

Kinetics of Contact Electrification between Metals and Polymers

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Kinetics of charge transfer between metals and polymers was studied using an analytical rolling-sphere tool. The rates of charge transfer were related to the area of contact between contacting surfaces and the tunneling current between them. The derived rate equations accounted for the experimentally observed sigmoidal charging curves. Furthermore, for a model system of steel spheres rolling on modified polystyrene supports, it was shown that the magnitudes of separated charges can be varied by adjusting the polymer's surface properties and/or ambient conditions.

1. Introduction

Contact electrification (CE)^{1,2} is the transfer of charge between two surfaces that are brought into contact, with or without friction and/or applied potential, and then separated. Although CE is, in the absolute sense, a small effect involving approximately only one in ten thousand surface atoms separating charge, it can give rise to surface charge densities on the order of 10^{-5} – 10^{-4} C/m² that are sufficient to cause breakdown of air or even common insulators. The buildup of charge caused by CE can produce electrical shocks, fires, explosions, mechanical jams, or damage of electronic equipment.^{3,4} At the same time, CE is key factor of many useful technologies such as photocopying,⁵ electrostatic spray-painting, and electrostatic precipitation,⁶ and has recently been used as a basis of dynamically self-assembling systems.^{7,8} Despite a long history of scientific investigation, the mechanisms of contact electrification between metals and dielectrics are not completely understood, largely because of the lack of sensitive and *reliable* experimental techniques. The literature has several examples where the same metal–dielectric system displayed conflicting charging behavior when studied by independent workers: in these cases both the magnitudes and polarities of the charges were claimed to be different.^{2,9–13}

We have recently described a versatile and sensitive tool for noninvasive measurement of charge that develops by CE on metallic spheres rolling in circular paths on dielectric surfaces. In previous work,^{14,15} we used this tool to (i) establish the polarities and maximal magnitudes of charges developed by CE on a range of polymeric supports, (ii) qualitatively relate the charging properties of the polymers to their chemical structures, and (iii) investigate the effects of relative humidity (RH) on the rates of CE charging in a model steel/polystyrene system. Here, we extend these studies to derive qualitative rate expressions for the *kinetics* of contact electrification between metals and polymers. The major experimental observation underlying our theoretical analysis is that the magnitude of charge, $Q(t)$, developed by CE increases sigmoidally with the time of sphere rolling, t . Importantly, for short times the rate of charge separation, \dot{Q} , is proportional to $Q^{4/3}$, indicating that the more

charged the polymer and the metal sphere are, the more readily they separate charge. We explain this counterintuitive effect by the dependence of \dot{Q} on the area of contact between the contacting surfaces and the tunneling current between them. In addition, for a model system of steel spheres rolling on pure and oxidized polystyrene (PS) surfaces, we show that \dot{Q} can be related to the concentration of charge-exchanging groups on the polymer's surface.

2. Experimental

(i) Apparatus. Figure 1a illustrates the experimental arrangement described in detail elsewhere.^{14,15} Briefly, a permanent, rectangular bar magnet of magnetization $M \approx 1000$ G cm⁻³ along its longest dimension rotated with angular velocity $\omega \approx 1000$ rpm at a distance ~ 1 cm below the surface of a flat polymer sheet (~ 100 μ m thick). A 1-mm ferromagnetic stainless steel sphere, either bare or covered with a thin layer of thermally evaporated gold or silver, was placed onto the polymer, and any adventitious charge was thoroughly neutralized with a piezoelectric gun. The entire assembly was housed in an electrically shielded hermetic chamber, in which temperature T was kept constant at 25 °C, and the relative humidity, RH, was adjusted to the desired level by introducing varying quantities of dry nitrogen gas (to obtain values of RH below ambient RH) or nitrogen gas saturated with water vapor (to obtain values of RH above ambient RH).

