of chemical reactions. Moreover, the charge density on the rubbed polymer could be accurately determined since a liquid can access the entire rubbed surface better than a solid.

Note that there is an important distinction between sensing the electrons on a dielectric surface with a chemical approach compared to conventional physical method with an electronic probe or Faraday cup. When the surface electrons are compensated partially or fully with physically adsorbed ions such as Na$^+$, the electrostatic measurement finds the overall charge (electron and ions), while the chemical technique is able to *selectively* detect only the electrons on the surface, independent of the counter ions. Therefore, an electron density determined by our chemical measurement is likely to be higher than the one obtained with conventional physical technique, depending on the degree of compensation. Such a clear distinction can be understood from the following experiment, closely related to one in electrochemical methodology called a 'coulostatic experiment.' Suppose two metal electrodes, e.g. of Au, are immersed in an electrolyte solution, e.g. water containing NaF. We assume the solution is deaerated and does not contain any purposely added or adventitious impurities that could undergo an electron transfer (redox or faradaic) reaction within the potential window where water is not reduced to hydrogen at the cathode and oxidized to oxygen at the anode (we also assume no oxidation of the Au). The cell in this potential region is essentially behaving as an electrolytic capacitor. If a potential of say 1 V is applied between the electrodes, both electrodes will become charged, with the magnitude of the charge dependent on the size of the electrodes and the nature of the electrolyte (but will largely be independent of the distance between the electrodes except for a small contribution of the so-called geometric capacitance), since the capacitance is controlled by the double layers at each electrode. The cathode will have electronic charge at the surface of the gold compensated by a double layer of ions on the solution side of the interface, and similarly positive electronic charge on the anode is compensated by its ionic layer. If the electrodes are now disconnected from the power supply, the electronic charge will remain (although it might slowly leak off through discharge of adventitious impurities, but the electrolytic capacitor will largely remain charged). If an appropriate reducible species is now injected into the solution, it will pick up the electronic charge from the negatively charged electrode (while a counter reaction will occur at the positive electrode). For example, if we assume the potential of the electrode changed by 0.5 V from the point where it was initially uncharged, it would have an amount of charge of the order of 0.5 V × 20 µF cm^{-2} = 10^{-5} C cm^{-2}, or 6×10^{13} cm^{-2}. If one of the electrodes is removed (emersed) from the solution into an inert atmosphere, although it will show no or negligible net charge, it

will still maintain the electronic charge in the metal at or near the relevant electrode potential. Note such emersion studies by bringing emersed electrodes into vacuum have been carried out and it has been shown that the electrode with its double layer can indeed be removed from the solution [51]. This electronic charge could be used to carry out a chemical reaction (oxidation or reduction) of a species whose standard potential is at the appropriate level (even if the electronic charge is compensated by ionic charge) and this redox reaction depletes the electronic charge. We give a brief overview of these studies below.

3.1. Electrostatic charges on contacted polymer surfaces

Examples of electrostatic phenomena on materials subjected to contact electrification are legion. We only give a few examples with the materials we used for the chemical testing. When a PTFE surface is rubbed or contacted with another substance, e.g. metal, glass, Nylon or PMMA, it becomes negatively charged, and its counterpart positively charged, as found with an electrometer [50,52]. These charged materials pick up a bits of paper or carbon powder held about 1 cm away. These light objects are uncharged but probably can be strongly polarized through electrostatic induction and thus are attracted to the charged polymer. When PTFE and PMMA are contacted in a predetermined pattern and then decorated with carbon (graphite) powder, the pattern becomes visible. For exam-
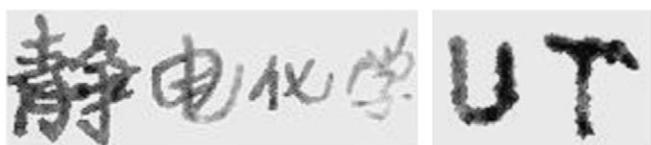
Fig. 1. After PTFE and PMMA rubbed each other in a predetermined pattern and were then placed near a carbon powder, the pattern became visible due to the carbon decoration: a term of 'electrostatic chemistry' in Chinese character was written on PTFE surface with a corner of PMMA plate and 'UT' was written on PMMA with a PTFE.

ple, a corner or point of a piece of PMMA can be used as a pen to write on a PTFE surface as shown in Fig. 1, in which the term 'electrostatic chemistry' was written on PTFE as the Chinese character. Similarly 'UT' could be written on PMMA with a PTFE point followed by carbon powder decoration. This, of course, is the general principle of the last stages of xerography (where charged toner is used).

The charge on rubbed PTFE is stable in the laboratory ambient, over many minutes. It is not uniformly distributed. If a rubbed sheet of PTFE is exposed to carbon powder, the distribution is clearly not uniform. In fact, some spots on the PTFE show significantly higher charge density than others as demonstrated by its effect on water drops in a syringe held above it. In this case, a charged PTFE disk was placed about 1 cm away from the tip of a syringe needle filled with water as shown in Fig. 2. Small water drops spontaneously came out and flew, one after another, from the syringe needle to separate spots on the PTFE probably because of electric field induced polarization of the water. These spots must have a higher charge density compared to other areas and thus exert a stronger attractive force on the water drops sufficient to overcome the surface tension at the needle tip. The water drops stopped coming out when the empty portion of the needle became so large that the charges on PTFE were no longer able to affect the surface tension. However, when the syringe was pushed slightly to refill the needle, water drops started to fly to the PTFE again. As before, they all landed on new spots and no two drops ever came to the same location. Note that each water drop stuck on the PTFE firmly without rolling across the surface as is often seen on uncharged, more hydrophobic, PTFE. As expected, no water drops would leave the syringe needle under the same conditions to a PTFE surface that was not intentionally charged by rubbing.

