Angewandte International Edition Chemie

VIP Contact Electrification

DOI: 10.1002/anie.201200057

Material Transfer and Polarity Reversal in Contact Charging**

*H. Tarik Baytekin, Bilge Baytekin, Jared T. Incorvati, and Bartosz A. Grzybowski**

Since the times of Volta,[1] scientists have strived to construct the so-called triboelectric series (TES) that would rank the contact-charging properties of various materials (Figure 1 a,b). While for contacting metals such ranking has been relatively straightforward,[1c,d,2] construction of a robust TES for bulk dielectrics has proven surprisingly challenging. In fact, the literature on the subject has been marred with irreproducible results, including situations where different polarities of charge have been reported by different laboratories for supposedly the same contact-charged materials.[3] Such ambiguities have been noted and discussed in Refs. [3f,7c,d,f]. Here, we show that contact charging of dielectrics cannot be predicted solely on the basis of their bulk properties—instead, it is necessary to account for the transfer of minute amounts of material between the contacting surfaces. Material transfer can lead to such counterintuitive phenomena as the reversal of charge polarity during contact charging, and is related to the differences in the mechanical properties of the contacting dielectrics.

For decades, the study of contact electrification has been mostly phenomenological in nature, rarely reporting more than the measurements/trends in the charges developed on macroscopic objects—not surprisingly, these studies have provided limited insights into the microscale phenomena underlying charging. It has only been relatively recently that surface characterization techniques have become available that allow for studying the changes in surface composition of the contact-charged surfaces with nanoscopic resolution. In this context, an important recent result from our group[4a] and others[3h,5] is that contact charging is not solely due to the transfer of charge carriers (be it electrons,[6a] ions,[3f,g] or both[6b]) between the surfaces but entails spatially inhomogeneous material transfer.[7] The patches of the transferred materials give rise to characteristic charge mosaics (i.e., regions of opposite polarities, (+) and (−)) on each of the contact-charged surfaces. Still, because the amounts of materials exchanged between the surfaces are very small (less than a microgram per square centimeter; see discussion later in the text), it remains unclear whether material transfer is just a secondary effect modifying only slightly the inherent charging properties of the bulk materials, or whether it can change the charging properties of the contacting materials

