Charge Partitioning at Gas−Solid Interfaces: Humidity Causes Electricity Buildup on Metals

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Isolated metals within Faraday cages spontaneously acquire charge at relative humidity above 50%: aluminum and chrome-plated brass become negative, stainless steel is rendered positive, and copper remains almost neutral. Isolated metal charging within shielded and grounded containers confirms that the atmosphere is an electric charge reservoir where OH^- and H^+ ions transfer to gas−solid interfaces, producing net current. The electricity buildup dependence on humidity, or hygroelectricity, acts simultaneously but in opposition to the well-known charge dissipation due to the increase in surface conductance of solids under high humidity. Acknowledging this dual role of humidity improves the reproducibility of electrostatic experiments.

The electrostatic behavior of dielectrics is not well understood, and this is largely due to a lack of consensus on the nature of species responsible for electrostatic charge buildup and dissipation.[1−6] Recent publications provide evidence for the participation of ions[6,7] and electrons[8,9] in electrostatic charging under various conditions. The effect of relative humidity (RH) on charge buildup and dissipation in dielectrics has been evidenced in recent papers from this laboratory[10−12] with an intriguing result: in many systems, charging is faster under high RH than in dry environments. This is in apparent conflict with common knowledge, according to which low humidity is conducive to the appearance of static electricity.

The effectiveness of high humidity to eliminate static charging from dielectrics is assigned in the literature to high surface conductance[13] through thick adsorbed water layers, but this widespread argument cannot explain the faster charge buildup under high humidity that has been observed in many systems studied under well-defined conditions.[10−12]

This work shows that the exposure of isolated metal samples to water vapor leads to charge buildup on the metal and presents an explanation based on water ion partitioning at the air−solid interface. The water vapor effect on metal charging was first observed in this laboratory during Faraday cup measurements to determine the charge on insulators. Charge measurements were in turn made to verify observations made in the Kelvin probe scanning microscope, showing a marked effect of RH on the ubiquitous charge distribution patterns observed on dielectrics and metals.[11]

There are reports in the literature showing that the corrosion potential of metals[14,15] changes when the surrounding humidity increases. However, changing air pressure and humidity cause a small flow of current (10^{-13} A) to and from a gold-plated brass electrode surface,[16] which was assigned to a Nernst voltage change due to metal ions dissolving in the water layer at the metal surface. However, neither case is currently clearly understood.

Results and Discussion

The electric charge on any isolated metal sample should remain equal to zero after the sample is grounded, as long as it is kept shielded from external fields except those due to exposure to high-energy ionizing radiation. In this case, charge builds up in the isolated metal, as in the Faraday cups used as radiation and electron detectors.[17,18]

When the metal sample is made out of brass (average composition: Cu 64.1%, Zn 35.9%, determined by X-ray fluorescence) or electrolytic copper mounted within but electrically isolated from an outer, grounded, hollow chrome-plated brass (CPB) cylinder (Supporting Information Figure S1), the charge drifts slowly to negative values, independent of RH. Changing the RH does not significantly change the rate of charge change, and this is highly reproducible, as shown in Figure 1 and SI Figure S2.

Different behavior is observed when the sample is a hollow cylinder made out of aluminum, stainless steel (SS), or CPB or when it is an SS screen. Under low humidity, charge drifts slowly as in the case of copper and brass, but as the humidity is increased, the charge changes significantly.

CPB and aluminum cylinders acquire negative charge as RH increases, as shown in Figure 2 and SI Figure S3. SS shows the