To get an estimate of the effective potential at the negatively charged spots on PTFE, a metal blade was placed on top of the PTFE and a bias voltage of 1000 V was applied between the blade and the metal needle on the syringe. This did not cause a flow of water drops, even after the syringe was pushed so that a small water drop was suspended at the end of the needle. When the blade was moved closer to the suspended drop so that it was about 1 mm
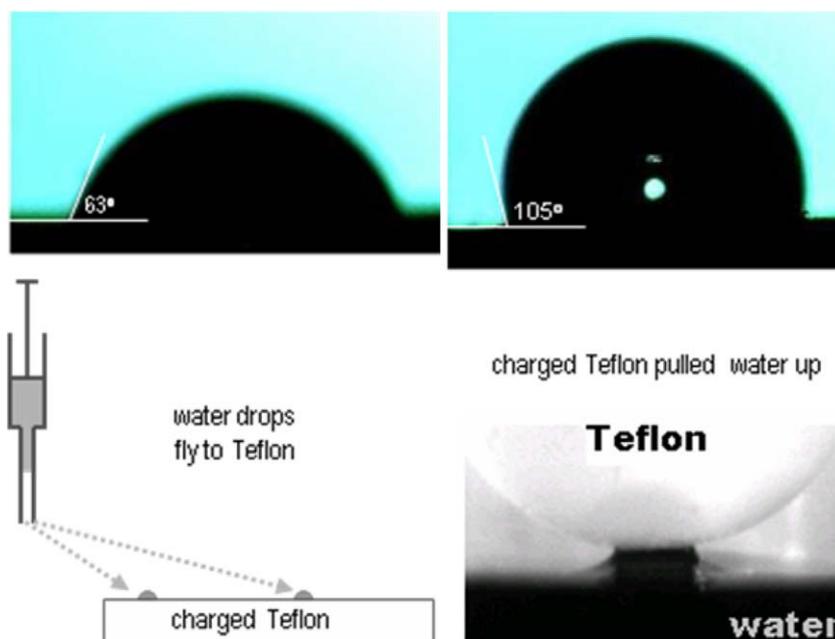
Fig. 2. Bottom left: a schematic diagram showing small water drops flying to a charged PTFE surface after rubbing with PMMA. Top left: an optical image of a water drop rested on a PMMA-rubbed PTFE showing a contact angle of 63°. Top right: an optical image of a water drop on an unintentionally treated PTFE surface showing a contact angle of 105°. Bottom right: an optical image of a PMMA-rubbed PTFE rod pulling water up from a pool that was dyed with black ink for easy focus.

away, the water drop still did not separate from the needle, but rather moved slowly toward the blade and briefly touched its edge and then retracted. Such a touch and retraction repeated every few seconds many times, but the drop never separated from the needle. This suggests that for a water drop to leave the metal needle, as it did to charged PTFE, a much higher bias voltage (e.g. 5–10 kV) is needed. Moreover, measurement with a goniometer showed drops that landed on the charged PTFE had a contact angle of about 63–70° in contrast to 100–105° for a water drop on PTFE surface that hadn't intentionally been subject to contact charging. Thus, electrostatic charging improves wetting of the hydrophobic surface of PTFE. Similarly, the edge of a charged PTFE rod was able to attract water and raise it by about 2 mm, as shown in Fig. 2 (right). The same phenomena were also observed with other polymers including PMMA, Nylon and polyethylene. Water can be polarized, charged or broken into droplets in response to external influences [53–55]. The visible effects described above clearly indicate that the charge density on the PTFE surface was quite high as will be discussed in the later sections.

3.2. Chemistry caused by electrostatic charges

The problem of studying chemical reactions of contact electrified dielectrics is that the number of surface charges is rather small, so rather sensitive analytical methods are required. This has probably been the main reason why this approach has not been explored earlier. The maximum amount of charge found in previous studies of contact electrification and in our work is at most 10^{13}–10^{14} cm^{-2} geometric (as opposed to true) area. This is equivalent to about 10^{-10} moles cm^{-2}, so either one has to use small volumes to contact large surface areas or devise methods that amplify the chemical signal. We have used both approaches.

An example of the first approach is when a small volume of solution containing a reducible species is brought into contact with a charged polymer. A chemical reaction will occur upon contact, if the charge carriers are electrons, in a manner analogous to a faradaic process at an electrode in conventional electrochemistry. Analysis of the chemical composition of the solution before and after the immersion of the charged polymer should provide an unambiguous answer to the nature of the charge carrier (electron or anion), and offers a unique opportunity for measuring the

charge density, energy, and spatial distribution on a polymer surface through analysis of carefully selected reactants and products with systematically varied redox potentials. For some electrochemical processes, especially for multielectron processes, the electrocatalytic nature of the surface is often important and it would be interesting to investigate whether such catalysis could be promoted on insulators. We have done little so far along these lines.