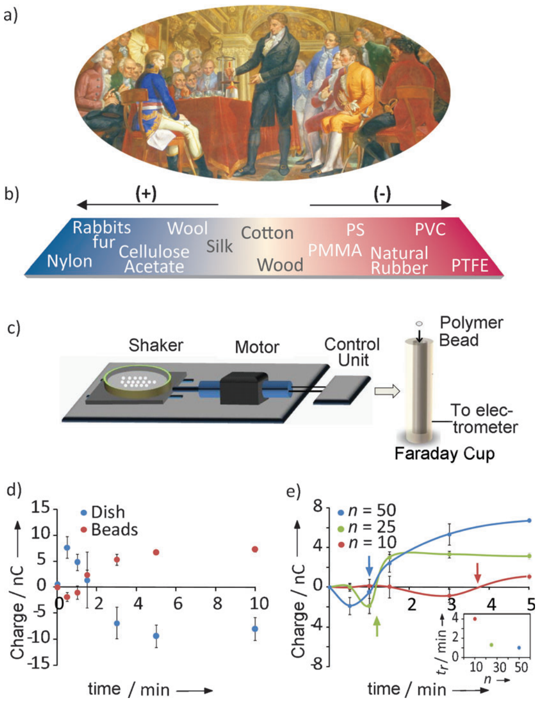

Figure 1. Construction of a triboelectric series for dielectrics is one of the oldest pursuits of modern science. a) Volta demonstrating "electrophorus", an electrostatic machine, to Napoleon who first honoured him with a medal and then raised him to the position of a Count and a Senator of the Realm of Lombardy.[19] (Portrait by Nicola Cianfanelli) b) A traditional triboelectric series of various dielectric materials (data adapted from Ref. [3g]). In this particular picture, the propensity of the material to charge negatively upon contact increases to the right (e.g., PTFE is expected to charge negatively when contacted with PS.). c) Illustration of experiments in which polymer beads are shaken against a polymeric dish (agitated by a LinMot shaker) and the charges developed on the beads and on the dish are measured by a Faraday cup connected to a high-precision electrometer (for details, see the Supporting Information). d) A typical charging curve for PTFE beads (here, $n=50$ beads, red markers show total charge on all beads) and the PS dish (blue markers) for different times of charging/shaking, t. e) Total charges on different numbers of beads ($n=10$ (red), 25 (green), 50 (blue)) plotted as a function of charging/shaking time, t. The markers correspond to experimental data, continuous lines serve to guide the eye. Arrows indicate times, t_r when the beads change polarity—as shown in the inset, these times decrease with n. In both (d) and (e), the error bars are based on the standard deviations of the bead charge distributions, averaged over five independent experiments for each condition.

---

[*] Dr. H. T. Baytekin, Dr. B. Baytekin, J. T. Incorvati, Prof. Dr. B. A. Grzybowski
Department of Chemistry and Department of Chemical and Biological Engineering, Northwestern University
2145 Sheridan Road, Evanston, IL 60208 (USA)
E-mail: grzybor@northwestern.edu
Homepage: http://dysa.northwestern.edu/

[**] This work was supported by the Non-equilibrium Energy Research Center (NERC) which is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0000989. We thank Bruker for supplying PeakForce QNM software. XPS and Raman spectra were taken in KECK-II and BIF facilities at NU. H.T.B. and B.B. contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200057.

substantially. The present study addresses this question with the help of several modern surface characterization techniques: various modalities of atomic force microscopy, AFM (to study not only surface topographies, but also mechanical properties of surfaces such as elastic moduli), Kelvin force microscopy, KFM (to visualize surface potentials), as well as X-ray photoelectron spectroscopy, XPS, and confocal Raman spectroscopy, CRS (to monitor changes in the surface composition).

We first consider experiments in which 1.6 mm polytetrafluoroethylene, PTFE, spheres (from 1 to 250) were shaken and therefore contact-charged in 8.5 cm-diameter polystyrene, PS, dishes (Figure 1c; for experimental details, see the Supporting Information). This system is especially convenient to study since, as discussed below, the elemental compositions and spectral characteristics of both polymers allow for unambiguous assignment of the two materials. According to the existing TES's, contact between PTFE and PS should always result in PTFE charging negatively and the PS, positively (Figure 1b). This was indeed observed for short charging times, as evidenced by the data shown in Figure 1d,e. However, for longer times, the magnitudes of charges on both the PTFE beads and the PS substrate started to decrease and after a few minutes, the polarities of the charges reversed—from there on, PTFE started charging positively and the PS negatively (Figure 1d). While this polarity reversal was observed for different numbers of beads used, n, the times at which polarity reversed, t_r, decreased with n (Figure 1e)—this trend will be an important piece of evidence in our mechanistic considerations below.

The observed reversal of charge polarity suggests that the very nature of contacting materials changes during the course of charging/shaking. The AFM topography plots in Figure 2a show that the surfaces become significantly rougher. In addition, the so-called AFM phase imaging (Figure 2b) indicates that material properties of the surfaces also change upon charging. However, phase images alone are not an unequivocal evidence of material transfer—this is so because this AFM modality visualizes domains of either different materials or of the same material but with different crystallinity.[8] Therefore, it could be argued that as the material gets rougher, it also changes its crystallinity locally—but no material transfer takes place. To rule this possibility out, we analyzed the surfaces by the so-called PeakForce Quantitative Nanomechanical Property Mapping® (QNM) atomic force microscopy,[9] which provides quantitative elastic property mapping of surfaces at the nanoscopic level. The collected maps of the DMT modulus (Young's modulus according to the Derjaguin–Muller–Toporov model[10]) of the polystyrene surface before (Figure 3a) and after charging (Figure 3b) identify the deposited PTFE as the darker-colored regions (corresponding to PTFE having lower modulus and higher deformation values than PS). Figure S1 in the Supporting Information provides additional evidence that submicrometer patches of PS materials are also being transferred onto PTFE. We observe that for both PS and PTFE surfaces, material transfer and the charge distributions are spatially inhomogeneous, in accordance with the mosaic model we described earlier.[4a,11] Also, the amounts of the

