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PAPER

# Absorption vs. redox reduction of $\text{Pd}^{2+}$ and $\text{Cu}^{2+}$ on triboelectrically and naturally charged dielectric polymers

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It has recently been reported that Teflon and polyethylene (PE) if rubbed by polymethylmethacrylate (PMMA) or Nylon as well as non-rubbed PMMA and Nylon induce “redox” reactions, including those of the reduction of  $\text{Pd}^{2+}$  and  $\text{Cu}^{2+}$  ions. On this basis, it was deduced that these dielectric materials may hold  $\cong 10^{13}$ – $10^{14}$  of “hidden” electrons  $\text{cm}^{-2}$ , a value at least three orders of magnitude higher than the charge that a dielectric surface can accumulate without being discharged in air. The “hidden” electrons were termed “cryptoelectrons”. In variance to these reports, we offer here an alternative interpretation. Our model is supported by X-ray photoelectron spectroscopy, contact angle and vibrating electrode (modified Kelvin probe) measurements performed on representative examples. Rubbing of the polymers was found to transfer polymer fragments between the rubbed surfaces altering their physical properties. The transferred polymer fragments promote adsorption of  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$  ions. It was found that Teflon and PE rubbed with PMMA and Nylon, and non-rubbed PMMA and non-rubbed Nylon do not induce “redox” reactions of  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$  ions but adsorb these ions on their surfaces. Furthermore, the earlier reported reduction of  $\text{Pd}^{2+}$  to  $\text{Pd}^0$  by electrons, as detected by catalytic activity of  $\text{Pd}^0$  in a Cu-plating bath, can be alternatively explained by reduction of adsorbed  $\text{Pd}^{2+}$  by the reducing agents of the bath itself. Based on these findings, we support the hypothesis that charging of dielectric polymers is due to ions or free radicals rather than electrons and there is no evidence to invoke a hypothesis of “cryptoelectrons”.

## 1. Introduction

Triboelectrification,<sup>5</sup> the electrification of dielectric materials upon rubbing, was known already in ancient Greece. Tribo-charge is used in several applications including photocopying and plastic separation.<sup>6</sup> However, it remains a matter of debate whether the tribo-charge is due to uncompensated ions,<sup>7–10</sup> free radicals<sup>11</sup> or free electrons.<sup>1–4,12</sup> Liu and Bard<sup>1–4</sup> reported, recently, that either pure or rubbed organic polymers can retain “hidden” electrons, at concentrations as high as  $\sim 10^{13}$ – $10^{14}$  electrons  $\text{cm}^{-2}$ , which are two orders of magnitude higher than the charge density that can be sustained on the surfaces of charged dielectrics in air. Moreover, they reported that PMMA and Nylon contain some “hidden” electrons that are partially or completely compensated by ions. Nevertheless, these electrons can be transferred to Teflon and PE upon rubbing and reduce a number of chemically active species  $\text{Pd}^{2+}$ ,  $\text{Fe}^{3+}$  to

$\text{Fe}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{H}^{+}$  and a chemo-luminescence reaction of tris-(2,20-bipyridine)ruthenium(II) perchlorate  $[\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2]$ .<sup>2,13</sup> Furthermore, positively charged PMMA can be recharged by exposure to an amalgam of sodium. The estimation of the density of electrons was deduced from suggested “redox” reactions. The “hidden” electrons were defined as “cryptoelectrons”.<sup>2,13</sup> Our interest in these reports was motivated by the ability of charged dielectric surfaces<sup>14</sup> to trigger nucleation of polar crystals, in general, and to induce freezing of super-cooled water, in particular. In previous studies we demonstrated that charged pyroelectric  $\text{LiTaO}_3$ ,<sup>14</sup> and certain polar crystals of  $\alpha$ -amino acids induce freezing of super-cooled water.<sup>15</sup> Following these reports we investigated the ability of “spontaneously” charged PMMA and Teflon, charged by rubbing with PMMA, to induce ice nucleation. In variance to the pyroelectric materials, no effect on water freezing was found. To highlight the differences in the ability to trigger ice nucleation between the polymers charged by rubbing and the pyroelectric crystals, we reinvestigated the reported “redox” reactions performed on representative polymer systems. We applied X-ray photoelectron spectroscopy (XPS), contact angle, vibrating probe (Kelvin probe) and we performed the reduction of  $\text{Pd}^{2+}$  ions to  $\text{Pd}^0$  by the formaldehyde in a copper-plating bath.

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In the previous reports see ref. 16 and 17 we presented preliminary results for the absence of reduction of  $\text{Pd}^{2+}$  and  $\text{Cu}^{+2}$  on Teflon rubbed by PMMA. Here we extend our studies to PMMA, Nylon and polyethylene rubbed with PMMA and Nylon.

Consequently, we reached an alternative explanation regarding the nature of the charge accumulated on the surfaces of dielectric polymers.<sup>1–4</sup>

## 2. Experimental

### 2.1 Sample preparation

Four different polymers were used: Teflon (Fluorosol), Polyethylene, PMMA (Palram Industries) and Nylon 6,6 (Alpha Chem). The samples were cleaned before each experiment to eliminate impurities on the surfaces.