Under the influence of the rotating permanent magnet, the sphere rolled on the polymer surface tracing a circular path.⁸ The rolling motion of the sphere resulted in the separation of charge between the sphere and the surface along its track. The magnitude of charge accumulated on the sphere increased with the time of rolling, and was measured using a 5-mm-wide metal electrode glued to the bottom of the dish and connected to an electrometer (Keithley 6517); the electrode was thus separated from the sphere by the thickness of the polymer sheet plus dish (~ 1 mm). Every time the charged sphere rolled over the electrode, it induced a charge, Q_{ind} , of opposite polarity in the electrode. The magnitude of this induced charge was proportional to the charge on the sphere, and was measured as Q_{m} (where $Q_{\text{m}} = -Q_{\text{ind}}$) by a digital electrometer connected to the electrode, and referenced to ground. Overall, the charge recorded by the electrometer was proportional to the charge developed on the rolling sphere.

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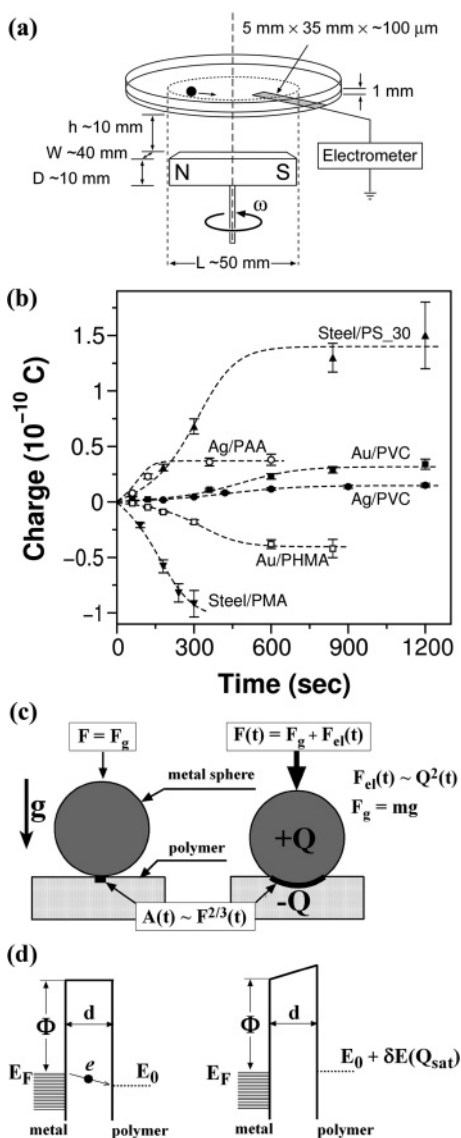


Figure 1. (a) Shows the scheme of the experimental arrangement and defines pertinent dimensions. (b) The experimental charging curves obtained for three different types of spheres (steel, steel coated with silver or gold) rolling on five different polymer substrates: poly(styrene) oxidized for 30 s (PS_30), poly(acrylic acid) (PAA), poly(vinyl chloride) (PVC), poly(hexyl methacrylate) (PHMA), and poly(methyl acrylate) (PMA). All charging curves have characteristic sigmoidal shapes irrespective of the chemical nature of the polymer or that of the contacting metal. Dashed lines are least-squares fits to the theoretical rate equation, $\dot{Q} = r(Q^2 + \lambda)^{2/3}(1 - Q/Q_{\text{sat}})$. Interestingly, best fits to all curves gave similar values of parameter λ (within 50%), reflecting the fact that masses of spheres (to which λ is related) used on all polymers are very similar. (c) Illustrates the deformation of polymer support caused by force, F , acting on the sphere. The total force F is a sum of two contributions: (i) the electrostatic force $F_{\text{el}} \propto Q^2$ between the charged sphere (here: positively), and the oppositely charged polymer surface, and (ii) the constant gravitational force, F_g , due to the mass of the sphere. The area of contact, A , increases with F as $A \propto F^{2/3}$, according to Hertz's law. (d) When the metal sphere and the polymer are brought in contact (left), charge carriers tunnel between the Fermi level, E_F , of the metal and some characteristic energy level, E_0 , of the dielectric.² Here E_0 is lower than the Fermi level, E_F and electrons tunnel into the surface states on the polymer. Typical height of the barrier for metal/polymer systems studied here, $\Phi \sim 5$ eV, is commensurate with the characteristic work function of stainless steel. The width of the barrier, d , is of atomic dimensions. The electric field developed by charge transfer raises the energy of the electrons in the polymer's surface states (relative to the Fermi level) by $\delta E(Q)$. When Q reaches its saturation value, Q_{sat} , the transfer of charge ceases (right).