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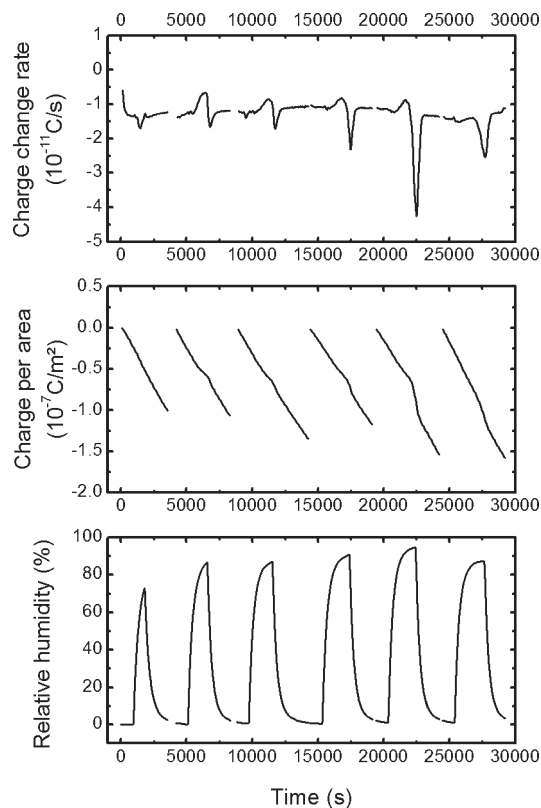
Figure 1. RH, charge per area, and charge change rate vs time plots for a brass cylinder during dry−wet−dry N_2 cycles.
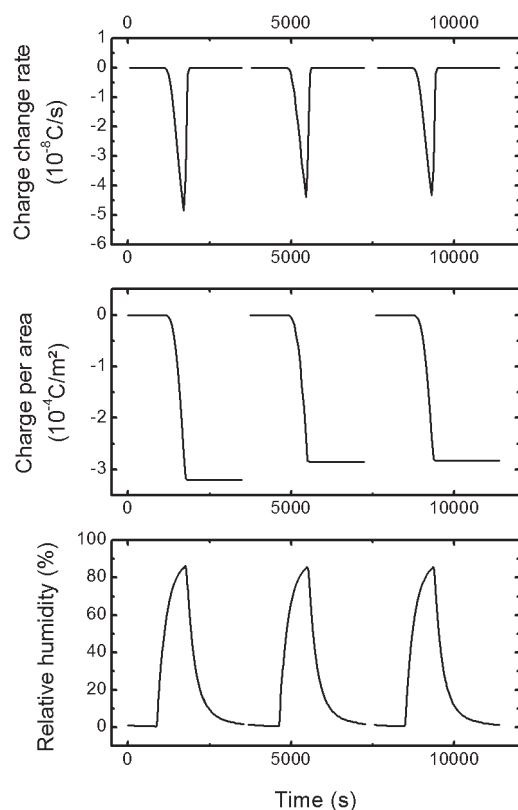

Figure 2. RH, charge per area, and charge change rate vs time plots for a CPB cylinder during dry−wet−dry N_2 cycles.

opposite behavior (SI Figure S4): as the RH increases, a positive charge increase is observed. In every case, successive experiments
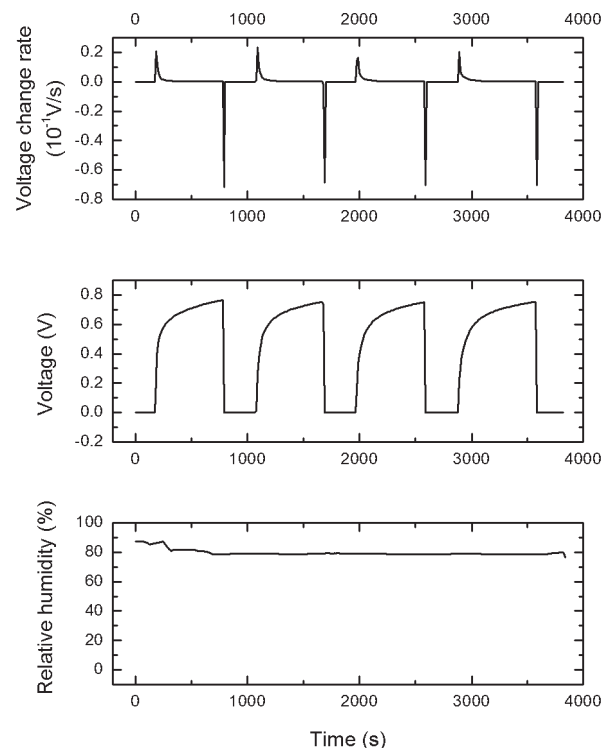

Figure 3. Charge−discharge cycles of the capacitor formed by two metal sheets (aluminum and SS) separated by a sheet of cellulose and enclosed within two cellulose sheets, within a humid N_2 atmosphere.

yield reproducible measurements that are an uncommon feature of electrostatic experiments.[1]

Rates of charge change thus vary pronouncedly with RH and the nature of the metal sample, as shown in SI Figure S5.

All these results point toward a connection between metal charging and water vapor adsorption. This assumption was verified by coating the aluminum and SS cylinders with silicone oil, which delays water vapor contact with the metal surface. Charge accumulation on coated metal is then negligible up to RH = 95%.

