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ARTICLE

Humidity Transforms Immobile Surface Charges into Mobile Charges during Triboelectric Charging

Phwey S. Gil and Daniel J. Lacks*[a]

Triboelectric charging – which children see when they rub balloons on their hair – has important consequences in many industries and natural phenomena. Despite its importance, the identity of the charge carriers that lead to triboelectric charging is uncertain. For polymers, previous x-ray photoelectron spectroscopy studies definitively show that bonds break during triboelectric charging. Others have argued that a pair of co-located bond breaks release a charged fragment that acts as the charge carrier for triboelectric charging. We describe an alternative process based on density functional theory results showing that charged fragments, in the presence of water, will react to form neutral fragments and H^+ or OH^- ions. These results show that a single bond break, which is more likely than a pair of co-located bond breaks, can then create tethered polymer fragments that in humidity will generate mobile H^+ or OH^- charge carriers for triboelectric charging.

Triboelectric charging is the transfer of charge that occurs between two substances that make physical contact and then separate. Triboelectric charging is ubiquitous and simple to demonstrate (e.g. rub a balloon against hair), and it has enormous consequences now – e.g., being the basis of major industries such as digital printing[1] and causing electrical discharges in combustible vapors and dusts that lead to dangerous explosions;[2] and in our natural history – e.g., a factor in the formation of planets[3] and the origin of life.[4] However, the identity of the charge carrier remains unknown in many cases, including the case for commonly-used polymer materials. Therefore, a fundamental challenge for understanding triboelectric charging is to identify what species are responsible transferring charge from one substance to another.

The role of mechano-chemistry (i.e. the concept that contact stress drives chemical reactions) has been historically acknowledged as a likely factor in triboelectric charging for polymer materials. For example, a 1962 article suggests that mechanical stress breaks chemical bonds to form "mechano-radicals", where these mechano-radicals can be a source for transferred charges.[5] X-ray photoemission spectroscopy (XPS),[6] infrared spectroscopy (IR) and electron spectroscopy imaging (ESI),[7] revealed that polymer fragments transfer during triboelectric charging, which led to the suggestion that the transfer of charged fragments ("mechano-ions") underlies triboelectric charging. Many subsequent XPS studies showed the same result.[8-14] Electron spin resonance measurements directly show the presence of mechano-radicals,[15] while force-microscopy and radical-scavenging experiments on triboelectrically charged surfaces[16,17] and density functional theory calculations[18] suggest the stabilization of mechano-ions by mechano-radicals.

These results, taken together, show that mechano-chemistry occurs during triboelectric charging. Experiments definitively show that contact stress breaks chemical bonds in a material during triboelectric charging. But how these broken bonds lead to charge transfer is less clear.

Many investigations surmise that charged fragments of a material are broken off from one surface, thus becoming mobile mechano-ions, and are transferred to another surface to lead to triboelectric charging. This process is shown schematically on the left side of **Scheme 1**. This idea is viable, as the amount of material transferred could reasonably be expected to carry the observed charge transfer,[6] and a recent study found that the magnitude of charge transferred correlates with the amount of material transferred.[14] However, there is no direct evidence that transferred materials were charged fragments, and therefore a different charge carrier may still be responsible for the triboelectric charging.

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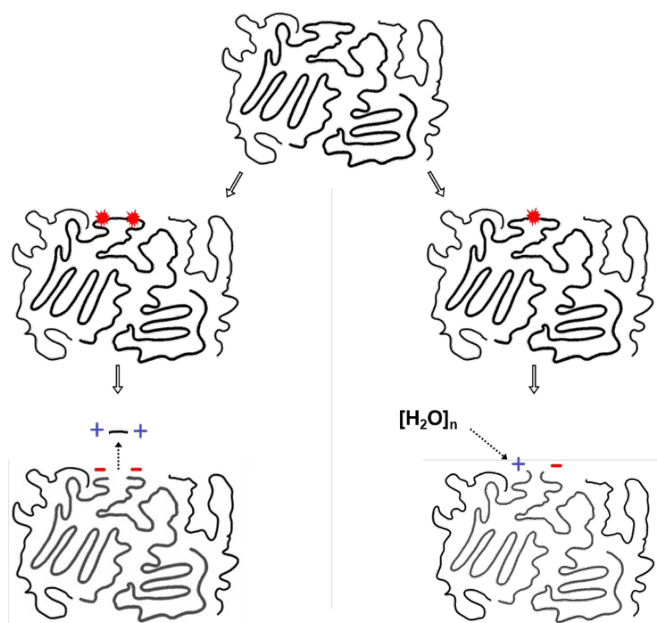
Scheme 1. Illustration of two ways that charge from a mechano-ion can transfer to another surface. Left: Polymers are entangled in the material surface, so it requires two bonds to break to release a mechano-ion, which could then transfer to the other surface. Right: A single bond breaks to create mechano-ions which react with water, generating mobile ions that can transfer to the other surface.