(ii) **Spheres.** Type 316, 1 mm stainless steel spheres from Small Parts (Miami Lakes, FL) were washed successively with methylene chloride, hexanes, methanol, and acetone, and were dried in an oven at 60 °C for 1 h. Spheres coated with gold and silver were prepared by thermally evaporating (Edwards Auto 306) an adhesion-promoting layer of chromium (30 nm at a rate of 0.2 nm/s), followed by evaporation of the desired metal (300 nm at a rate of 0.2 nm/s) onto stainless steel spheres. Mechanical agitation of the spheres during evaporation of metal ensured complete and even coverage of the metal on the surfaces of the spheres. The finished spheres were stored under an atmosphere of dry nitrogen gas until use to prevent unwanted oxidation and/or contamination of the surfaces.

(iii) **Polymers.** Solutions of polymers were obtained from VWR, Aldrich, and PolySciences. Films of PS, PHMA, and PMA were cast from solutions of toluene; those of PAA were cast from aqueous solutions. Films of PVC were obtained from Small Parts. All cast films ($\sim 100 \mu\text{m}$) were dried in an oven (60 °C, ~ 1 mmHg, ~ 12 h) followed by a vacuum oven (60 °C, ~ 1 mmHg, ~ 12 h). The surfaces of PS were oxidized by UV light and ozone (UVO oxidation) using a Boekel Model 135500 UV-ozone cleaner in which a mercury lamp emits UV light across a wide range of wavelengths that photosensitizes the surface of PS and excites molecular oxygen to form ozone. The surfaces of PS were UVO oxidized and then placed under a stream of nitrogen gas (~ 10 s, to remove excess ozone) immediately prior to use.

3. Results and Discussion

a. Sigmoidal Kinetics of Charging – Generic Case. Figure 1b shows the experimental charging curves recorded for three different types of spheres (steel, steel coated with silver or gold) rolling on five different polymer supports: poly(methyl acrylate), PMA; poly(hexyl methacrylate), PHMA; poly(vinyl chloride), PVC; poly(acrylic acid), PAA; polystyrene oxidized for 30 s, PS_30. All curves have characteristic sigmoidal shapes irrespective of the chemical nature of the polymer or that of the contacting metal (for steel/PMA system, the curve terminates at ~ 0.1 nC before reaching a plateau, when the attractive electrostatic force between the sphere and the polymer is greater than the motive magnetic force, so that the sphere adheres to the surface and stops rolling¹⁶). The shapes of the charging curves can be explained qualitatively by accounting for the increase in the area of contact and the decrease in the tunneling current between the contacting surfaces during CE.

(i) **Area of Contact, A .** The larger the area of contact between the metal and the polymer, the more surface groups of the polymer can participate in CE,¹⁶ and the higher the amount of charge transferred per unit time^{17,18} (also see Supporting Information). In the rolling-sphere tool, the charged sphere is pressed against an oppositely charged surface by an electrostatic force¹⁹ $F_{\text{el}}(t) \propto Q^2(t)$ as well as a constant gravitational force, $F_g = mg$, due to the sphere's mass, m (Figure 1c). Under the influence of these two forces, the compliant polymer deforms and the area of contact increases. We note that because the surfaces are always rough to some extent, the *true* area of contact, on the atomic scale, is different (smaller) than the apparent area; it's been shown by others, however, that the apparent and true areas are proportional to one another.¹ Also, as we verified by the Nomarski-mode microscopy, the polymer surfaces show no discernible physical deformations after the removal of the sphere and return to their initial, undeformed states. It is thus reasonable to assume that the degree of surface deformation caused by the rolling sphere is small, and that the

polymers obey Hook's law. In particular, for a sphere, A scales with the total exerted force, $F = F_{el} + F_g$, according to the Hertz law^{20,21} as $A \propto F^\gamma$ where $\gamma = 2/3$. Therefore, the area of contact scales with the charge on the sphere, Q , as $A \propto (F_{el} + F_g)^{2/3} \propto (Q^2 + \lambda)^{2/3}$, where λ is some constant.