3.2.1. Reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$

When a solution containing $Fe(CN)_6^{3-}$ was brought into contact with charged PTFE, $Fe(CN)_6^{4-}$ was produced [50]. As shown in Fig. 3 a steady-state current plateau that is proportional to the $Fe(CN)_6^{3-}$ concentration appeared in the cyclic voltammogram at an ultramicroelectrode for the initial solution. However, the height of the reduction wave decreased and an anodic one appeared after the solution had contacted charged PTFE tape. This new plateau corresponded to $Fe(CN)_6^{4-}$ in the solution and clearly indicated that the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ took place on charged PTFE. Note that some $Fe(CN)_6^{4-}$ might also adsorbed or be lost during the PTFE contact, since the net current was slightly smaller after the contact (Fig. 3). In a well controlled experiment, 16 pieces of PTFE septa (total geometric area ~36 cm^2) were charged by contacting with PMMA and then immersed briefly one after another into 1 mL of an aqueous solution containing 0.2 mM $Fe(CN)_6^{3-}$ and 0.1 M KCl. The current plateau for $Fe(CN)_6^{3-}$ reduction dropped by 23%, corresponding to an electron density of 7.7×10^{14} cm^{-2} (geometric area) on the charged PTFE septa assuming a 100% reaction efficiency. Note that contacting the solution with uncharged PTFE never showed detectable production of $Fe(CN)_6^{4-}$. In all the experiments, more $Fe(CN)_6^{3-}$ was reduced to $Fe(CN)_6^{4-}$ with a greater area of charged PTFE, independent of the shape, size and source of the PTFE. The results are consistent with electrons being involved in the charge/discharge processes. The electrode potential of $Fe(CN)_6^{3-/4-}$ is +0.36 V vs. NHE, so the energy of the electrons in the PTFE was at least more negative than this value. The reduction of K^+ in this solution, which would lead to hydrogen evolution, occurs at a much more negative potential, -2.92 V, and we found no evidence for this reaction. Note that the negative electronic charge on PTFE following contact with PMMA might attract K^+ counter ions that effectively shield the
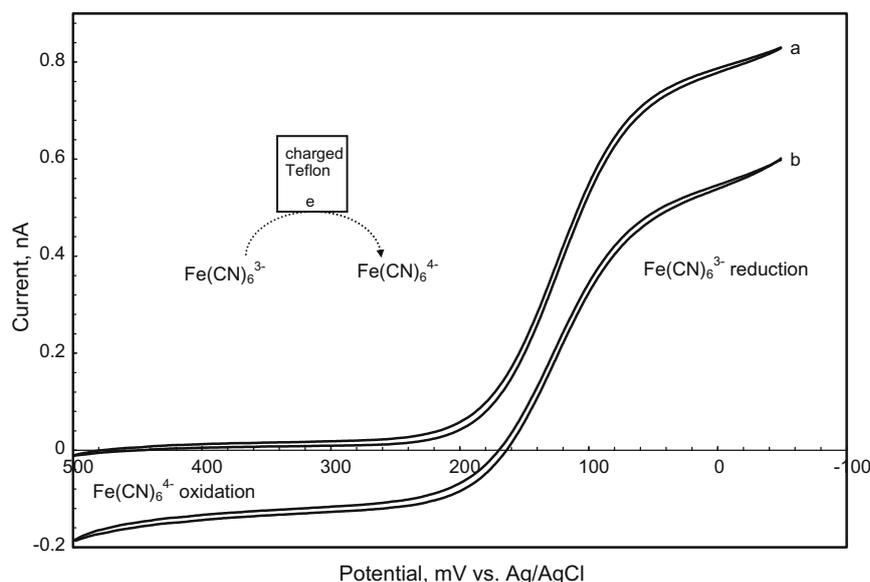
Fig. 3. $Fe(CN)_6^{3-}$ was reduced by charged PTFE to $Fe(CN)_6^{4-}$. Cyclic voltammograms (10 mV/s) at a 23 μm diameter glass-encased Pt ultramicroelectrode in water containing 0.2 mM $Fe(CN)_6^{3-}$ and 0.1 M KCl before (a) and after (b) the immersion of PTFE tapes charged with PMMA by rubbing.

electrons from being sensed by a probe of net surface charge. However, just as in electrochemistry, this does not seriously change the ability of the electrons to react with a reducible species like $Fe(CN)_6^{3-}$. Therefore, a higher charge density may be determined by a chemical measurement compared to that determined by a physical (electrostatic) measurement under the same conditions.

In very similar experiments, polyethylene (PE) of different kinds, after contact with PMMA also reduced $Fe(CN)_6^{3-}$ and showed an average electron density of 7.9×10^{13} cm^{-2} (geometric area) assuming 100% reaction efficiency [52]. This density is about 10 times smaller than charged PTFE, consistent with PE being listed above PTFE in the triboelectric series [56–58], although different surface roughness could also be a factor.

3.2.2. Metal deposition

Another electron transfer reaction studied was metal deposition. When PTFE or PE (after contact with PMMA or Nylon) was immersed into a solution containing metal ions (e.g. 1 mM Ag_2SO_4, saturated $PdCl_2$, or 1 mM $CuSO_4$) followed by washing with deionized water, small deposits ($\sim$10 μm spots) of Ag, Pd or Cu metal could be seen under an optical microscope [50,52]. Cu deposition on PTFE was confirmed by energy dispersive X-ray spectroscopy (EDS) as shown in Fig. 4. A Cu peak in EDS was seen on each spot examined and no Cu was found in control experiments with uncharged PTFE. The F and C peaks in Fig. 4 originate from the area beneath the Cu spot that was thin enough for the electron beam to penetrate, since the scanned area for the EDS was smaller than the Cu spot. The peak height of F relative to C appeared much larger in EDS scans obtained on bare PTFE compared to the Cu deposited one, suggesting that perhaps F was deficient beneath the Cu spot. The O peak shown in Fig. 4 suggests that Cu in the spot might be partially oxidized. However, a small O peak in EDS was also seen with a bare PTFE surface. When a small drop of 1 mM $CuSO_4$ was purposely placed on PTFE 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 PTFE and not ions. After the PTFE deposition experiment, the optical absorbance of the Cu^{2+} in the solution decreased upon immersion and removal of the PTFE, as