Teflon was rinsed by acetone, ethanol (both spectroscopic grade, from Sigma), deionized water (18 M $\Omega$  cm) and then treated with high pressure oxygen plasma (March Plasma 250 W, 1.2 Torr of  $\text{O}_2$ , 20 min) to remove possible residues. The samples were 0.5 mm thick and of a rectangular shape with a top surface area of 0.5 cm<sup>2</sup>. The polyethylene samples were rinsed in water. The samples had a 1 cm<sup>2</sup> top surface area. The PMMA samples were rinsed in ethanol and water. The samples were 2.5 mm thick and had a 1 cm<sup>2</sup> top surface area. The Nylon samples were rinsed in water. The samples had a 1 cm<sup>2</sup> top surface area and were 1.6 mm thick. Rubbing was performed by hands with a load of 0.3–0.5 N, 10–15 strokes each time in a room, in which temperature was maintained within the range of 23–25 °C and humidity 50–70%. The experiments involving analysis of the Teflon surface were repeated at least ten times with similar results. The experiments involving analysis of the PE surface were repeated at least five times. The experiments involving analysis of Nylon and PMMA surfaces were repeated at least twice with identical results at different days because XPS analysis of Nylon or PMMA requires long degassing time (two to three weeks).

### 2.2 Characterization

An XPS study was conducted with Kratos AXIS-HS and AXIS-Ultra spectrometers, both using a monochromatic Al-K $\alpha$  source (1486.6 eV) at 10–75 W. The base pressure was  $\sim 1 \times 10^{-9}$  Torr, but with PMMA pressure increased to  $\sim 10^{-8}$  Torr. An electron flood Gun (eFG) was used for stabilizing the surface potential, which took 10–60 min to achieve. For final energy-scale calibration, we referenced the substrate signals in each sample to Handbook data,<sup>18</sup> such that surface contaminating moieties were not arbitrarily forced to have any pre-assumed value. Specifically, the main carbon peak in PMMA, PE and Nylon was set to 285.0 eV and that of the Teflon to 292.48 eV.

Surface charge density was deduced by modified Kelvin probe measurements (vibrating electrodes). A small (2 mm) vibrating electrode (Kelvin probe) was placed at a distance (5 cm), larger than the dimensions of the measured sample e.g. Teflon (0.2  $\times$  0.2  $\times$  0.1 cm) placed on a large (8  $\times$  15 cm) metallic plate. Two measurement modes were used. (a) The

compensation voltage,  $U$ , corresponding to zero current between the plate and the electrode was measured as a function of distance,  $d$ , between the sample and the electrodes. This potential corresponds to the potential that the trapped charges at the dielectric surface (approximated as a point charge) create at the electrode location. Applicability of the point charge approximation was confirmed by a perfect fit to  $U(d) = C/d$ , where  $C$  is a constant. Since for a point charge  $U = A\sigma/(4\pi\epsilon_0 d)$  where  $A$  is the top area of the sample,  $\sigma$  is the charge density on the top surface and  $\epsilon_0$  is the dielectric permittivity of vacuum, the charge density can be calculated as  $\sigma = 4\pi\epsilon_0 C/A$ . (b) The AC voltage,  $\phi$ , generated in a vibrating electrode was measured as a function of distance,  $d$ . The ratio  $E = \phi/x$ , where  $x$  is the amplitude of vibration of the electrode (estimated to be  $\sim 1$   $\mu\text{m}$ ), gives an electric field at a given point. It was found that the dependence  $\phi(d)$  perfectly follows  $\phi(d) = C/(d - d_0)^2 + B$ , where  $C$ ,  $B$  and  $d_0 \ll d$  are constants. Since  $E = \phi/x = A\sigma/(4\pi\epsilon_0 d^2)$ , the charge density can be estimated as  $\sigma = 4\pi\epsilon_0 C/(xA)$ .

## 3. Results

### 3.1 Ice nucleation on negatively charged and discharged PMMA

Following the results reported in ref. 1–4, 14, and 15, we decided to test the capability of negatively charged PMMA to affect ice nucleation. PMMA discharged by an ion antistatic gun was used as a reference. We were particularly attracted to this system because, as reported, it may be utilized repeatedly by recharging it negatively by sodium amalgam.

To identify the real uncompensated charge, we measured the surface charge density on PMMA by a vibrating electrode and found that the surface of non-treated PMMA is negatively charged with an equivalent density of  $\sim 10^{10}$  el cm<sup>–2</sup>. The PMMA rubbed with Teflon changes its surface charge from negative  $\sim 10^{10}$  el cm<sup>–2</sup> to a positive one of a similar density. Observed charge densities are fully consistent with the limitation imposed by the electrical breakdown of air<sup>10</sup> at  $E_b = 3$  kV mm<sup>–1</sup>;  $\sigma = E_b\epsilon_0 \approx 2 \times 10^{10}$  el cm<sup>–2</sup> ( $\epsilon_0$  is the dielectric permittivity of vacuum). Kelvin probe data also show that PMMA rubbed by Teflon remains positively charged after being treated with 5% Na amalgam. This result suggests that contact of PMMA with Na amalgam does not charge it by electrons, in variance to what was reported in ref. 2.

Ice nucleation experiments were performed using the setup described in ref. 14. To ensure reproducibility, the experiments were carried out in a clean room at fixed temperature (20 °C) and humidity (50  $\pm$  10%). No differences in the freezing point of supercooled water between charged and discharged PMMA were observed in all experiments (> 30 tests).