(ii) *Probability of Charge Transfer, P .* Abundant experimental evidence suggests that charge separation between metals and dielectrics proceeds via tunneling.^{2,11} It has been shown that this tunneling can be well approximated as one-dimensional (i.e., as a charge transfer between infinite parallel surfaces) and across a rectangular potential barrier.^{1,22} The values of work functions Φ_M of the metals used in this study are 5.05 eV for 316 stainless steel,²³ ~ 5.4 eV for gold, and ~ 4.7 eV for silver.²⁴ In the case of polymers, the values of Φ_{pol} are around 5.0 eV^{23,25,26} (e.g., 5.48 eV, for polystyrene²³). In metals, Φ_M measures the difference between the vacuum energy level and the Fermi level.¹ E_F . In polymers, the quantity Φ_{pol} is the difference between the vacuum energy level and the energy, E_0 , of the polymer's localized surface states.^{2,11,27} Depending on the relative magnitudes of E_F and E_0 , electrons can flow either from the polymer into the metal, or in the opposite direction. For example, in the steel/polystyrene system, $E_F > E_0$ and when the sphere and the polymer are brought into contact, electrons tend to flow out of the filled Fermi level of the metal into the empty surface states of the polymer (Figure 1d).²⁸

The probability, P , of charge transfer (per unit area of contact) between the metal surface and a polymer is proportional to the tunneling current, I_t ,²⁸ which is given by^{29,30} a product of the voltage difference (bias) between two adjacent materials, U , and the transmission coefficient across the barrier, T ; that is, $I_t \propto UT(\Phi, d)$. Here, the voltage bias is proportional to the difference between the Fermi level in the metal and the surface states in the polymer, $eU \propto \Delta E = E_f - E_0$. The transmission coefficient is approximated as $T(\Phi, d) \approx \exp(-2dk)$, with $\kappa(\Phi) = \sqrt{2m_e\Phi/\hbar}$, where m_e denotes the mass of an electron, d is the width of the barrier (i.e., the distance between the surface of the polymer and the sphere), and Φ is the barrier height,³³ $\Phi \approx \Phi_M \approx \Phi_{pol}$. This height is, to a good approximation, independent of the charge, Q , on the sphere. To see this, consider the density of surface charges on the sphere, σ , generated during the process of CE. Since the maximal amount of charge collected on the sphere is on the order of 10^{-10} C and the sphere's surface area is $\sim 10^{-6}$ m², it follows that $\sigma \sim 10^{-4}$ C/m². The additional electric potential due to the charge transfer is calculated as $V_{el} \propto d\sigma/\epsilon_0$, where ϵ_0 stands for the electric permittivity of the vacuum. Assuming that d is of atomic dimensions (Angstroms), it can be estimated that this additional potential raises the energy barrier by $\Delta E_{el} \sim 10^{-1}$ eV, negligible compared to the height of the barrier, $\Phi \sim 5.0$ eV. Thus, it is reasonable to assume that the transmission coefficient, T , does not depend on Q and, consequently, that the probability of charge transfer is a function of the bias potential, $\Delta E(Q)$, only.