Fig. 4. Cu deposited on charged PTFE. EDS of a Cu film on PTFE that was rubbed with PMMA and then briefly immersed into a 1 mM $CuSO_4$ solution, causing the reaction $Cu^{2+} + 2e \rightarrow Cu$ (and leaving the solution negatively charged with excess SO_4^{2-} ions). Insert shows an image of the film taken with an optical microscope. Cu films were formed only on a few isolated spots probably through a surface diffusion and aggregation of Cu atoms instead of consecutive electron transfer to attain the nucleation of multiple Cu ions on the same point.

shown in Fig. 5. The concentration change corresponded to an average charge density of about 8×10^{14} cm^{-2} (geometric area). When the deposited Cu on PTFE was dissolved in nitric acid, analysis of the Cu concentration by absorbance yielded a charge density up to 7.6×10^{14} cm^{-2}, about the same as that found in the preceding experiments. This is a rather high surface density and is about the same as the atom density on an atomically smooth Si surface [59].

3.2.3. pH change and hydrogen production

When PMMA-rubbed PTFE was immersed into 3 mL of a 0.1 mM HCl solution, the solution pH increased. For example, after 37 pieces of PTFE septa were rubbed with PMMA disks and then briefly immersed into solution one after another, the solution pH increased from 4 to 6.2. While this experiment does not distinguish between ion (OH$^-$) or electron transfer, the observation of hydrogen gas demonstrates that electron transfer is involved. Indeed, hydrogen was detected by UHV mass spectrometry. In this case, D_2O was used and samples were prepared inside a glove box. Charged PTFE tape was introduced through a PTFE 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. 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, while a control experiment carried out under the same conditions without contact to charged PTFE showed only a flat baseline [50].

3.2.4. Amplified responses

The Cu deposition effect could be amplified by using the available charge on PTFE and PE in an electroless deposition mode. In electroless deposition, a solution of a metal ion, e.g. Cu^{2+}, and a reductant, e.g. formaldehyde, will deposit metal, e.g. Cu, only in the presence of the proper catalyst, such as Pd. Thus it is only necessary for the contact electrification charge to form seed metal catalysts, which then spontaneously will form a much larger deposit of Cu when it contacts the electroless plating bath. For example, after a PTFE surface was rubbed with the edge of a PMMA 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 act as catalysts for Cu deposition. When it was washed and immersed into a Cu plating bath containing $CuSO_4$, $KNaC_4H_4O_6$, NaOH, and formaldehyde [60], Cu was deposited on PTFE in the same pattern as shown in the insert of Fig. 5, i.e. the initial charge was 'developed' as in a photographic image. This suggests that one can charge the PTFE surface in a designed pattern and then metallize it to form a desired structure, which may be of interest in applications [61].

Similarly, mass Cu deposition on PE could also be accomplished [52]. For example, following the plating of Pd in the way as described above, a PE rod was washed and then placed into a Cu plating bath, a large amount of Cu deposition was observed as shown in Fig. 6, only where the PE was charged by rubbing with PMMA.

3.2.5. Chemiluminescence (CL) generation

Chemiluminescent reactions can be very sensitive, since light emission is measured without any input of light, and that has been the basis of many electrogenerated chemiluminescent (ECL)-based redox reactions [62]. This type of CL can be generated through an 'oxidative reduction' process in a solution containing a coreactant and a luminophore molecule, where both of them are first reduced at an electrode. The reduced coreactant decomposes to form a highly oxidizing species that in turn reacts with the reduced form

Fig. 5. Cu plated on charged PTFE. Optical absorbance of 1 mM CuSO$_4$ solution before and after contact with charged PTFE. Insert shows an optical image (167 × 225 μm^2) of Cu lines formed by electroless deposition on PTFE in a designed pattern in a separate experiment. (Plating of Pd, followed by deposition of Cu in a catalyzed chemical reaction.)

Fig. 6. Top right: an optical image showing Cu deposited on the end of a PMMA-rubbed PE rod and no Cu plated on other surface that was not rubbed. Top left: an optical image showing Cu deposited on untreated inner surface of a Nylon tube. No Cu was found on the PE-rubbed outer surface and the end. Bottom: enlarged optical image (0.8 × 0.43 mm^2) of the Cu film on the Nylon inner surface.

Fig. 7. Relative intensity of chemiluminescence as a function of time when a PMMA-rubbed PE rod dipped into a MeCN/H$_2$O (1:1, v/v) mixture containing 2.5 mM S$_2$O$_8$$^{2-}$ and 0.25 mM Ru(bpy)$_3$$^{2+}$. Insert shows the reaction mechanism.

of the luminophore. Ultimately the redox reaction produces an emitting excited state and CL. Thus the electrochemical reduction of a mixture of tris(2,2′-bipyridine)ruthenium (II) perchlorate [Ru(bpy)$_3$(ClO$_4$)$_2$] and the coreactant, sodium peroxydisulfate, Na$_2$S$_2$O$_8$ in an acetonitrile (MeCN)/water (1:1, v/v) mixture leads to emission, from the reaction of Ru(bpy)$_3$$^+$ and SO$_4$$^{\cdot-}$. This reaction also occurs when PMMA-rubbed PTFE or PE is immersed in this solution. Fig. 7 shows the emission when a PE rod first rubbed with PMMA and then immersed in 0.25 mM Ru(bpy)$_3$(ClO$_4$)$_2$ and 2.5 mM Na$_2$S$_2$O$_8$, with CL at the μA level. Note in this example that some air bubbles were trapped at the PE/solution interface and

blocked some of the charged area. As those bubbles moved around and eventually escaped, more electrons became available and generated the irregular CL spikes shown in Fig. 7. As expected, when either of these reagents alone was present in the solution, the CL was barely seen above the background upon charged PE introduction on the same scale. This result is again consistent with the charges on PE being electrons. Note that same result was also obtained with PMMA-rubbed PTFE [50], and Nylon-rubbed PTFE and PE [52].