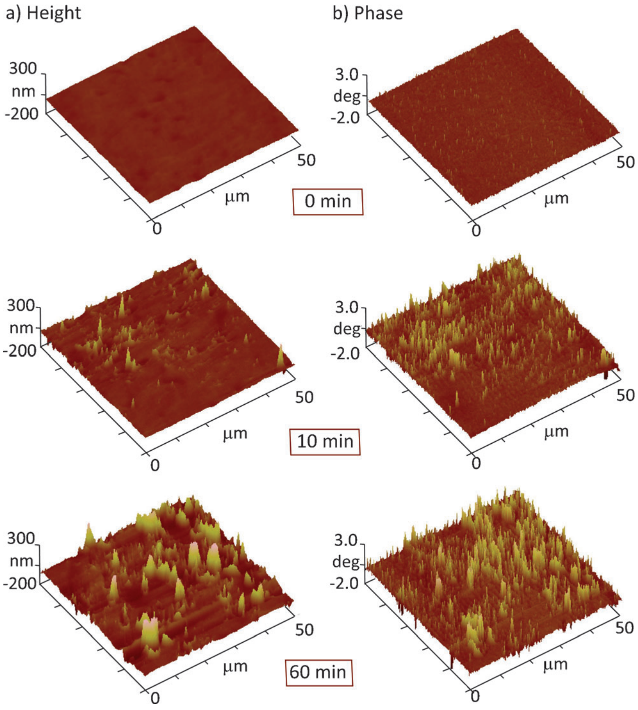

Figure 2. The surface roughness increases during contact charging. Changes in the surface roughness are visualized using AFM in the a) height and b) phase modes. The images here are for the PS surface charged against 50 PTFE beads for 0, 10, and 60 mins. The roughness, as determined from the images is $R_{\mathrm{RMS}} = 5.07$ nm, 17.2 nm, and 52.5 nm, respectively.

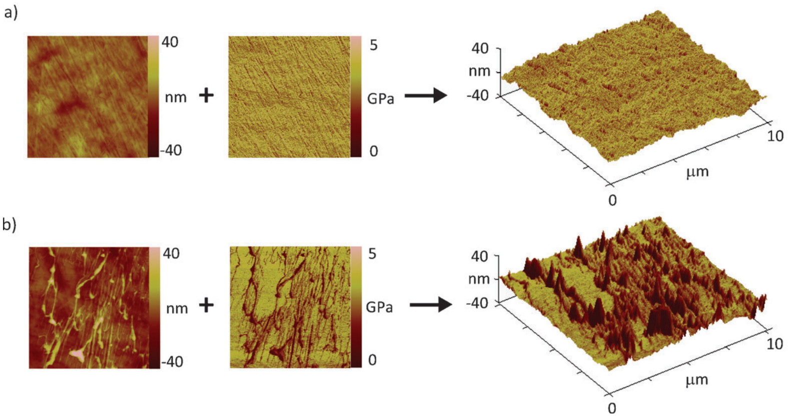

Figure 3. AFM height and AFM-Peakforce QNM DMT modulus maps determine the identity of the transferred material. From left to right: height, DMT modulus maps, and 3D height maps with DMT modulus skin (i.e., topography from height maps, color scale from modulus maps) for the PS dish surface a) before charging and b) after 60 min shaking/charging against 50 PTFE beads. The transferred material is clearly identified as PTFE, since it has a lower modulus compared to PS (see also Figure S2 in the Supporting Information for quantitative determination of polymer moduli by AFM). The imaged area is 10 µm × 10 µm for all maps.

materials being transferred are very small (on the order of around 5 $\mu g\,cm^{-2}$ on PS dish in 1 hour), as determined by weighing the PTFE beads on a high precision balance before and after the charging/shaking experiments. Finally, at least in some images we collected (see Figure S1 in the Supporting Information), the regions where material transfer is detected by DMT and the regions of most pronounced changes in surface charge (by KFM) correspond to one another suggesting that the pieces of transferred polymers are charged (likely because of the breaking of bonds, see Ref. [4]).