Charge density of these polymers is similar to the maximum charge densities that can be achieved on a pyroelectric surface: LiTaO<sub>3</sub> can uphold  $\sim 10^{10}$ – $10^{11}$  electrons cm<sup>–2</sup> and undergoes rapid discharge if heating and cooling generate higher charge density. In this view, surfaces charged by contact electrifications are not expected to be similarly useful for controlling crystallization from aqueous solutions.

### 3.2 Transfer of material between polymers upon rubbing

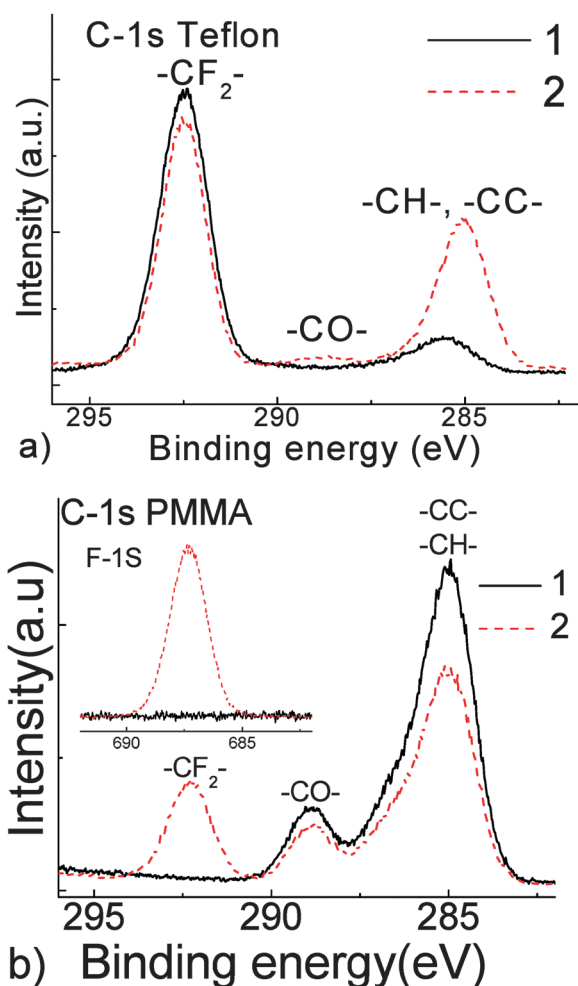
We examined the effect of triboelectrification on the polymer surfaces of representative polymer systems: Teflon rubbed with PMMA and Nylon rubbed with Teflon or PE. The surfaces of the polymers were analyzed by X-ray Photoelectron Spectroscopy (XPS). The spectrum of pure Teflon (Fig. 1a) (solid) shows  $\text{-CF}_2\text{-}$  groups at 292.48 eV and ( $\text{-CH-}$  and  $\text{-CC-}$ ) groups at  $\sim 285$  eV. The XPS spectrum of non-rubbed PMMA (Fig. 1b, solid) shows two peaks at 288.8 eV and 285 eV corresponding to the  $\text{-CO-}$  and ( $\text{-CH-}$ ,  $\text{-CC-}$ ) respectively. The spectrum of rubbed Teflon with PMMA is shown in Fig. 1a (dashed). In addition to the peaks of Teflon, there is a peak at 288.8 eV corresponding to the carbonyl ( $\text{-CO-}$ ) group of PMMA. Moreover, the intensity of the  $\text{-CH-}$  and  $\text{-CC-}$  peak (285 eV) increased substantially in comparison to the Teflon before rubbing, from 0.16 to 0.70 relative to the  $\text{C}^{\text{F}}$  signal, implying transfer of PMMA groups to the Teflon surface. Similarly  $\text{-CF}_2\text{-}$  groups of Teflon were transferred to the surface of PMMA, as follows from the appearance of a

$\text{-CF}_2\text{-}$  peak at 292.45 eV and a fluorine peak at 689.5 eV (shown in the inset of Fig. 1b). The surface of PMMA acquires  $\sim 6 \text{ \AA}$  of  $\text{-CF}_2\text{-}$  fragments and the surface of Teflon acquires at least  $\sim 16 \text{ \AA}$  of non-fluorinated carbons.