Comparing all of the combinations among these four polymers under study, the highest charge density was obtained on the PMMA-rubbed PTFE surface, which, as expected, also generated the strongest CL under the same conditions. A potential analytical application was demonstrated for electrostatic charge generated CL, which we have called 'electrostatic chemiluminescence (ESCL).' The ESCL dependence on the concentrations of Ru(bpy)$_3$$^{2+}$ and
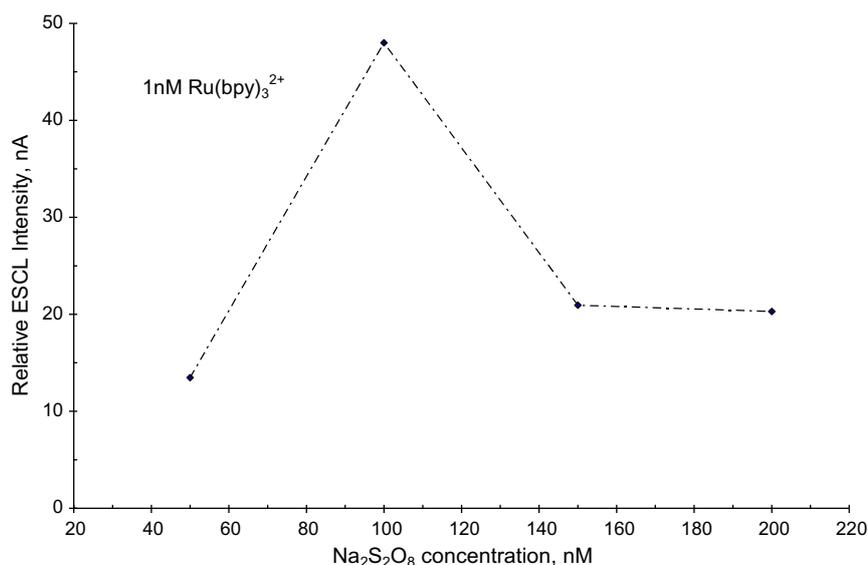
Fig. 8. Charged PTFE produced chemiluminescence. Relative ESCL intensity generated by charged PTFE as a function of $Na_2S_2O_8$ concentration in MeCN/H_2O solution (1:1 by volume) with 1 nM Ru(bpy)$_3^{2+}$.

Table 1

Emission Intensity as a function of [Ru(bpy)$_3^{2+}$] and [$S_2O_8^{2-}$] in CH_3CN:H_2O (1:1, v/v) averaged from 10 measurements.

[Ru(bpy)$_3^{2+}$]	[$S_2O_8^{2-}$]	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	1500 nM	93
100 nM	10 μM	176
1 μM	180 μM	594

$S_2O_8^{2-}$ was studied , similar to previous ECL studies [63]. For 1 nM Ru(bpy)$_3^{2+}$, the ESCL increased with $S_2O_8^{2-}$ concentration up to roughly 100 nM (Fig. 8), and then the emission dropped off sharply, probably because of quenching of Ru(bpy)$_3^{2+*}$ by $S_2O_8^{2-}$ as reported earlier [64]. Similar results were obtained for different concentrations of Ru(bpy)$_3^{2+}$ over a range of five orders of magnitude. Table 1 shows the maximum ESCL response at a given Ru(bpy)$_3^{2+}$ concentration from separate measurements for each mixed with 4 to 5 different concentrations of $S_2O_8^{2-}$. At 0.1 nM Ru(bpy)$_3^{2+}$ a clear ESCL signal was seen that was well above the background level.

Since the electrostatic charges on the PTFE surface were generated through rubbing with PMMA, reproducibility of these measurements was a concern. A series of measurements showed that the ESCL intensities did not vary significantly over 10 separate experiments (two different solutions with the same composition and PTFE rods of the same size and shape, 5 new rubbings for each) with 1 nM Ru(bpy)$_3^{2+}$ and 100 nM $S_2O_8^{2-}$ and yielded an averaged signal of 49 nA with a standard deviation of 5.8 nA as shown in Fig. 9. Note that the rubbing (in air) was stopped when discharge sounds were heard, always accompanied with small sparks that lit up the rubbed PMMA surface and edges and clearly seen with the naked eye in a dark room. This was a good indication to ensure reproducible results, since the charges were probably indicative of a charge-saturated PTFE surface at which point further rubbing may only produce additional discharges. Contact without rubbing generated the ESCL but with a lower intensity.

