Electrostatic Interactions

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The Absence of Redox Reactions for Palladium(II) and Copper(II) on Electrostatically Charged Teflon: Relevance to the Concept of "Cryptoelectrons"**

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Triboelectrification[1] (electrification upon rubbing) of dielectric materials,[2] one of the most ancient and commonly observed forms of electricity, has a number of useful and practical applications, such as triboelectrostatic separation of plastics,[3] as well as numerous adverse effects related to uncontrolled charge accumulation and subsequent discharge. Nevertheless, the mechanism of charge transfer between two dielectric materials remains a matter of debate that is centered upon two different views: transfer of ions[4–6] or transfer and trapping of electrons.[7] To support the latter view, Liu and Bard recently reported that a high density of electrons, which they defined as "cryptoelectrons", were present on a dielectric surface and could be detected by inducing "redox" reactions including reduction of Cu^{2+} and Pd^{2+} ions.[8–12] On the basis of these reactions, they estimated the electron density on Teflon (polytetrafluoroethylene, PTFE) that was rubbed by PMMA (polymethylmethacrylate),[8] and on pure PMMA[9] to be $\geq 10^{13}$ electrons cm^{-2}.

Our interest in charged dielectrics stems from the attempt to utilize them for nucleation of polar crystals as a possible alternative to pyroelectric surfaces that we used earlier to suppress or promote ice nucleation.[13,14] As a part of this work, we provide direct evidence, based on X-ray photoelectron spectroscopy (XPS), that the surface charge created on these surfaces does not reduce copper and palladium ions. Instead, rubbing Teflon with PMMA causes material exchange and promotes adsorption of copper ions from aqueous solutions onto the rubbed Teflon; this process can be misinterpreted as an electrochemical reduction. These data challenge the role of cryptoelectrons in these reactions.

One of the arguments supporting the existence of cryptoelectrons is their supposed ability to reduce Cu^{2+} and Pd^{2+} from aqueous solutions.[8,9] Copper reduction was deduced from two factors: a) the decrease in the intensity of the blue color of a 0.1 mmol solution of Cu^{2+} ions that is brought into contact with Teflon rubbed by PMMA; this is not observed with Teflon not rubbed by PMMA; and b) the presence of metallic copper on the surface of the Teflon as detected by energy-dispersive X-ray fluorescence spectroscopy (EDS).[8] The Pd reduction was inferred from Pd^0-catalyzed copper plating onto a PMMA-rubbed Teflon surface that is brought into contact with a saturated solution of $PdCl_2$ and then immersed in a chemical copper plating bath[8,9,15] containing formaldehyde.

We investigated the Teflon and PMMA surfaces before and after rubbing by using X-ray photoelectron spectroscopy (XPS), and found that the surface of PMMA acquires approximately 25–60% of a monolayer of CF_2 fragments and the surface of the Teflon acquires at least 25% of a nonfluorinated carbon monolayer, which is significantly more than any residue observed before rubbing (Figure 1a,b). Since both materials are polymers having a high molecular weight, this exchange[6,16] must be accompanied with the breaking of chemical bonds and the formation of a chemically polar active species. The transfer of polar (containing C=O groups) PMMA species to the Teflon surface should change the physical and chemical properties of the surface, including a decrease of the water-contact angle[10] and ability to adsorb ions, such as Cu^{2+} and Pd^{2+}.[8] Therefore, one can offer alternative interpretations of the experiments supporting the hypothesis of cryptoelectrons proposed by Liu and Bard.[8–11]

The oxidation states of copper and palladium were analyzed by XPS, which is a less aggressive probe compared to the electron beam in EDS. On the surface of the Teflon that was rubbed by PMMA, immersed in $CuSO_4$ (1 mmol), and then rinsed thoroughly, copper was found in the +2 oxidation state; for immersion of a similarly treated Teflon surface in $PdCl_2$/HCl (0.2 mmol) the palladium was also in the +2 oxidation state (Figure 2a,b). Similarly, only Cu^{2+} and Pd^{2+} are found on the Teflon, which was charged and then discharged with an antistatic gun. The quantity of copper and palladium corresponds to 10–30% (ca. $(1\text{–}3\times10^{14})\,cm^{-2}$) and 1–5% (ca. $(1\text{–}5\times10^{13})\,cm^{-2}$) respectively, of a monolayer.[17] Furthermore, treating the surface containing Pd^{2+} ions with a 1% formaldehyde solution[15] causes their reduction to Pd^0 (Figure 2b).