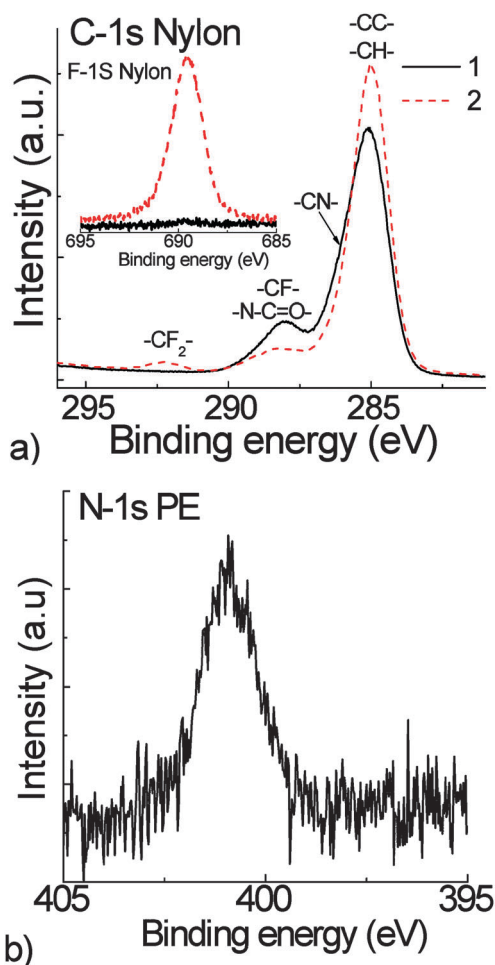
A similar analysis was carried out for Teflon and PE rubbed with Nylon. The C-1s spectrum of pure Nylon is shown in Fig. 2a, solid line. It consists of three overlapping peaks: ( $\text{-CC-}$ ,  $\text{-CH-}$ ) at 285.0 eV,  $\text{-CN-}$  peak at 286.0 eV and the peak of carbonyl-group attached to the nitrogen atom  $\text{-N-C=O-}$  at 288.05 eV. A peak of N-1s is observed at 399.8 eV (not shown). Nylon rubbed with Teflon (Fig. 2a, dashed) shows, in addition to Nylon peaks, the  $\text{-CF}_2\text{-}$  peak at 292.2 eV and the  $\text{-CF-}$  peak at 288 eV. A fluorine peak is observed at 689.5 eV (inset, Fig. 2a), which implies the transfer of Teflon on Nylon. Similarly, polar groups of nylon are being transferred to polyethylene with coverage of a few monolayers. Nylon XPS peaks were observed on the rubbed PE surfaces (not shown). The N-1s line shown in Fig. 2b indicates transfer of  $\text{-CN-}$  and  $\text{-N-C=O-}$  from Nylon to PE.

### 3.3 Change of physical properties upon rubbing

The transfer of polar groups from PMMA and Nylon to Teflon and PE changes the physical properties of the rubbed polymers,



**Fig. 1** (a) XPS C-1s line of Teflon before (1—solid) and after (2—dashed) rubbing with PMMA. Rubbing causes transfer of non-fluorinated carbon species from PMMA to Teflon;<sup>16</sup> (b) XPS C-1s and F-1s (inset) line of PMMA before (1—solid) and after (2—dashed) rubbing with Teflon. Rubbing causes transfer of  $\text{-CF}_2\text{-}$ -containing species from Teflon to PMMA.



**Fig. 2** (a) XPS C-1s and F-1s (inset) line of Nylon before (1—solid) and after (2—dashed) rubbing with Teflon. Rubbing causes transfer of  $\text{-CF}_2\text{-}$ -containing species from Teflon to Nylon; (b) XPS N-1s of PE after rubbing with Nylon.



as demonstrated by the contact angle measurements, and the ability of these surfaces to adsorb Cu and Pd ions.

**3.3.1 Contact angle.** Liu and Bard reported differences in contact angle between non-rubbed Teflon and Teflon rubbed with PMMA. They interpreted the reduced contact angle as a result of electrostatic charging on the rubbed Teflon.<sup>3</sup> The transfer of polar groups to the surfaces of the hydrophobic polymers might provide an alternative interpretation for this difference. A way to differentiate between the two mechanisms is to measure changes in contact angles on the rubbed polymers. Since the charged surfaces are discharged by water, one anticipates that the contact angle on these charged surfaces should increase with time. On the other hand, would the reduction in the contact angle be induced by the transferred polar groups, it should remain unchanged. The contact angle measurements of water drop on non-rubbed Teflon, Teflon rubbed with PMMA (1–5) and Teflon rubbed with Nylon (6–10) (Table 1) were carried out. The contact angles did not change during the period from several hours to several days, suggesting that the change in the contact angle is due to transferred polar groups.

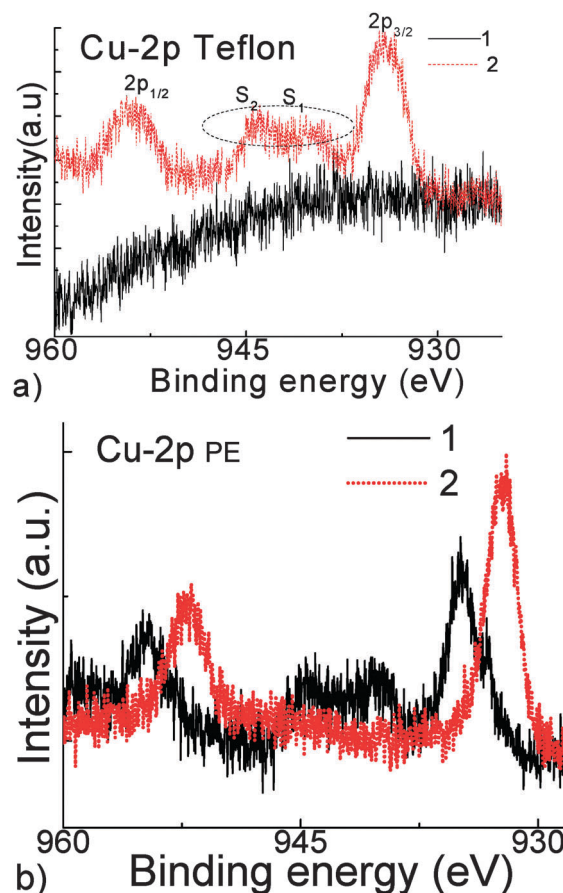
### 3.3.2 Adsorption vs. “redox” reaction of $\text{Cu}^{2+}$ and $\text{Pd}^{2+}$ .