We present computational results showing that a different mechano-chemical effect will also occur, which we argue is more likely to lead to transferred charges. The creation of mobile mechano-ions, as described above, requires a pair of bonds to break in a polymer chain, where the locations of the pair of broken bonds are sufficiently close such that there are no chain entanglements in between them (left side of **Scheme 1**). In contrast, this paper describes a process where the creation of mobile ions requires only one bond to break in the polymer chain, as illustrated by the process shown on the right side of **Scheme 1**. It is statistically more probable to have one bond in a polymer chain break, rather than for two bonds to break in proximate locations – thus, we argue that the process based on one broken bond is more likely to be important than the process based on two broken bonds. However, when there is one broken bond the fragment may be charged but it remains tethered to the surface and thus immobile.

We show that a tethered polymer mechano-ion created from one broken bond is unstable in the presence of water. Water is ubiquitous in our atmosphere, and in general adsorbs onto surfaces, even if the surface is hydrophobic.[19,20] We carry out density functional theory (DFT) calculations[21] to show that water and mechano-ions undergo acid-base charge exchange reactions. These reactions neutralize the charge of the tethered, and thus immobile, mechano-ions while producing mobile charges (as H^+ or OH^- ions) stabilized by surrounding water molecules.

A rigorous simulation of mechanochemical processes during contact of two surfaces is far beyond current computational capabilities – a large number of atoms are needed to describe surfaces of polymers materials; the timescale that two surfaces move with respect to each other is orders of magnitude longer than the timescales of molecule-level processes such as bond-breaking; and yet quantum mechanical methods are needed to consider bond-breaking.
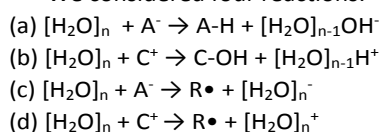
For this reason, we consider a simplified system that can be rigorously addressed. We model a polymer molecule which has been cleaved to form an anionic fragment (A^-) and a cationic fragment (C^+). Each ion is modeled as an isolated fragment of polyethylene (PE), polytetrafluoroethylene (PTFE), or polydimethylsiloxane (PDMS), as shown in **Figure 1**. PE, PTFE, and PDMS are materials that are commonly studied in triboelectric charging experiments.

We examine how these fragments interact with a small cluster of water molecules; we choose to use a small cluster of water molecules rather than bulk water, as we believe the cluster more suitably mimics the nature of adsorbed water.
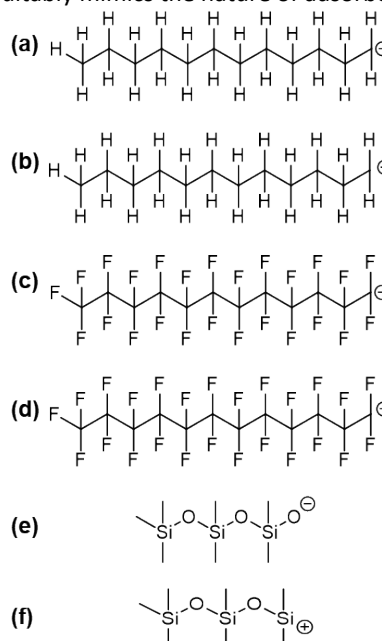
Figure 1. Chemical structure of model **(a)** PE mechano-anion, **(b)** PE mechano-cation, **(c)** PTFE mechano-anion, **(d)** PTFE mechano-cation, **(e)** PDMS mechano-anion, and **(f)** PDMS mechano-cation.