With another set of samples that served as a reference, we have found that the XPS probe (X-ray plus a low-energy electron flood gun[18]) does not noticeably affect the oxidation state of copper. Although it does not cause oxidation of Pd^0, it does cause partial reduction of oxidized palladium after exposure to both factors of the XPS probe for at least an hour (Figure 2b).

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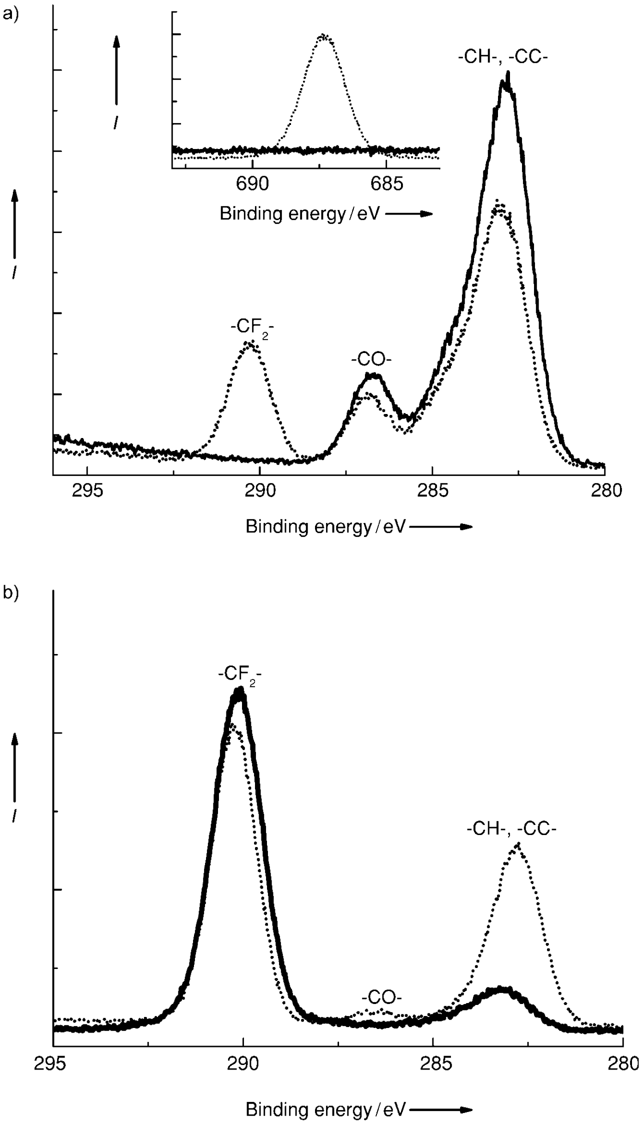

Figure 1. a) XPS C 1s and F 1s (inset) lines of PMMA before (solid line) and after (dotted line) rubbing with Teflon. Rubbing causes transfer of (CF_2)-containing species from Teflon to PMMA. b) XPS showing traces for C 1s of Teflon before (solid line) and after (dotted line) rubbing with PMMA. Rubbing causes transfer of nonfluorinated carbon species from PMMA to Teflon.

These findings indicate that Teflon rubbed with PMMA causes absorption of Cu^{2+} and Pd^{2+} without any change in their oxidation state. The actual amount of Cu^{2+} and Pd^{2+} is a strong function of material exchange during the rubbing and rinsing processes.

One has to emphasize that Teflon that is not rubbed by PMMA has much lower potency in adsorbing Cu^{2+} ions, which is in agreement with the results reported in references [8,9], but is probably related to the absence of PMMA residues. The superior ability of PMMA-rubbed Teflon to adsorb Cu^{2+} and Pd^{2+} ions on its surface can also be a result of the polar groups present in PMMA.[19]

We point out that although Pd/Pd^{2+} has one of the highest standard redox potentials (+0.92 V), it cannot be reduced by a static charge in detectable quantities, and it is therefore highly unlikely that cryptoelectrons are responsible for the reduction of a less-active species, such as Cu/Cu^{2+} (0.34 V), as we show, as well as for the examples from Liu and Bard[8,9] [including Fe^{2+}/Fe^{3+} (0.36 V) and chemo luminescence of a mixture of tris(2,20-bipyridine)ruthenium(II) perchlorate $[Ru(bpy)_3(ClO_4)_2]$ and sodium peroxydisulfate $(Na_2S_2O_8)$ in an acetonitrile/water (1:1 v/v; −1 V)].