In ref. 1 and 3 it has been reported that Teflon rubbed with PMMA, in variance to non-rubbed Teflon, induces discoloration of  $\text{CuSO}_4$  solutions. This discoloration effect was interpreted as a reduction of the Cu ions by the charge created on the Teflon upon triboelectrification and it was supported by Energy Dispersive Spectroscopy (EDS).<sup>1,3</sup> The transfer of PMMA to Teflon suggests a mechanism of preferred adsorption of the Cu and the Pd ions on the modified surfaces of these polymers. In order to differentiate between these two mechanisms, we measured the oxidation states of Cu and Pd by XPS, which is a less aggressive method than EDS. It also provides a sensitive mean of the oxidation states of ions. In order to assure that the XPS beam covers the entire rubbed surface, the experiments were also performed along rubbed marked lines.

XPS lines of Cu-2p and Pd-3d show that both ions are in the 2+ oxidation state (Fig. 3–6). The question of probe-induced oxidation/reduction (irradiation by an X-ray source and by a low-energy electron flood gun<sup>19</sup>) was studied thoroughly, comparing various exposure times and source conditions at different analysis spots and samples. After long exposures, reduction of the ions was observed under the beam but oxidation was not observed. The radiation induces some

damage to the polymers,<sup>20</sup> e.g. the creation of free fluorine or  $\text{CF}_1$  groups in the Teflon but does not cause oxidation of Pd or Cu.

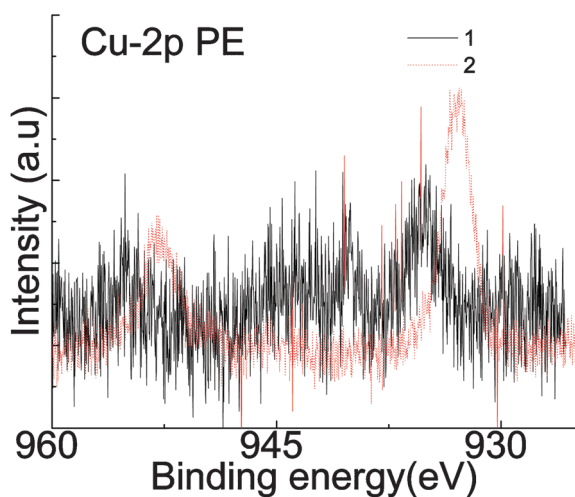
*Adsorption vs. reduction of  $\text{Cu}^{2+}$ .* The following systems for copper reduction by electrification were prepared and analyzed: non-rubbed Teflon and Teflon rubbed with PMMA or with Nylon; non-rubbed PE and PE rubbed with PMMA or with Nylon; non-rubbed PMMA and PMMA rubbed with Teflon; and non-rubbed Nylon and Nylon rubbed with Teflon. All samples were immersed in  $\text{CuSO}_4$  solution (1 mM), rinsed and finally analyzed by an optical microscope and XPS. All samples were scanned meticulously under an optical microscope in a dark field mode, to detect the presence of (red) metallic copper particles but none were observed. Subsequently, an XPS analysis was performed, showing typical  $\text{Cu}^{2+}$  spectra, characterized by the presence of satellite peaks (circled Fig. 3a): Cu-2p lines of Teflon rubbed with PMMA show the doublet at 934.1 eV (Cu 2p<sub>3/2</sub>) and 953.9 eV (Cu 2p<sub>1/2</sub>) and two shake-up S1 and S2 features of  $\text{Cu}^{2+}$ .<sup>21</sup> The quantity of copper corresponds to 10–30% of a monolayer ( $\sim (1-3) \times 10^{14} \text{ cm}^{-2}$ ). Furthermore, XPS data show the



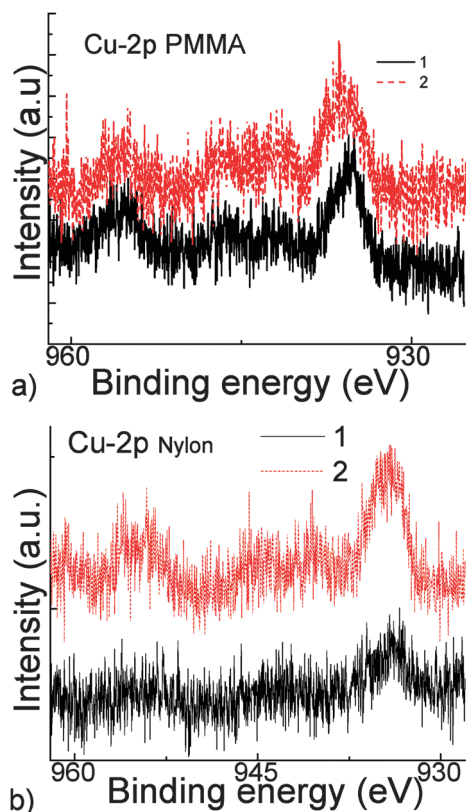
**Fig. 3** XPS Cu-2p line of (a) non-treated Teflon (1—solid) and Teflon rubbed with PMMA (2—dashed).<sup>16</sup> The position of the main peak and the presence of the satellite peaks (circled) indicate that copper is in the oxidation state 2+; (b) PE rubbed by PMMA (1—solid) at the beginning of the measurement, (2—dashed) after prolonged (2 hours) exposure to the X-ray plus flood-gun beams, showing partial reduction to  $\text{Cu}^0$ .