4. Additional considerations

4.1. Charges in solution

We have demonstrated that charged polymers can behave as 'single electrodes' and that a variety of chemical species can be reduced by electrostatic charges on polymer surface, when the negative charges, produced through contact electrification with other polymers, were transferred to solution species. However, as opposed to these reactions in a conventional electrochemical cell, where reduction reactions at cathodes are exactly balanced by oxidations at the anode, with single electrode electron-donating polymers, the solution should become negatively charged upon contact due to the presence of uncompensated anions. This concept seems to go against the basic idea that, *at equilibrium*, solutions are generally considered electrically neutral, as implied by the well-known electroneutrality condition widely applied in equilibrium calculations. However, in fact, charged solutions are quite common, e.g. in electrospray mass spectroscopy [65] and the classic Kelvin water drop experiment [53]. We have confirmed solution charging on polymer contact by a direct electrostatic measurement. In the experiment, a sensitive electrometer was connected to two identical cells, which were made of aluminum foil and were well insulated from ground, both containing the same solution of 1 mM $CuSO_4$. The voltage, measured with an electrometer, was initially zero between those two cells as expected. After a PTFE or PE rod rubbed on a PMMA plate was dipped into the solution in one cell (avoiding contact with the Al foil), a stable voltage of over 100 V was measured on the electrometer, with the cell where the polymer dipped at the negative potential. This voltage persisted even after the PTFE or PE was removed from the solution.

4.2. Origin of the electrostatic charge

All of the above reduction chemical reactions indicated that the charge carriers on PMMA-rubbed PTFE surface were most reasonably explained as electrons. Where did those electrons come from? The results suggest that electrons of the appropriate energy to carry out the reactions were transferred from PMMA to PTFE during rubbing, that is, PMMA is the initial electron donor (e.g. as opposed
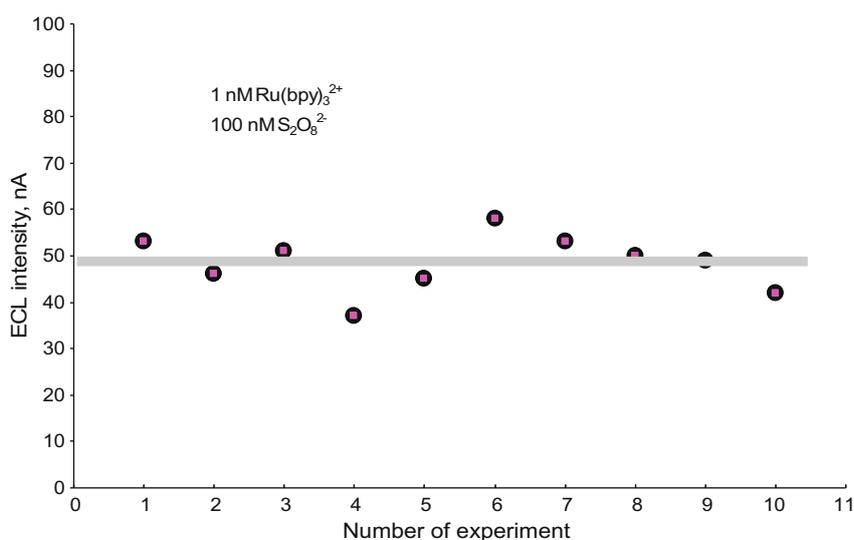
Fig. 9. Reproducibility of charged PTFE generated chemiluminescence in MeCN/H$_2$O solution (1:1 by volume) containing 1 nM Ru(bpy)$_3^{2+}$ and 100 nM Na$_2$S$_2$O$_8$.

to electrons being generated by breaking bonds during the contact). If that is the case, then a native PMMA piece that had not been contacted with PTFE or another electron acceptor, i.e. had not been depleted of available electrons, should be capable of carrying out these same reactions. Indeed we have found that PMMA itself can carry out the same reactions as those observed with contacted PTFE [66]. These include metal plating (via Pd-catalyzed electroless Cu deposition) (Fig. 10), reaction with Fe(CN)$_6^{3-}$, and ESCL experiments. When the total amount of reduced Fe(CN)$_6^{3-}$ was divided by the overall surface area of the PMMA tube contacted, an average electron density of 4.5×10^{13} cm^{-2} was obtained. This is essentially the same as the total electrostatic charge density on an atomically flat mica surface contacted with silica determined with a different technique [67]. Similarly, native Nylon, which also was capable of charging polymers like PTFE or PE, would also carry out these reactions [52]. To see whether a PMMA surface depleted of electrons on contact with PTFE could still cause metal deposition, a fresh PMMA tube was rubbed with PTFE tape, then dipped into a PdCl$_2$ solution briefly as before, followed by washing and immersion into an electroless Cu plating bath for different time periods. No Cu was observed on the PTFE-rubbed PMMA tube and the blue color in the solution did not fade even when the PMMA was left in the bath for over 6 months. Similar results were obtained with Nylon as shown in Fig. 6. These results demonstrate that native PMMA (and Nylon) can produce reduction reactions, but that when they are depleted of the required surface electrons (called 'cryptoelectrons') [66] either by contact with PTFE or by oxidation in the chemical reaction, they will not carry out these reactions. It is reasonable that these electrons are passed to PTFE or PE on contact electrification.