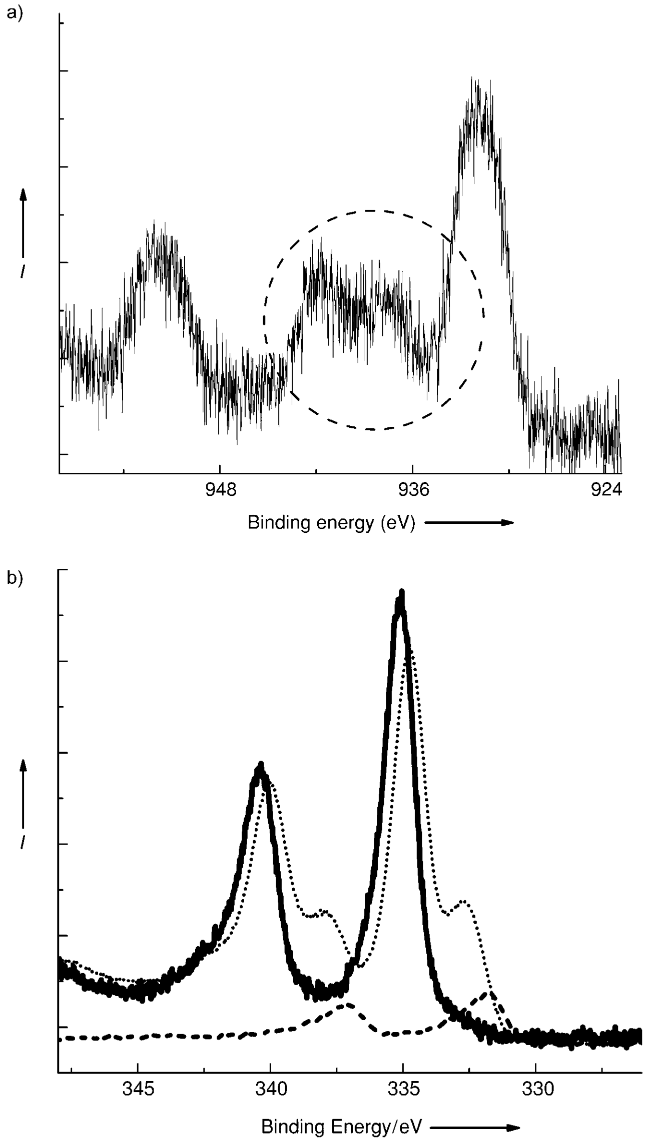

Figure 2. a) XPS showing traces for Cu 2p of Teflon rubbed with PMMA and treated by 1 mmol $CuSO_4$ solution. The position of the main peak and the presence of the satellite peaks (circled) indicate that copper is in the oxidation state +2; b) XPS showing traces for Pd 3d of Teflon rubbed with PMMA and treated with $PdCl_2/HCl$ (0.2 mmol) solution. Solid line: beginning of the measurement (< 20 minutes) showing a dominant Pd^{2+} signal; dotted line: the same sample after prolonged exposure (2 hours) to the X-ray plus electron irradiation, thus showing partial reduction to Pd^0; dashed line: a sample treated with 1 % solution of formaldehyde in NaOH (0.1 mol) after the $PdCl_2/HCl$ treatment, thus presenting the early exposure only to the XPS probe where a dominant Pd^0 signal is seen.