**Table 1** Contact angle of Teflon rubbed with PMMA (1–5) and Nylon (6–10)

		Teflon not rubbed	As-rubbed (30 s)	Rubbed + 50–60 h
1	PMMA	131	108	105 (60 h)
2	PMMA	119	92	102 (60 h)
3	PMMA	117	98	102 (60 h)
4	PMMA	115	107	103 (60 h)
5	PMMA	104	88	87 (60 h)
6	Nylon	119	103	99(50 h)
7	Nylon	122	110	105(50 h)
8	Nylon	122	104	101(50 h)
9	Nylon	134	118	120(50 h)
10	Nylon	120	101	104(50 h)

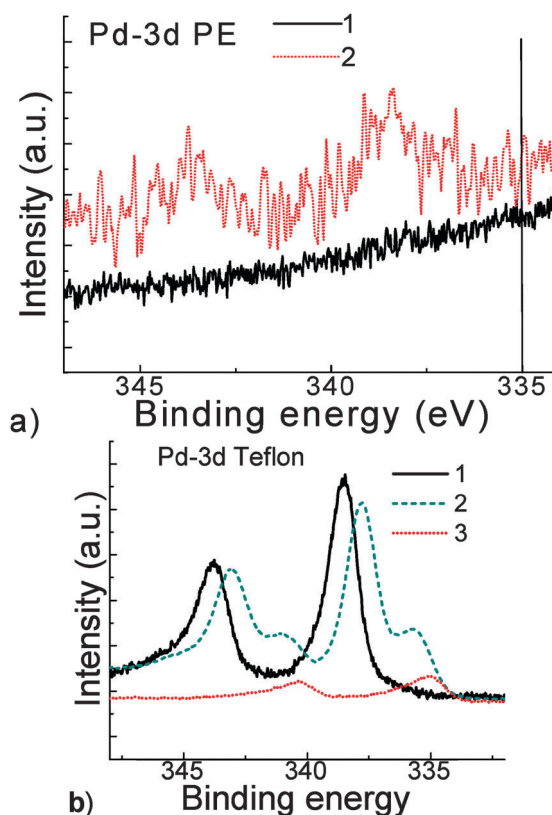


**Fig. 4** XPS Cu 2p lines of PE rubbed by Nylon after treatment with  $\text{CuSO}_4$  (1—solid) at the beginning of the measurement (2—dashed) after prolonged (hours) exposure to the X-ray plus flood-gun beams, showing partial reduction to  $\text{Cu}^0$ .



**Fig. 5** XPS Cu-2p line of (a) PMMA pure (1—solid), rubbed by Teflon (2—dashed); (b) Nylon pure (1—solid), rubbed by Teflon (2—dashed).

presence of oxidized sulfur, in a similar amount as that of copper. The signal of sulfur decreases with time, which is a known effect under the XPS probe. The XPS analysis indicated that non-rubbed Teflon did not adsorb Cu ions (Fig. 3a, solid-line). Teflon rubbed with PMMA (Fig. 3a, dashed) and Teflon rubbed with PMMA and then discharged with



**Fig. 6** XPS Pd-3d line of (a) PE dipped in a solution of  $\text{Pd}^{2+}$ : (1—solid) PE not rubbed; no Pd adsorption; (2—dashed) rubbed by PMMA. The theoretical energy of  $\text{Pd}^0$  is marked by the line at 335.1 eV. (b) Teflon rubbed with PMMA immersed in Pd solution (1—solid) at the beginning of the measurement (minutes), showing a dominant  $\text{Pd}^{2+}$  signal; (2—dashed) the same sample after prolonged (two hours) exposure to the X-ray plus electron irradiation, showing partial reduction to  $\text{Pd}^0$ ; (3—dotted) a sample treated by 1% solution of formaldehyde in NaOH (0.1 mol), showing complete reduction to  $\text{Pd}^0$ .<sup>16</sup>

antistatic gun (not shown) adsorb  $\text{Cu}^{2+}$  ions. This result implies that the tribo-charge does not reduce  $\text{Cu}^{2+}$  ions. This also implies that the polar groups transferred to Teflon from PMMA by rubbing are responsible for the adsorption of  $\text{Cu}^{2+}$  ions.

The XPS analysis area in our instrument is  $\sim 0.5$  mm in diameter. To scan the entire surface on which  $\text{Cu}^0$  may be present, we confined the search area by rubbing Teflon with PMMA along two perpendicular lines forming a cross. Only  $\text{Cu}^{2+}$  ions but not metallic copper particles were found along these lines. Independently, no copper particles were observed along these lines either by EDS or by optical microscopy. Similar results were obtained with pure PE and PE rubbed by PMMA (Fig. 3b).

The effect of the XPS probe on the oxidation state of Cu was also tested. Fig. 3b shows Cu-2p lines of PE rubbed with PMMA at the beginning of the measurement (solid) and after 2 hours of exposure to the XPS probe (dashed). The disappearance of shake-up peaks S1 and S2 and the shift of  $2p_{3/2}$  and  $2p_{1/2}$  main peaks toward lower energy clearly indicate the reduction of  $\text{Cu}^{2+}$  (Fig. 3b, dashed). The preservation of the

area under the curves 1 and 2 in Fig. 3b indicates the absence of copper diffusion during the measurement.