These observations raise the possibility of producing electricity by charging metals under high humidity, which was verified by building a simple device made of stacked sheets of filter paper, aluminum, filter paper, SS, and filter paper in this order. These stacks or "piles" are just capacitors with some singular features: electrodes are made out of two metals that are always coated with oxides showing different adsorptive abilities, separated by a porous dielectric with a high capacity to absorb water vapor. They were mounted within a closed aluminum box that was grounded and kept within a Faraday cage, and the two electrodes were connected to an electrometer. The voltage between the two metal sheets increases steeply when the humidity increases, and it tends to level off on charged electrodes, as shown in Figure 3, to be dissipated when electrodes are short-circuited (SI Figure S6). Charging and electrode short-circuiting are repeated many times, with good reproducibility and without any evidence of an irreversible change.

Charge buildup on metals under high humidity, as described in this work, is a novel example of electrostatic charging at the solid−gas interface, and it can be understood by making an analogy to the well-known behavior of solid surfaces within liquid water: they always acquire charge by some mechanism such as specific ion adsorption or ionizable group dissociation.[19]

Aluminum, chromium, and SS acquire charge under high humidity and are well known for their resistance to oxidation, which is due to the coating metal oxides that protect the highly reactive metals in the bulk from the atmosphere. Water vapor adsorbs in the oxide layers, causing a number of structural changes.[20]

Al and Cr oxides are amphoteric, reacting with acids and bases. Aluminum oxides on metal contain OH and O sites with Brönsted/Lewis acid−base properties that are fairly independent of the oxidation procedure,[21] but dry aluminum oxide usually shows marked acidic character.[22] Hydroxyl groups in mixed chromium−aluminum oxides prepared by the sol−gel technique to be used as catalysts show the opposite acid−base behavior: chromium oxide sites are acidic , but aluminum oxide sites are basic.[23] This means that when the two oxides are formed together, H⁺ binds preferentially to Cr oxide but Al oxide rather collects hydroxyl ions from the aqueous medium. Water itself is amphoteric, acting as an acid or a base, under various conditions.

An explanation of charge buildup on metals can thus be presented as follows: adsorbed water molecules contribute OH⁻ or H⁺ ions to the oxide-coated metal surface, depending on its nature and state and thus imparting excess overall charge to the isolated metal. According to this view, metal charging under high humidity is the outcome of one or more concurrent acid−base surface reactions, for instance,

$$S + H_2O = S_{(OH^-)} + H^+ \quad \text{or} \quad S + H_2O = S_{(H^+)} + OH^- \quad (1)$$
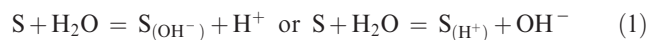
where S represents surface sites and the H⁺ or OH⁻ ions formed are released to the atmosphere, bound to desorbed water molecule clusters.

H⁺ or OH⁻ ions derived from adsorbed water may also pre-exist in the gas phase as ionic water clusters.[24] Whenever the ion concentration in the gas phase is significant, their adsorption should also contribute charge to the metal, but in the present case, the atmosphere is contained within a grounded box where gas-phase ions can be discharged.

Thus, the adsorption and desorption of water carries charge to and from the metal surface, depending on the acid−base nature of its oxide layer, imparting positive or negative charge to the metal. Unfortunately, the current status of knowledge on the structure and especially on the specific acid−base properties is still insufficient to establish a detailed correlation between charge buildup and the metal surface structure. This was recently acknowledged as follows: "the structure of the first water layer in contact with the surface, including the possibility of dissociation into OH and H groups, remain largely unanswered".[20]

These results strengthen the role of atmospheric water as a charge reservoir for solids, which was initially proposed only for dielectrics but is now extended to metals. A schematic description of the charge exchange mechanism is in Scheme 1.