Although the redox reactions, which are proposed as a tool for estimating the charge produced by rubbing Teflon with PMMA, apparently do not take place, the electrification is known to occur. Therefore we independently measured the charge residing on the PMMA and the Teflon before and after rubbing using a vibrating electrode technique (Kelvin probe). The data from the Kelvin probe shows that the surface of the nontreated PMMA is negatively charged with an equivalent density of approximately 10^{10} electrons cm^{-2}. The nonrubbed Teflon is positively charged with an equivalent density of approximately 10^{8} electrons cm^{-2}. However after rubbing with PMMA, Teflon acquires negative charges of approximately 10^{10} electrons cm^{-2}, which decreases to approximately 10^{8} electrons cm^{-2} after 40 minutes in dry air. The PMMA rubbed with Teflon changes its charge from negative (ca. 10^{10} electrons cm^{-2}) to a positive one of similar density. This PMMA sample remains positively charged after being treated with 5 % Na amalgam, thus implying that the contact between PMMA and amalgam does not lead to detectable charge transfer.[9]

One has to emphasize that although the observed charge densities on PMMA and Teflon are much smaller than those deduced from redox reactions reported by Liu and Bard, our observations are fully consistent with the limitation imposed by the electrical breakdown of air of $E_b = 3$ kV mm^{-1}:[5] $\sigma = E_b \varepsilon_0 \approx 2 \times 10^{10}$ el cm^{-2} (ε_0 is a dielectric permittivity of vacuum). This is similar to the maximum charge densities that can be achieved on other dielectric surfaces, for instance pyroelectrics. Surfaces of inorganic pyroelectrics (like $LiTaO_3$) can uphold approximately 10^{10}–10^{11} electrons cm^{-2} but undergo rapid discharge if the higher charge density is generated by heating and cooling. In this view, surfaces charged by contact electrifications are not expected to be similarly useful for controlling the nucleation of polar crystals. We confirmed this expectation by measuring ice nucleation on pure PMMA and on Teflon rubbed with PMMA under conditions described in our previous work,[13,20] and found the results to be indistinguishable.[21]

In conclusion, our XPS and Kelvin probe data are complementary to those reported by Liu and Bard,[8–11] but offer an alternative interpretation, which is based on material transfer and ion adsorption. Therefore, the static charge might be due to uncompensated ions[4,5] rather than cryptoelectrons.

Experimental Section

All experiments with Teflon (Fluorseals) were carried out with three types of samples: a) rinsed by acetone, ethanol (both spectroscopic grade, from Sigma), and deionized water (18 MΩ cm), and then treated for 20 min with high-pressure oxygen plasma (March Plasma 250 W, 1.2 Torr of O_2, 20 min) to remove possible residues. Each rinsing was done in ultrasonic bath for 5 min. b) Sample of the type (a) rubbed manually by PMMA. c) Sample of the type (b) treated by antistatic (Zerostat 3, MILTY, Sigma). All samples were of rectangular shape with a 0.5 cm^2 surface area and 0.5 mm thickness.

PMMA (Palram Industries) samples were rinsed in ethanol and water, similar to Teflon. The samples had a 1 cm^2 surface area and 2.5 mm thickness.

Ice nucleation experiments were performed using the setup described in Ref. [13]. To ensure reproducibility, the experiments were carried out in a clean room at a fixed temperature (20 °C) and humidity (50 ± 10 %). No differences in the freezing points between charged (b) and discharged (c) samples of Teflon were observed any of the experiments (> 30 tests).

Kelvin probe (vibrating electrodes). A small (2 mm) vibrating electrode (Kelvin probe) was placed at a distance (5 cm) that was greater than the dimensions of a charged plate of Teflon (0.2 × 0.2 × 0.1 cm) placed on a large (8 × 15 cm) metallic plate. Compensation voltage corresponding to zero current between the plate and the electrode 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 perfect 1/distance decay of the voltage. Since the mobility of the charge on the dielectric surface is small, the average charge density was obtained by dividing the absolute charge deduced from the compensating voltage over the top are of the dielectric sample.

An XPS study was conducted on Kratos AXIS-HS and AXIS-Ultra spectrometers, using a monochromatic Al-Kα source at 10–75 W. The base pressure was ca. 1×10^{-9} Torr, but with PMMA the pressure was ca. 10^{-8} Torr. An electron flood gun (eFG) was used for stabilizing the surface potential, which took 15–60 min to achieve. Therefore, the question of beam-induced oxidation/reduction was studied thoroughly by comparing various exposure times and source conditions at different analysis spots and samples. A tendency to reduce surface metal ions was observed, but oxidation was never observed. Radiation-induced damage to the polymers[22] was observed to a much lesser extent, for example, the creation of fluorine free or CF1 groups in the Teflon.

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[21] The difference in the ability of electrets to affect ice nucleation may be due to two reasons. Firstly, the charge density on electrets is about two magnitudes 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.

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