The presence of material transfer in the PTFE/PS system is further corroborated by two spectroscopic techniques—Raman confocal imaging and X-ray photoelectron spectroscopy—which feature signals characteristic for both of the charging polymers. Specifically, the Raman confocal maps (Figure 4a) of charged PTFE and PS both show C-H absorption bands around 1000 cm^{-1} which is only present in the Raman spectra of PS.[12] We observe that similar to the AFM imaging, both charged surfaces are patchy due to material transfer (uncharged polymers show only flat maps). Individual Raman spectra in Figure 4b indicate that these patches are composed of different materials—patches featuring the 1000 cm^{-1} band correspond to PS transferred onto PTFE, and those featuring the 732 cm^{-1} band correspond to PTFE transferred onto PS. Furthermore, the XPS data in Figure 4c demonstrate a gradual increase (with the time of charging/shaking) in the intensity of the F1s peak (located at 691 eV and characteristic of PTFE) on the PS surface. At the same time, XPS spectra of the PTFE beads (Figure 4d) feature a slight increase in the C—C and C—H signals at 285 eV (with respect to the C—F signal at 291 eV) indicating the material transfer of PS onto PTFE. Interestingly, the rate of material transfer—measured by the rates at which the ratio of the F1s and C1s peaks change—is faster for the transfer of PTFE onto PS than for the transfer of PS onto PTFE.

Taken together, the above experiments confirm bidirectional material transfer, albeit with different rates. This transfer continues steadily for times longer than the times of polarity reversal, t_r (compare the time dependencies in Figure 5a vs. the charging curves in Figure 1e)—this observation implies that the non-monotonous charging curves in Figure 1d and e are not solely because of material transfer but originate from a competition between the transfer of charge and the transfer of material. A plausible scenario can be then narrated as follows (Figure S3a in the Supporting Information). Initially, for native polymers, the charge is transferred such that PS charges positively and PTFE negatively (note: many studies[6a,13] suggest that electrons are being transferred). At the same time, however, PS is being covered with pieces of PTFE, while PTFE is covered with pieces of PS—as this material transfer continues, the identity of the surfaces reverses. Because, as we have shown earlier, the effects of contact charging are predominantly due to a tens-of-nanometer-thin surface layer (see Refs. [4] and [13]), this mutual coating effectively translates into the dish becoming PTFE-like, and the bead, PS-like. Thereafter, the dish charges negatively and PTFE positively. The proposed scenario agrees with the observed trend in the polarity reversal times, t_r versus the number of beads, n (Figure 1e). Specifically, as more beads are being shaken, they "teflonize" the PS surface more rapidly than when fewer beads are used—consequently, the effects of material transfer leading to polarity reversal manifest themselves at earlier times (Figure 1e versus Figure S3b in the Supporting Information).