Experiments with similar results were obtained by rubbing Teflon (not shown) and PE (Fig. 4) with Nylon. Again one finds the doublet of Cu and shake-up S1 and S2 peaks. The amount of  $\text{Cu}^{2+}$  found on the surface of PE rubbed with Nylon is  $\sim 1\text{--}2\%$  of a monolayer.

XPS spectra were also acquired on the surfaces of non-rubbed PMMA and non-rubbed Nylon and those rubbed by Teflon (Fig. 5a and b). The copper was found in the state of oxidation  $2+$ , indicating adsorption of metallic Cu due to polar groups.

**Adsorption vs. reduction of  $\text{Pd}^{2+}$ .** The reduction  $\text{Pd}^{2+}/\text{Pd}^0$  (0.92 V vs. NHE) was also investigated in ref. 1–4. The formation of  $\text{Pd}^0$  was monitored by considering the fact that pure  $\text{Pd}^0$  operates as a catalyst in the copper reduction in a Cu-plating bath. We analyzed this reaction in the following systems: non-rubbed Teflon and Teflon rubbed with PMMA or Nylon, non-rubbed PE and PE rubbed with PMMA or Nylon and non-rubbed Nylon. Non-rubbed and tribo-charged polymers were immersed in  $\text{PdCl}_2\text{:HCl}$  solution (0.2 mM), rinsed and analyzed by XPS. Fig. 6a shows the XPS Pd-3d lines of PE treated with  $\text{Pd}^{2+}$  solution non-rubbed (1—solid) and rubbed with PMMA (2—dashed). One can see that Pd is not adsorbed on non-rubbed PE (1), but after rubbing with PMMA, PE adsorbs  $\text{Pd}^{2+}$  ions. Spectrum (2) shows the doublet of Pd at 338.3 eV ( $\text{Pd } 3d_{5/2}$ ).

The quantity of palladium corresponds to  $1\text{--}5\%$  ( $\sim (1\text{--}5) \times 10^{13} \text{ cm}^{-2}$ ) of a monolayer. A smaller amount of  $\text{Pd}^{2+}$  was also observed on the surface of Teflon and PE rubbed with Nylon as well as on pure Nylon (not shown).

Fig. 6b illustrates adsorption of  $\text{Pd}^{2+}$  on the surface of Teflon rubbed with PMMA at the beginning of measurement (1—solid) and after few hours (2—dashed), highlighting the partial reduction of Pd due to the XPS probe. A similar sample, treated in Pd solution, was subsequently immersed in 1% formaldehyde solution<sup>22</sup> and measured by XPS (3—dotted), which clearly revealed reduction of  $\text{Pd}^{2+}$ . In separate experiments, when  $\text{Pd}^{2+}$  was added to a solution of the Cu-plating bath, which contains formaldehyde, tartaric acid, NaOH and  $\text{CuSO}_4$ ,<sup>22</sup> the  $\text{Cu}^{2+}$  was reduced to  $\text{Cu}^0$ . These results imply that reduction of  $\text{Pd}^{2+}$  ions to  $\text{Pd}^0$  takes place in the copper-plating bath and not by charge accumulated on the surfaces.

**3.3.3 Charge density measurements.** To estimate uncompensated charge available for water freezing experiments and to verify formation of triboelectrification charge for the “redox” reaction experiments, surface charge density,  $\sigma$ , was measured by a vibrating electrode technique (Kelvin probe, Section 2.2) on non-rubbed PMMA and PMMA rubbed with Teflon, non-rubbed Nylon and Nylon rubbed with Teflon and non-rubbed Teflon and Teflon rubbed with PMMA or Nylon (Table 2).

PMMA is negatively charged with an equivalent charge density of  $\sim 10^{10} \text{ el cm}^{-2}$ , it becomes positively charged, with equivalent charge density, upon rubbing with Teflon. Non-rubbed Teflon is positively charged with an equivalent charge density of  $\sim 10^8 \text{ el cm}^{-2}$ . However, after rubbing with

**Table 2** Charge density values

$\text{el cm}^{-2}$	Not rubbed	Rubbed Teflon	Rubbed PMMA	Rubbed Nylon
Teflon	$+10^{10}$	$\times$	$-10^{10}$	$-10^{10}$
PMMA	$-10^{10}$	$+10^{10}$	$\times$	$\times$
Nylon	$-10^9$	$+10^9$	$\times$	$\times$

PMMA, Teflon acquires a negative charge of  $\sim 10^{10} \text{ el cm}^{-2}$ , which decreases to  $\sim 10^8 \text{ el cm}^{-2}$  within 40 minutes in dry air. Similarly, Teflon rubbed with Nylon becomes negatively charged with a charge density of  $\sim 10^{10} \text{ el cm}^{-2}$ .

## 4. Discussion and conclusions

Experiments performed with charged dielectric materials demonstrate that in variance to the pyroelectric materials,<sup>14</sup> they do not induce ice nucleation. The difference in the ability of dielectric polymers to affect ice nucleation may be due to two reasons. Firstly, the charge density on dielectric polymers is about two orders of magnitude lower than what pyroelectrics can deliver. Secondly, upon heating and cooling, pyroelectrics generate surface charge *continuously*, as long as the temperature continues changing, whereas the charge of electrets is neutralized almost immediately after contact with water.