We considered four reactions:

(a) $[H_2O]_n + A^- \rightarrow A\text{-}H + [H_2O]_{n-1}OH^-$

(b) $[H_2O]_n + C^+ \rightarrow C\text{-}OH + [H_2O]_{n-1}H^+$

(c) $[H_2O]_n + A^- \rightarrow R\bullet + [H_2O]_n^-$

(d) $[H_2O]_n + C^+ \rightarrow R\bullet + [H_2O]_n^+$

In each reaction, water clusters of various sizes ($[H_2O]_1$, $[H_2O]_3$, or $[H_2O]_5$) react with the anionic fragment (A^-) or the cationic fragment (C^+) of PE, PTFE, or PDMS. Reactions (a) and (b) are acid-base reactions that convert the ionic charges of mechano-ions into H^+ or OH^-. Reactions (c) and (d) are electron transfer reactions where the mechano-ions are neutralized to radicals ($R\bullet$) while water gains or loses an electron.

Density-functional theory is used to calculate the energy of reaction (ΔE) for the above reactions. The calculations address the case where the reactants start out separated and the products end up separated; the calculated ΔE accounts for the change in potential energy for bringing the separated reactants to proximity, exchanging atoms and/or electrons, and then

separating the products. A negative ΔE indicates that the reaction is thermodynamically favorable.

The calculations are carried out with the 6-31G(d,p) basis set[22] and the B3LYP density functional;[23-25] this functional has been shown to be accurate for neutral and charged water clusters of various sizes.[26] Open shell calculations are used in order to be able to model reactions (c) and (d) that have radical species with an unpaired electron. Geometry optimizations are carried out before calculating the energy of each species - the optimized structure and the energy of each species are detailed in the **Supplemental Information**. Avogadro software[27] is used to prepare the initial atomic coordinates, and Gaussian 09 software[28] is used to carry out the electronic structure calculations.

A water molecule can donate an H$^+$ to the mechano-anion,
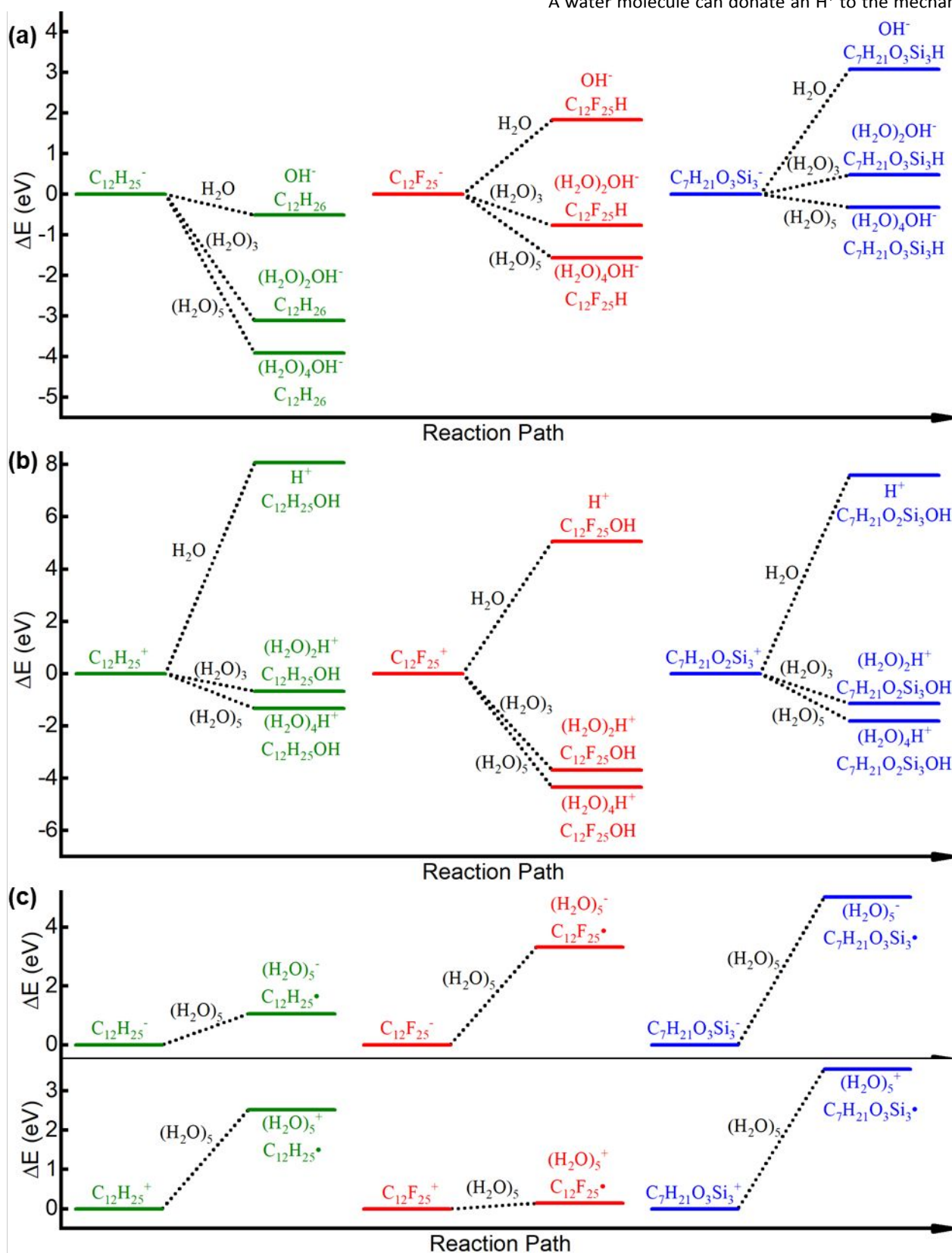
Figure 2. Change in energy as water **(a)** reacts with mechano-anions to produce OH$^-$, **(b)** reacts with mechano-cations to produce H$^+$, **(c)** exchanges an electron with mechano-ions to produce (H$_2$O)$_5^-$ or (H$_2$O)$_5^+$. Green shows the reactions with PE, red shows the reactions with PTFE, and blue shows the reaction with PDMS.