As the contact charging progresses, the electric field grows and the energy of the surface states in PS is raised, relative to the Fermi level in metal (note that if the initial bias potential, ΔE , is negative, electrons migrate from the polymer to the metal, and as charging progresses the energy of surface state in the polymer is lowered relative to E_F). Consequently, the bias potential becomes smaller (Figure 1d). The increase $\delta E(Q)$ in the energy of the surface states is approximated as² $\delta E(Q) \approx d\sigma/\epsilon_0 \propto Q$. It follows that the electric field due to the separated charges reduces the initial energy bias, ΔE , according to $\Delta E(Q) = \Delta E - \delta E(Q) \propto 1 - Q/Q_{sat}$, where Q_{sat} stands for the saturation charge corresponding to the condition³⁴ $\Delta E(Q_{sat}) =$

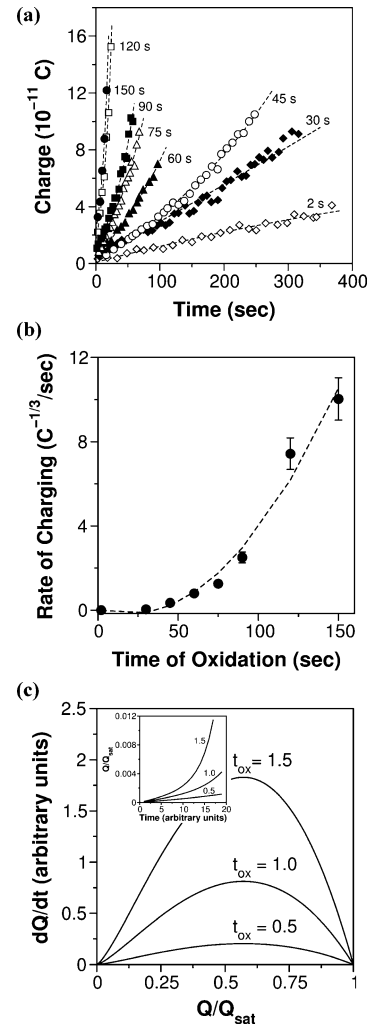


Figure 2. (a) Charging curves for steel beds rolling on PS oxidized with UVO (radiation from Boekel model 135500 plasma cleaner) to different extents; RH = 15% for all curves. The times of oxidation (t_{ox} , in seconds) are given next to the curves. Each curve is an average of two independent experiments; experimental errors are of the order of the marker size. Dotted lines are the least-squares fits to the solution of the rate equation, $\dot{Q} = r(Q^2 + \lambda)^{2/3}(1 - Q/Q_{sat})$, which was solved numerically with the initial condition $Q(t = 0) = Q_0$, and r , λ , Q_{sat} , and Q_0 being the fitting parameters. Graph in (b) has the experimentally observed quadratic dependence of the rate coefficients, r , on the times of surface oxidation, $r \propto t_{ox}^2$. (c) Curves have the theoretical rate of charging plotted against the relative magnitude of the separated charge, Q/Q_{sat} for three different values of t_{ox} . At early stages of charging (approximately, left to the dashed vertical line), the rates of charging vary quadratically with t_{ox}^2 as observed in experiment; later, rates decrease and ultimately go to zero (cf. Figure 1b). Insert: Charging curves obtained by integrating the rate equation agree well with those observed experimentally for early times of the charging process (cf. Figure 2a).

0 (i.e., when the transfer of charge ceases.) Overall, the transfer probability varies with the magnitude of the separated charge as $P(Q) \propto 1 - Q/Q_{sat}$.

(iii) *Qualitative Rate of Contact Charging.* From the above discussion it follows that the amount of charge separated between the contacting metal and polymer surfaces per unit time is proportional to the probability of charge tunneling per unit area of contact multiplied by the total area of contact. Mathematically, the rate of charge transfer (the rate equation) can be written out as $\dot{Q} = r(Q^2 + \lambda)^{2/3}(1 - Q/Q_{sat})$, where the proportionality coefficient, r , depends on the surface properties of the polymer substrate (e.g., degree of oxidation of the surface