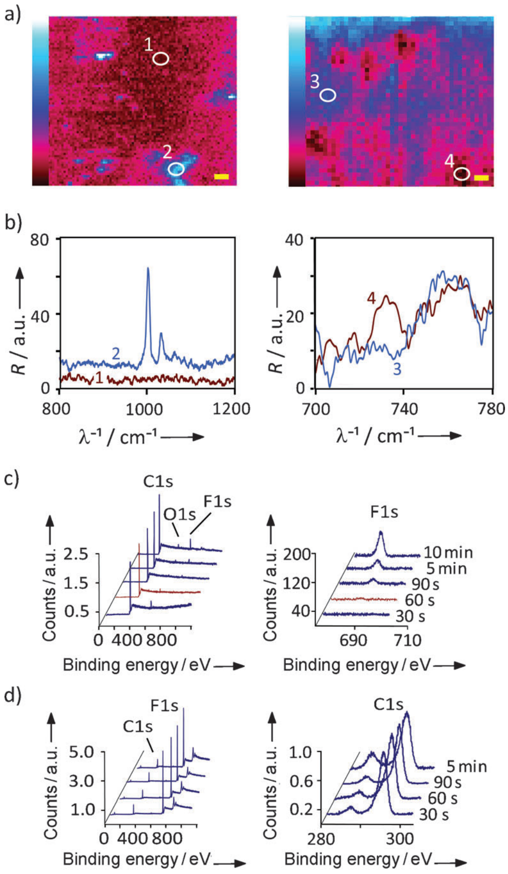

Figure 4. Spectroscopic verification of material transfer between contact-charged PTFE and PS. a) Raman confocal images of PTFE beads (left) and PS dishes (right) after $t = 30$ min of charging. The dark red regions in both images, where there is no peak for PS at 1000 cm^{-1}, can be identified as PTFE and blue-white regions where the peak is clearly observed, are PS. On both surfaces, micrometer-sized domains of the other/transferred material are detected. (scale bar = 1 μm, left, and 0.5 μm, right) b) Individual Raman spectra from the regions numbered in (a) compare the intensity of the PS characteristic band at 1000 cm^{-1} at regions 1 and 2 and of the PTFE-specific band at 732 cm^{-1} at regions 3 and 4. c,d) XPS survey (left) and high-resolution spectra (right) of c) PS dishes and d) PTFE beads at different shaking times, t. Bidirectional material transfer is evidenced by a gradual increase in the intensity of the PTFE-specific F1s signal at 691 eV on PS and a slight increase (relative to the F1s peak) of the PS-specific C1s signal at 285 eV on PTFE.

A question that immediately presents itself is whether material transfer and polarity reversal are features universal to other types of contact-charging materials. The answer depends crucially on the ability of the surfaces to exchange materials—one possible criterion here is the relative softness of at least one of the contacting materials. For example, in the PS/PTFE and the PS/PVC pairs (Figure 5a,b), PTFE and PVC are significantly softer (DMT modulus = 0.55 GPa and