Water and water ions are ubiquitous: water fits into many crystalline structures, it solvates positive and negative ions, and it is soluble, albeit to a limited extent, in nonpolar media. The difficulty of removing the last traces of water from any solid surface

Scheme 1. Mechanism for Charge Transfer from the Atmosphere to the Metal Surface[a]
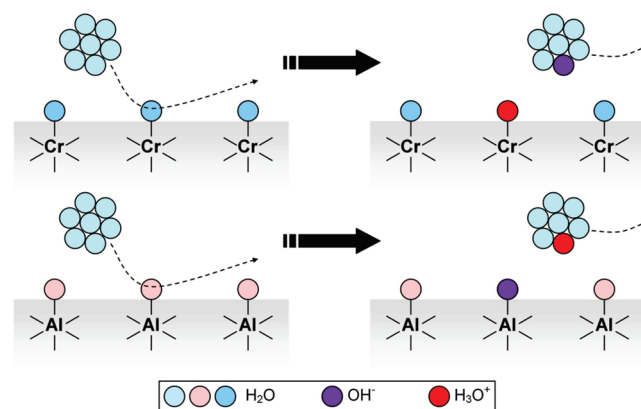
[a](Top) Formation of positive charge over a basic oxide. (Bottom) Formation of negative charge over an acidic oxide. Neutral water molecules are amphoteric, reacting differently with different oxides according to their acid−base properties.

at room temperature has long been known,[25] and traces of water in material surfaces and the bulk receive daily attention from many experimenters, from high-vacuum users to thermoplastics processors.[26,27]

Acknowledging aqueous ion partitioning at interfaces and applying this concept in other contexts may eventually help us to understand many intriguing phenomena, from the "steam electricity" that received attention from Faraday and Volta but was ultimately forgotten without being understood to the formation and (in)stability of atmospheric electricity.[28,29]

Because all surfaces relevant to environmental problems are covered by water forming thinner or thicker layers, it is certainly important to know that the growth of adsorbed water layers on most surfaces contributes to changing their electrical state.[30]

Finally, the present results suggest a new approach to capturing electricity from the atmosphere, an objective that has been eluding a number of scientists and inventors. It is quite convenient that metals can be used as traps for atmospheric charge because they can easily transfer charge to devices and circuitry. However, the present findings may help to design new protective measures for electrical circuits on every size scale.

Experimental Section

Faraday cups consist of open-ended, hollow metal cylinders placed within an outer CPB cylinder (20.0 cm length, 5.0 cm outer diameter (o.d.), and 0.05 cm wall thickness (w.t.)). Samples of 20.0 cm length, 3.8 cm o.d., and 0.16 cm w.t. (CPB: 0.05 cm w.t.; copper: 3.5 cm o.d., and 0.07 cm w.t.) were polished, washed with ethanol, and air dried, whereas the SS screen (17.1×3.3 cm², 400 mesh) and NiCr yarn (31.7819 g, 0.0825 cm ϕ) were washed with ethanol and air dried. Separation between cylinder walls was 0.57 cm (except for copper, 0.72 cm). Silicone-coated SS and aluminum cylinders were also immersed in silicone oil, followed by allowing the excess oil to drip off. Cylindrical samples and the outer cylinder were held together (and isolated) by three polyethylene foam rings mounted between the cylinders, as shown in

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Supporting Information Figure S1. The steel screen and NiCr yarn are supported by a stick of polyethylene, which hangs from the top end of the outer cylinder. This is grounded, and the isolated samples are connected to the input of a Keithley 6514 electrometer. The setup is vertically placed within a grounded aluminum box with fittings for gas circulation and kept within a Faraday cage. RH is measured with a Minipa MTH-1380 thermo-hygrometer connected to a PC. The metal samples are initially grounded. After the connection to ground is removed, charge is measured as a function of time, starting at RH $\approx$ 0. After 15 min under dry N_2, water-saturated nitrogen is admitted to the chamber for a specific amount of time. Then, dry nitrogen is admitted again for 30−60 min, the sample is grounded, and another dry−wet−dry N_2 cycle is started.

Capacitors were built by using cellulose sheets (30.0 × 30.0 cm^2, 0.20 mm thick, 80 g m^{-2}, 3 μ porosity) to separate and enclose 14 mesh Al and 400 mesh SS screens (25.0 × 25.0 cm^2). The capacitance was 9.68 nF. The stack was rolled and fastened with a rubber band and mounted within an aluminum box, and the metal sheets were connected to the electrometer in parallel with a 3.3 μF polyester capacitor.

Supporting Information Available: Scheme of the experimental setup. RH, charge per area, and charge change rate versus time plots for copper, aluminum, and SS cylinders during dry−wet−dry N_2 cycles. Rates of charge change versus RH plots for different metal samples. Scheme of the charge buildup and discharge of electrodes in the capacitor formed by two metal sheets. This material is available free of charge via the Internet at http://pubs.acs.org.