TABLE 1: Qualitative Summary of the Influence of Various Parameters on the Rates of Contact Charging

parameter	influence on \dot{Q}	comments
area of contact, A	$\dot{Q} \uparrow$ as $A \uparrow$	The exponent in the area term depends on the geometries of the contacting surfaces (e.g. $A \propto Q^2$ for a cylinder or a flat surface). ^{20,21}
tunneling current, I_t	$\dot{Q} \uparrow$ as $I_t \uparrow$	The higher the difference between the energies of the Fermi level of the metal and the energy of the polymer's surface states, the higher the rate of charging
relative humidity, RH	$\dot{Q} \uparrow$ as $RH \uparrow$	For polymers whose surface reorganizes upon adsorption of water and below their glass transition temperature. ^{14,15}
	$\dot{Q} \downarrow$ as $RH \uparrow$	More "common" behavior observed with polymers that do not reorganize (e.g. polyethylene charges less rapidly when RH increases ^{14,15}). Water dissipates charge.
number of surface groups, N	$\dot{Q} \uparrow$ as $N \uparrow$	The surface groups dominate CE, and a given polymer can be made to charge positively <i>or</i> negatively depending on the chemical identity of these groups. ¹⁴
temperature, T	$\dot{Q} \uparrow$ as $T \uparrow$	Usually, the charging rate increases ¹⁴ with T , as the temperature enhances transfer of electrons to/from the surface states ² of a polymer.
	$\dot{Q} \uparrow$ as $T \downarrow$	Atypical behavior observed with polymers containing water (e.g., poly(allylamine or poly(acrylic acid)) ¹⁴ . As T is lowered, water mobility in the polymer matrix decreases and reduces charge dissipation - hence, higher the rate of charge accumulation.
acidity of the atmosphere, pH	$\dot{Q} \uparrow$ or \downarrow as pH \uparrow	This trend depends on the protonation state of the charge-exchanging groups. If protonated form participates in charge transfer, increasing pH decreases \dot{Q} ; if deprotonated form is implicated, \dot{Q} increases when pH is increased. ¹⁵

or ambient conditions; vide supra). Integration of this equation with respect to time reproduces characteristic sigmoidal charging curves. Dashed lines shown in Figure 1b are the least-squares fits to this equation, obtained by numerical integration with initial condition $Q(t=0) = Q_0$ (Q_0 stands for the initial charge on the sphere), and with quantities r , λ , Q_{sat} , and Q_0 used the fitting parameters. In the early stages of CE, when Q is small compared to Q_{sat} , the process of charge transfer is dominated by an increasing area of contact; in this regime, the rate equation predicts stronger-than-linear growth of Q with time, with the initial slope of the charging curve proportional to the rate coefficient, r , (Figure 1b and also Figure 2c). As Q approaches Q_{sat} , the bias potential decreases, and so does the tunneling current; ultimately, the rate of charging goes to zero (Figure 2c).

b. Factors Influencing the Kinetics of Charging – Model Steel/Polystyrene System. While the generic kinetic equation captures the qualitative aspects of contact charging in metal/polymer systems, it does not explain whether and how the rate of charge separation can be controlled by chemical or physical means. The ability to do so could be useful, for example, in designing self-assembling systems^{7,8,32} in which objects interact via time-dependent potentials mediated by contact electrification, or in controlling the accumulation of static electricity on various types of industrially important polymer coatings.^{3,4}

To date, we have identified and studied^{14,15} several factors that influence CE: type and degree of surface modification, relative humidity, temperature, and acidity of the atmosphere (Table 1), of which the first two are probably the easiest to control experimentally. In the following, we illustrate how two of these factors can be incorporated into the rate coefficient, r , in the generic rate equation for a model system of steel spheres rolling on oxidized polystyrene supports. We chose this system because procedures for controllable surface modification of polystyrene are straightforward^{33–36} to carry out, and because we had part of the data describing the dependence of \dot{Q} on the relative humidity (RH) available from our previous studies.¹⁵ While the experiments we analyze here pertain to a specific metal/polymer pair, we suggest, in subsection iv below, that some observations can be extrapolated to other metal/polymer systems.