as described by reaction (a). The reaction products are a neutral

oligomer and an OH⁻ ion that is hydrated by any remaining water molecules in the cluster. The results for ΔE are shown in **Figure 2(a)**. For PE, the ΔE is negative even when the OH⁻ ion is not hydrated by water molecules; for PTFE and PDMS, the ΔE is positive when the OH⁻ ion is not hydrated. The ΔE becomes more negative (more thermodynamically favorable) as the size of the water cluster increases. For the case that two water molecules can hydrate the OH⁻ ion, the ΔE becomes negative for PTFE, although it remains positive for PDMS. When four water molecules hydrate the OH⁻ ion, the ΔE is negative for all three polymers studied.

A water molecule can donate an OH⁻ ion to the mechano-cation, as described by reaction (b). In this case, the reaction products are a neutral oligomer and an H⁺ ion that is hydrated by any remaining water molecules in the cluster. The results for ΔE are shown in **Figure 2(b)**. Here, the ΔE is positive for all polymers when the H⁺ ion is not hydrated. This reaction becomes more thermodynamically favourable as the water cluster gets larger. When two or more water molecules hydrate the H⁺ ion, the ΔE is negative for all three polymers studied.

We believe that entropic effects would steer the thermodynamics to be in favor of the acid-base reactions. The reaction breaks a bond in water and creates a bond with the polymer − the change in configurational entropy would be balanced in this part of the process. The reaction leads to a water cluster that contains an ion that is distinguishable from other water molecules, increasing the configurational entropy.

Both acid-base reactions become more favourable with increasing number of water molecules. Likely, the same reactions would carry out in bulk water as well in humid air.

We also examined reactions (c) and (d) where an electron is transferred between water and the mechano-ions. In these cases, the reaction products are a neutral radical oligomer and a water cluster with ±1 electron. The results for ΔE are shown in **Figure 2(c)**. The ΔE of this reaction is always positive, even when the largest water cluster was considered.

To conclude, water is ubiquitous, so it plays a role in most cases of triboelectric charging that occur in the Earth's atmosphere. It is amphoteric, so it can act as an acid or a base, reacting with mechano-anions to generate negative mobile charges (OH⁻) or reacting with mechano-cations to generate positive mobile charges (H⁺). Our results and arguments concur with previous experimental results that show that the presence of water enhances charge transfer[29-32] and the results that highlight the importance of acid-base properties of surfaces in their interaction with water.[33-36]

We argue that it is statistically more probable for single bonds in polymer chains to break and create tethered mechano-ion on the polymer surface, rather than for two bonds to break and create mobile mechano-ions. Our density-functional theory calculations show that tethered mechano-ions will react with adsorbed water to generate mobile charges that can act as charge carriers in triboelectric charging. This is an effect that likely acts in concert with, and not necessarily exclusive to, other mechanisms that can drive triboelectric charging.

Conflicts of interest

There are no conflicts to declare.

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$[H_2O]_n$

Ionic material fragments created by contact stress will react with water to create ions that can transfer between surfaces.