4.2.1. Recharging of depleted PMMA

In vacuum contact electrification, PMMA surfaces can be reversibly charged, discharged and recharged between positive and negative in cycles by consecutive contacts with metals with different work functions [68], and a wide distribution of electronic states on a PMMA surface were proposed [69]. Note that we found that fully discharged PMMA could not carry out reduction reactions. For example, after a Fe(CN)$_6^{3-}$ solution passed through a fresh PMMA tube and Fe(CN)$_6^{3-}$ was reduced to Fe(CN)$_6^{4-}$ as described above, the same tube was then kept in the lab environment for 2 months. A repeat of the experiment at that time
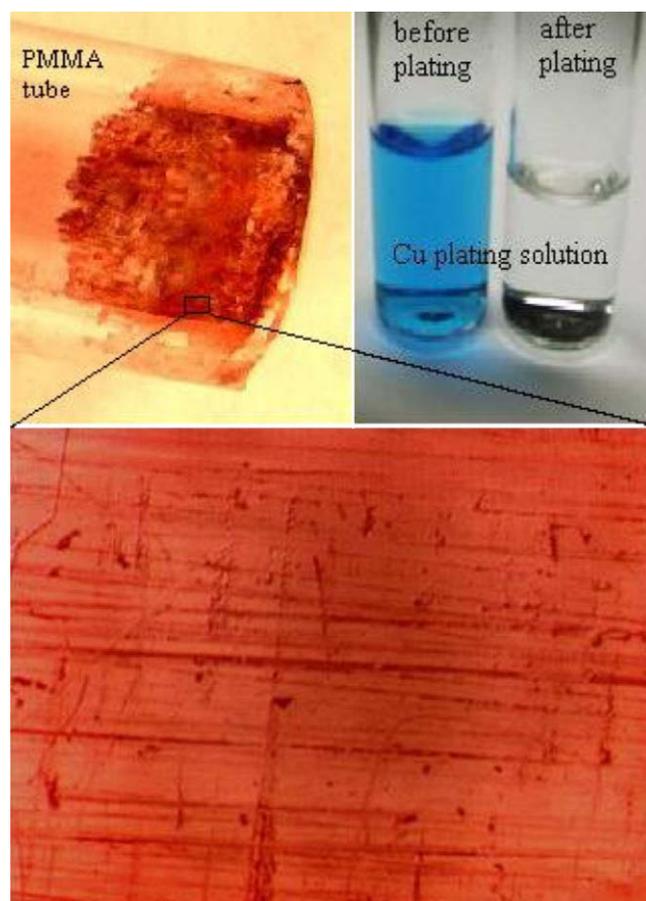
Fig. 10. Copper plated on untreated PMMA surface. Upper left: an optical image of copper film deposited on a PMMA tube inner surface. No Cu was seen on the outer surface that had been previously contacted with PTFE. Bottom: enlarged image of the copper film (0.8 mm × 0.6 mm) where features such as lines reflect the surface structure of the tube instead of scratches. Upper right: images of two glass test tubes containing copper plating solution before and after the plating. Blue color of the solution disappeared following the deposition.

showed essentially no Fe(CN)$_6^{4-}$ formation. After another 6 months, still no Fe(CN)$_6^{4-}$ was detected. Thus the PMMA tube, once depleted of its cryptoelectrons did not recharge on standing,
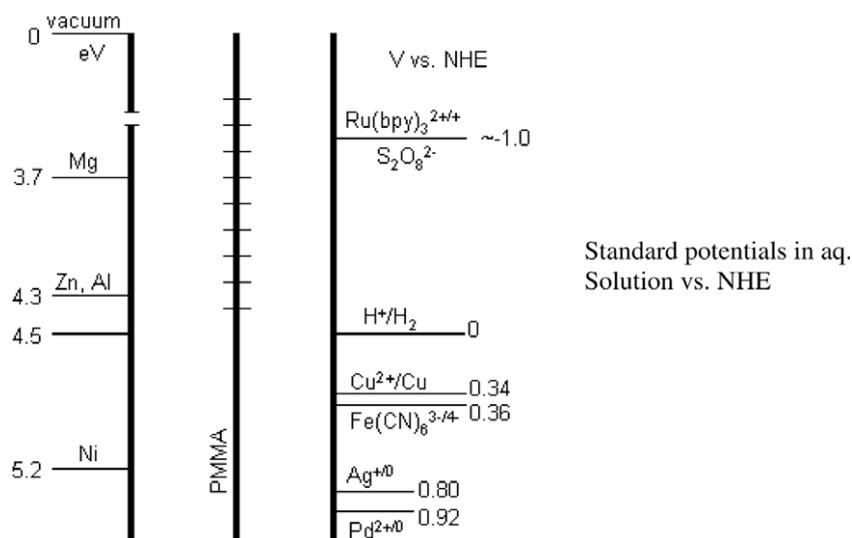
Fig. 11. Proposed energy states on a PMMA surface in relation to several standard redox potentials on the right and metal electron work functions on the left. Note the antibonding (conduction band) levels of PMMA would be above the vacuum level and the bonding (valence band) levels would be at about 8 eV.

e.g. from adventitious reductants in the air or cosmic rays. An attempt was made to recharge the PMMA by a suitable reductant [66]. In this case, the depleted PMMA tube inner surface was thoroughly washed with deionized water and dried with an argon flow. Then 0.8 mL of 0.3% w/w sodium amalgam was passed through the tube. Following this, the tube was contacted with the $Fe(CN)_6^{3-}$ solution as described early. The amount of $Fe(CN)_6^{4-}$ produced was about 10 times higher than that with a fresh tube. This indicates that the PMMA tube was recharged and able to carry out reduction reactions again. In a separate experiment, a Na amalgam recharged PMMA tube was dipped into a saturated Pd^{2+} solution briefly, then washed and immersed into an electroless Cu platting bath as described above. Cu quickly deposited on the internal recharged surface of the tube and, in less than 20 s, could clearly be seen with naked eye, indicating that the electron density on the recharged surface was significantly higher than that of a fresh tube consistent with the results of $Fe(CN)_6^{3-}$ reduction. As expected, Cu deposition was not seen on the tube's outer surface that had been depleted previously and never touched the amalgam for recharging. Although one cannot exclude the possibility that small amounts of amalgam may be left on the surface, e.g. in small cracks and defects, we found in the plating experiment that the deposition of metal covered the whole recharged surface immersed into the plating bath and not just a few spots where possible residues of the amalgam might be located. Thus with both contact electrified PTFE and native PMMA, the ability to carry out reduction reactions depends on the 'state of charge' of the surface.