(i) *Phenomenological Trends.* The starting point for the current analysis was a set of experiments in which we studied the initial phase of CE of steel spheres rolling on PS surfaces

oxidized to different extents and at constant values of RH (Figure 1a). All charging curves in this regime were well approximated by the generic rate equation with charging rates, r , increasing approximately quadratically with the time of surface oxidation, t_{ox} where $\dot{Q} \propto t_{\text{ox}}^2(Q^2 + \lambda)^{2/3}(1 - Q/Q_{\text{sat}})$, as shown in Figure 2b. In addition, our previous results¹⁵ indicate that, for a given value of t_{ox} , the rate of charging increases linearly with RH. These results suggest that the constant of proportionality in the generic rate equation depends on both the number of the chemical functionalities introduced onto the surface by oxidation and on the amount of surface water adsorbed onto the oxidized surface from a humid atmosphere.

(ii) *Surface Density of Charge-Exchanging Groups, N .* Chemical groups on the surface of the polymeric support have a major role in determining the mechanisms and magnitudes of charge transfer.¹⁴ In case of PS, the charging characteristics depend on the number of oxidized surface groups,¹⁵ and the non-oxidized phenyl moieties do not significantly contribute to charging (i.e., non-oxidized PS charged only marginally; cf. curve labeled "2 s" in Figure 2a). Using contact angle measurements, we demonstrated that this increase is a linear one; the cosines of the contact angles (both advancing, receding, and sessile) of water on oxidized PS surfaces were linear functions of t_{ox} . Through Young's equation,²⁰ these cosines can be related to the interfacial free energies and, subsequently, to the numbers of hydrophilic groups introduced onto the surface during oxidation, $\cos \theta \propto N(t_{\text{ox}})$.³⁷ It follows that $N(t_{\text{ox}}) \propto t_{\text{ox}}$.

(iii) *Amount of Surface Water, W .* The counterintuitive increase of the rate of charging with RH is a result of reorganization of PS surface in response to the adsorbed water (below glass transition of PS, T_g (PS) ≈ 100 °C). Water "pulls out" polar side chains from the bulk of the polymer to minimize the free energy of the PS/water interface.^{38,39} As either t_{ox} or RH increase, so does the amount of adsorbed water, W . The more water on the surface, the larger the degree of surface reorganization, and the higher the concentration of polar groups that separate charge with the metal surface, consequently, the higher the rate of charge transfer. Using ellipsometry, it was established that W varied approximately linearly with both RH and t_{ox} , $W \propto t_{\text{ox}}RH$.

(iv) *Rate Equation.* The expression for the rate of charging in the steel/PS system can be written out as a product of contributions due to N , W , surface area and the tunneling current, $\dot{Q} = f(T, pH, \dots)RH t_{\text{ox}}^2(Q^2 + \lambda)^{2/3}(1 - Q/Q_{\text{sat}})$, in which function

f contains possible contributions of other variables (e.g., temperature T and pH) that were kept constant in our experiments. This equation is in agreement with experimental data (Figure 2b,c).

(v) *Generalization to Other Systems.* Based on these and our previous^{14,15} observations, we suggest that factorization of rate equations into multiplicative terms due to different physical and/or chemical parameters can provide a viable *einsatz* for deriving, or at least approximating, rate laws in different metal/polymer systems. Table 1 lists several trends we identified of how the rates of charging respond to parameter changes. While these trends are only qualitative in nature, they can be of practical utility in guiding a rational design of materials of desirable charging characteristics.

4. Conclusions

In summary, contact electrification between metals and polymers is a complicated process that depends on several, equally important contributions. The present study is the first one in which the kinetics of contact charging was studied with precision sufficient to derive a general model of CE between a metal and a compliant dielectric. The major virtues of this model are that it (i) accounts qualitatively for the shapes and polarities of the charging curves (ii) relates these shapes to the electronic properties of the contacting materials, and (iii) suggests how the changes in external parameters affect the magnitudes of separated charges. Aside from its fundamental interest, we envision this work to be useful in engineering of materials and coatings that separate charge in controllably and to desired degrees.

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Supporting Information Available: Experimental verification that charge separation between the metal and the polymer surfaces is proportional to the compressive force between them. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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