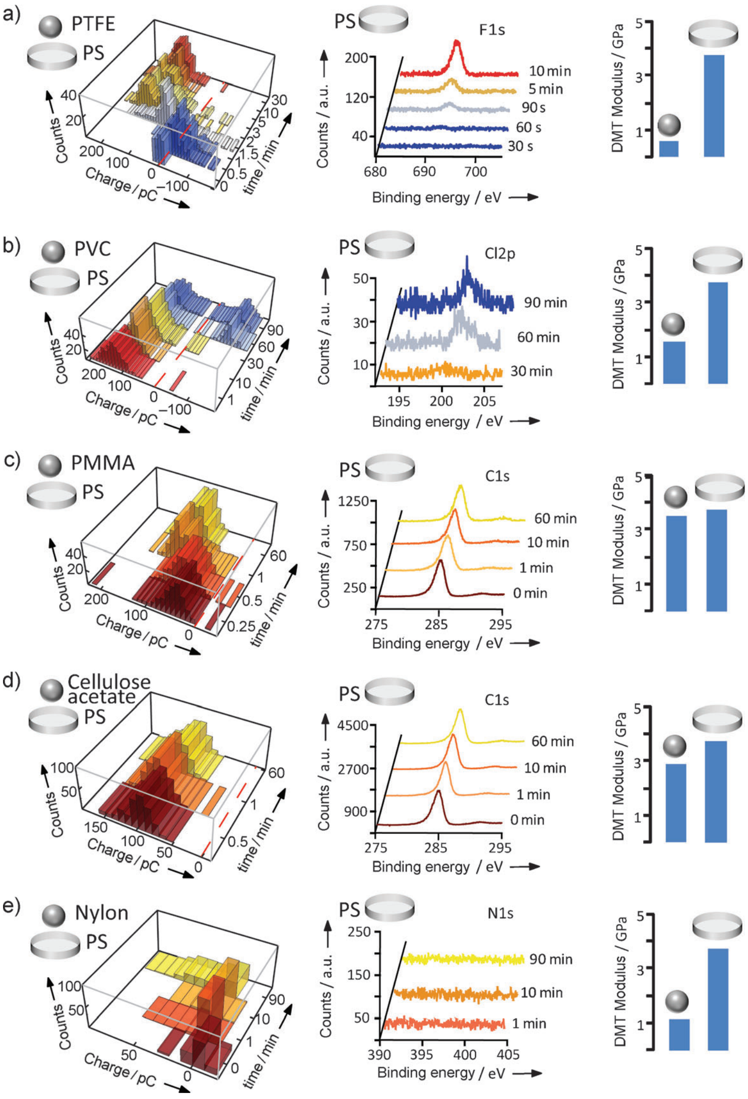

Figure 5. Relating polarity reversal to material properties. The histograms in the leftmost column have the distributions of charges on the beads at various times of charging. Red dashed lines correspond to zero charge; each distribution is based on the analysis of five independent experiments, each with 50 beads. The plots in the middle column have the HIRES-XPS spectra recorded at different times of charging. The spectra are recorded for the harder of the two polymers in each pair and focus on the regions where characteristic peaks appear (or would be expected to appear, had a noticeable material transfer taken place). The schemes in the rightmost column give the DMT moduli of the contacting polymers. a,b) The soft PTFE and PVC beads both transfer onto the harder PS, and both change polarity during charging. We note that the times at which the characteristic F1s peak at 691 eV in (a) and the Cl2p peak at 200 eV in (b) become clearly discernible are commensurate with the times of polarity switch in the charge histograms for these materials. c,d) The harder PMMA and cellulose acetate do not transfer material onto hard PS and do not change polarity during CE. In the XPS spectra, the C1s peaks from C=O and C-O for PMMA or cellulose acetate at 287–290 eV do not appear even after 60 min. e) Nylon is a notable exception to the hard/soft trend other materials follow. Although being relatively soft, it does not transfer onto harder PS and the nylon beads do not reverse polarity. For nylon, DMT modulus does not account properly for its high cohesive energy.

1.54 GPa, respectively) as measured by AFM PeakForce QNM, Figure S2 in the Supporting Information) than PS (3.75 GPa). Consequently, in both cases, there is a predominant material transfer from PTFE or PVC (also see the discussion earlier in the text) onto PS—the changing identity of the surfaces participating in CE ultimately manifests itself in polarity reversal. A very different situation is observed when both contacting surfaces are hard, for example, in pairs involving cellulose acetate (2.84 GPa), PMMA (3.52 GPa), or PS (3.93 GPa) (see Figure 5c,d)—in this case, there is very little material transfer from/to either of the contacting surfaces and no polarity reversal is observed even at very long times.

While the DMT softness/hardness criterion works well for the majority of materials we tested, we also found a notable exception to this rule that reflects the multifaceted nature of the material wear/transfer at the nanoscale. This exception is nylon, the contact charging characteristics of which have been, incidentally, amongst the most debated cases in the literature on contact electrification.[14] As shown in Figure 5e, although nylon beads are relatively soft (DMT modulus 1.12 GPa), they charge only up to around 50 pC (compared to around 150–200 pC for other polymers) when shaken in hard PS dishes (3.75 GPa). In addition, even after 90 min, there is no noticeable material transfer from nylon onto the PS (or, as a matter of fact, from PS onto nylon). While this behavior cannot be explained on the basis of the DMT moduli, it can be rationalized by taking into account the cohesive energy,[15] which describes the interchain attractions and scales inversely with the square of the wear rate of polymers[16] (such that it can be linked to the material transfer rate). Importantly, for nylon, the cohesive energy is about one order of magnitude higher than that of other polymers we used,[16] such that ripping off pieces of material from this surface onto other polymers is difficult. Hence, no appreciable material transfer takes place and no polarity reversal is observed.