4.3. Nature of the electrostatic charge on polymers

All the experimental results shown above are consistent with electrostatic charges on non-ionic polymers being electrons and that electron transfer occurs in contact electrification. PMMA and Nylon behave as electron donors to PTFE and PE. What is the nature of the electrons on the donor polymers (e.g. the physical location and molecular environment of such electrons) and their energy levels on a typical potential scale? In terms of the sites for the cryptoelectrons, there are several general possibilities. (1) *Impurities*; however these are small (<0.1 ppm) for PMMAs used in this work and the powders, for example, should not be contaminated substantially. (2) *Additives;* however these were not intentionally introduced in the manufacture for all of the PMMA samples used. (3) *Cosmic rays* which in principle could excite electrons to produce trapping sites; however, the total number of those energetic particles are too low to make a meaningful contribution. (4) *End groups* on the polymer chains that originate in the polymerization of monomers; however for polymers with the molecular weights studied here, such end groups would represent only about 0.1% or less. (5) *Unique sites* created by special configurations of the chains or intrinsic molecular ion states formed in a charge transfer reaction; however, similar electron transfer capability was found with totally different polymers of polyamide (Nylon) and PMMA. (6) *Surface states* induced by mechanical breakage of bonds. Such states should be able, depending on their nature, to accept or donate electrons to other substances upon contact. Surface damage could occur during formation of the polymer, handling, or by rubbing or contact with other surfaces.

In terms of the energy level(s) of the cryptoelectrons in PMMA, we can examine the potentials of the various redox reactions that we carried out (Fig. 11). The most negative reaction involved the reduction of $Ru(bpy)_3^{2+}$, which, on the basis of measurements in acetonitrile, would have a potential of about −1 V vs. NHE in water, so an occupied electronic energy level on the PMMA surface would be above (more negative than) this value and any chemical species with a redox potential below this could be reduced. In contact electrification experiments, PMMA and Nylon are usually placed at or near the top in several triboelectric series [56–58], becoming positively charged upon contact with other dielectrics and most metals, where the amount transferred charge increased with increasing metal work function [69,70]. Based on the electron transfer mechanism for contact electrification, PMMA and Nylon have higher tendency to donate electrons to contacted materials compared to other polymers. Thus, contacting PMMA with Zn or other metals with a larger work function cause the PMMA to become positively charged. However, contacting PMMA with Mg with a small work function produces negatively charged PMMA [69]; this is generally consistent with the energy level suggested by the solution phase experiments (Fig. 11). This analysis agrees with the results that PMMA surface could be reversibly charged, and discharged between positive and negative in repeated cycles with consecutive contacts with metals of different work functions [68].

Moreover, the usual measurement of charge with an electrometer results only in the determination of the total charge (electronic and ionic), while the chemical approach determines only the electronic component. Systematic investigation of polymers and other dielectrics is currently underway to examine the generality of this behavior. Such studies will help in the development of 'single electrode electrochemistry' [71] where a charged dielectric can play the role of a charged metal. Although the available charge in PMMA from the cryptoelectrons is small, of the order of 10^{-10} mole equivalents cm^{-2}, it is sufficient to cause surface modification of the material. The chemical effects would be even more important if the involved species were catalytic. PMMA and PE are widely used, for example in medical implants where inertness in the biological environment is important [72,73], and it is perhaps appropriate to consider the possibility that reactions by cryptoelectrons can have detectable effects.

5. Conclusions

Polymer charging by contact electrification, and probably more generally with dielectrics, can occur by several different mechanisms, which accounts for the lack of agreement of a huge body of studies with a general, all-inclusive mechanism. As discussed at the start of this perspective, in general, solid surfaces are characterized by both ionic and electronic charge, and the same is probably true with polymers. Moreover, polymers have a wide range of properties, from polyelectrolytes with exchangeable ions, to non-ionic ones, like PTFE and PE, where ions would be thought to play a less important role, to conjugated polymers, where electron transfer processes are clearly important. Perhaps a useful analogy is the reactions that occur at the interface between two immiscible electrolyte solutions (ITIES), where both electron and ion transfer have been shown to occur [74].

We contend that chemical probes are a powerful approach to understanding contact electrification for non-ionic polymers and that these experiments demonstrate that the electron is the charge carrier that is transferred from one insulator to another during contact electrification. Surface electron density could be precisely determined through a quantitative analysis of the chemical species that was reduced upon contact with charged insulator. The energy distribution of the electron on the charged surface could be probed by systematical measurements of redox reactions using a variety of chemical species with different redox potentials. Electronic states may exist on the surface or in the bulk [75] of insulating polymers, and accessible states can be charged and discharged reversibly through contact with different metals or solutions containing appropriate molecules. Efforts to obtain further independent evidence about the surface states on polymers and expand the scope of this concept are under way in our laboratory. An important challenge is obtaining a molecular level understanding of the charging sites on the surface of dielectrics.

Acknowledgments

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