Charge on the surface of non-rubbed Nylon and Nylon rubbed with Teflon is smaller than the charge created on pure PMMA mentioned above. Pure Nylon is negatively charged with charge density  $\sim 10^9 \text{ el cm}^{-2}$ . Upon rubbing with Teflon it becomes positively charged with similar charge density.

The nature of the charge accumulated on organic dielectric materials, either charged spontaneously or charged by triboelectrification, as deduced from the “redox” reactions, was reinvestigated by applying analytical tools that differ from those applied in ref. 1–4. Surface analysis performed on selected representative systems shows that rubbing of Teflon and PE with PMMA or Nylon promotes the transfer of material in both directions as shown in Fig. 1 and 2.<sup>9,23</sup> The transfer of negatively charged groups from PMMA and Nylon to the hydrophobic polymers changes their physical properties. This was demonstrated by contact angle measurements, showing the absence of changes in the contact angle of rubbed Teflon either with PMMA or with Nylon (Table 1). In addition, it was observed that the transfer of polar groups from PMMA and Nylon to the surfaces of Teflon and PE improves the ability of these surfaces to adsorb Pd and Cu ions and thus provides an alternative explanation to the suggested “redox” reactions. Support for the adsorption mechanism is provided by the XPS measurements, which demonstrated that both the Cu and Pd are in the  $2+$  oxidation state on the tribo-charged Teflon and PE surfaces (Fig. 3, 4, and 6). Similar adsorption of Cu was observed on the charged non-rubbed PMMA and Nylon as shown in Fig. 5. Adsorption of ions by Teflon rubbed with PMMA provides a different interpretation of the experiments on the discoloration of  $\text{CuSO}_4$  solutions.

The actual amount of adsorbed  $\text{Cu}^{2+}$  and  $\text{Pd}^{2+}$  is a function of the material exchange during rubbing and thoroughness of rinsing. Surface coverage of  $10\text{--}30\%$  of monolayer of  $\text{Cu}^{2+}$  and  $1\text{--}5\%$  of monolayer of  $\text{Pd}^{2+}$  can be achieved by adsorption from the dilute aqueous solutions.



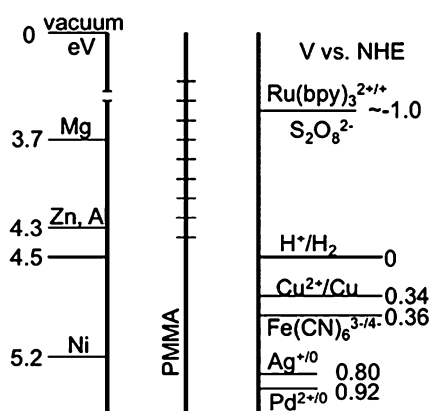


Fig. 7 Standard line of "redox" potentials. Reprinted with permission from ref. 2.

The use of the copper-plating bath cannot be considered as evidence for the reduction of the Pd ions by the cryptoelectrons, since these ions themselves can be reduced by formaldehyde in the copper-plating bath (Fig. 6b) and catalyze the Cu plating of the surfaces as shown by XPS.<sup>1–4</sup> The absence of Cu<sup>0</sup> was also demonstrated by an optical microscope, and SEM/EDS and XPS analysis was performed by scanning Teflon samples along lines rubbed with PMMA.

According to the diagram (Fig. 7) by Liu and Bard,<sup>2</sup> Pd<sup>2+</sup>/Pd<sup>0</sup> has one of the highest standard "redox" potentials (+0.92 V vs. NHE) and, yet, reduction of Pd<sup>2+</sup> does not take place by static charge in detectable quantities. Therefore, it is highly unlikely that electrons are responsible for the reduction of less electropositive species, such as Cu<sup>2+</sup>/Cu<sup>0</sup> (0.34 V), as we show here, or in other examples reported in ref. 1 and 2 (including Fe<sup>3+</sup>/Fe<sup>2+</sup> (0.36 V) and chemo-luminescence of mixture of tris(2,20-bipyridine)ruthenium(II) perchlorate [Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>] and sodium peroxydisulfate Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in an acetonitrile (MeCN)/water (1 : 1, v/v) (–1 V)). We would like, however, to point out that this conclusion is based on the assumption that the reduction of Pd<sup>2+</sup> and Cu<sup>2+</sup> by the products of material exchange during rubbing is not kinetically controlled.

Finally, we measured the charge on the surface of pure and rubbed polymers by a vibrating electrode (Kelvin probe). The amount of charge on polymers does not exceed 10<sup>10</sup> electrons cm<sup>–2</sup>. Moreover, it shows that PMMA positively charged after rubbing with Teflon and cannot be charged negatively by sodium amalgam.<sup>2</sup>

In conclusion, we report here an alternative model for the "redox" reactions reported in ref. 1–4. On the basis of these findings, we maintain that the model of cryptoelectrons is not supported by the experimental evidence and other models of triboelectrification should be considered.<sup>8–10,11,24</sup> Furthermore, out of non-rubbed Teflon, PE, Nylon and PMMA, only Nylon and PMMA may develop static charge spontaneously because these two polymers contain polar groups which may give rise to some amount of uncompensated ions at their surfaces.<sup>2,4</sup> Future studies should concentrate on the elucidation of structure of the different species present on the surfaces of pure PMMA and Nylon, which create the charge on these polymers, and the species, which are transferred to other polymers during the processes of triboelectrification.

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