The overall picture that emerges from our experiments is that contact electrification cannot be understood solely on the basis of charge flow. Instead, it is the combination of charge flow and transfer of minute amounts (around a microgram per square centimeter) of material between the contacting surfaces. Perhaps the chief reason why after several centuries of research there has been no coherent description of CE is that this phenomenon depends not only on the electronic properties of the contacting materials but also on their elastic[10,17] and topographical[18] characteristics. We believe that the most promising outcome of our study is that the relative softness/hardness of the contacting materials can at least guide intuition about the contact-charging characteristics and possible polarity reversal. Future studies on contact charging should take into account the molecular and nanoscale mechanics and the corresponding changes in the structure of materials. Only with such a microscopic understanding at hand, will it be possible to construct a truly coherent and predictive triboelectric series.

Received: January 3, 2012

Keywords: contact electrification · material transfer · mechanical properties · surface analysis

---

[1] a) W. Gilbert, *De Magnete*, *Vol. 2* (Ed.: P. Short), London, **1600**; b) J. Wilcke, *Philos. Trans. R. Soc. London* **1759**, *11*, 401; c) A. Volta, *Proc. R. Soc. London* **1800**, *1*, 27 – 29; d) A. Volta, *Philos. Trans. R. Soc. London* **1800**, *90*, 403 – 431; e) M. Faraday, *Experimental Researches in Electricity*, *Vol. 2*, R. & J. E. Taylor, London, **1843**, pp. 2075 – 2145.

[2] IUPAC definition of contact potential difference (Volta potential difference): The electric potential difference between one point in the vacuum close to the surface of M1 and another point in the vacuum close to the surface of M2, where M1 and M2 are two uncharged metals brought into contact. *IUPAC Compendium of Chemical Technology*, 2nd ed., **1997**.

[3] a) A. Coehn, *Ann. Phys.* **1898**, *300*, 217 – 232; b) A. Coehn, U. Raydt, *Ann. Phys.* **1909**, *335*, 777 – 804; c) S. P. Hersh, D. J. Montgomery, *Text. Res. J.* **1955**, *25*, 279 – 295; d) J. Henniker, *Nature* **1962**, *196*, 474 – 474; e) C. K. Adams, *Nature's Electricity*, Wiley, New York, **1987**, pp. 63; f) A. F. Diaz, R. M. Felix-Navarro, *J. Electrost.* **2004**, *62*, 277 – 290; g) L. S. McCarty, G. M. Whitesides, *Angew. Chem.* **2008**, *120*, 2218 – 2239; *Angew. Chem. Int. Ed.* **2008**, *47*, 2188 – 2207; h) D. J. Lacks, R. M. Sankaran, *J. Phys. D* **2011**, *44*, 453001; i) N. Knorr, *AIP Adv.* **2011**, *1*, 022119.

[4] a) H. T. Baytekin, A. Z. Patashisnki, M. Branicki, B. Baytekin, S. Soh, B. A. Grzybowski, *Science* **2011**, *333*, 308 – 312; b) M. Sakaguchi, Y. Miwa, S. Hara, Y. Sugino, K. Yamamoto, S. Shimada, *J. Electrost.* **2004**, *62*, 35 – 50; c) M. Sakaguchi, S. Shimada, H. Kashiwabara, *Macromolecules* **1990**, *23*, 5038 – 5040.

[5] a) M. Sow, R. Widenor, A. Kumar, S. W. Lee, D. J. Lacks, R. M. Sankaran, *Angew. Chem.* **2012**, DOI: 10.1002/ange.201107256; *Angew. Chem. Int. Ed.* **2012**, DOI: 10.1002/anie.201107256; b) R. Pham, R. C. Virnelson, R. M. Sankaran, D. J. Lacks, *J. Electrost.* **2011**, *69*, 456 – 460.

[6] a) C. Y. Liu, A. J. Bard, *Nat. Mater.* **2008**, *7*, 505 – 509; b) L.-H. Lee, *J. Electrost.* **1994**, *32*, 1 – 29.

[7] a) W. R. Salaneck, A. Paton, *J. Appl. Phys.* **1976**, *47*, 144 – 147; b) J. Lowell, *J. Phys. D* **1977**, *10*, L233 – L235; c) G. S. P. Castle, *J. Electrost.* **1997**, *40 – 41*, 13 – 20; d) S. Matsusaka, H. Maruyama, T. Matsuyama, M. Ghadiri, *Chem. Eng. Sci.* **2010**, *65*, 5781 – 5807; e) S. Piperno, H. Cohen, T. Bendikov, M. Lahav, I. Lubomirsky, *Angew. Chem.* **2011**, *123*, 5772 – 5775; *Angew. Chem. Int. Ed.* **2011**, *50*, 5654 – 5657; f) M. Williams, *AIP Adv.* **2012**, *2*, 010701.

[8] J. Tamayo, R. García, *Appl. Phys. Lett.* **1997**, *71*, 2394 – 2396.

[9] a) B. Pittenger, N. Erina, C. Su, *Quantitative Mechanical Property Mapping at the Nanoscale with PeakForce QNM*, *Bruker Application Note* **2010**; b) A. Rosa-Zeiser, E. Weilandt, S. Hild, O. Marti, *Meas. Sci. Technol.* **1997**, *8*, 1333 – 1338; c) O. Sahin, S. Magonov, S. Chanmin, C. F. Quate, O. Solgaard, *Nat. Nanotechnol.* **2007**, *2*, 507 – 514; d) J. Adamcik, A. Berquand, R. Mezzenga, *Appl. Phys. Lett.* **2011**, *98*, 193701.

[10] B. V. Derjaguin, V. M. Muller, Y. P. Toporov, *J. Colloid Interface Sci.* **1975**, *53*, 314 – 325.

[11] M. M. Apodaca, P. J. Wesson, K. J. M. Bishop, M. A. Ratner, B. A. Grzybowski, *Angew. Chem.* **2010**, *122*, 958 – 961; *Angew. Chem. Int. Ed.* **2010**, *49*, 946 – 949.

[12] T. E. Bridges, M. P. Houlne, J. M. Harris, *Anal. Chem.* **2004**, *76*, 576 – 584.

[13] a) J. A. Wiles, M. Fialkowski, M. R. Radowski, G. M. Whitesides, B. A. Grzybowski, *J. Phys. Chem. B* **2004**, *108*, 20296 – 20302; b) J. A. Wiles, B. A. Grzybowski, A. Winkleman, G. M. Whitesides, *Anal. Chem.* **2003**, *75*, 4859 – 4867.

[14] a) L. Jian, L. Ning, S. Yang, J. Wang, M. Hua, *Tribol. Lett.* **2009**, *36*, 199 – 208; b) A. R. Akande, J. Lowell, *J. Electrost.* **1985**, *16*, 147 – 156.

[15] a) B. B. Sauer, G. T. Dee, *Macromolecules* **2002**, *35*, 7024 – 7030; b) K. Oharat, S. Uchiyama, *J. Phys. D* **1992**, *25*, 94 – 99.

[16] P. Giltrow, *Wear* **1970**, *15*, 71 – 78.

[17] a) H. Hertz, *J. Reine Angew. Math.* **1881**, *92*, 156 – 171; b) K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. R. Soc. London Ser. A* **1971**, *324*, 301 – 313; c) D. Maugis, *Contact, Adhesion and Rupture of Elastic Solids*, Springer, Berlin, **2000**.

[18] a) F. P. Bowden, D. Tabor, *Proc. R. Soc. London Ser. A* **1939**, *169*, 391 – 413; b) F. P. Bowden, D. Tabor, *The Friction and Lubrication of Solids*, Oxford University Press, Oxford, **2001**; c) B. N. J. Persson, F. Bucher, B. Chiaia, *Phys. Rev. B* **2002**, *65*, 184106.

[19] B. Dibner, *Allessandro Volta and the Electric Battery*, Franklin Watts, New York, **1964**.