



Short communication

Where is water in the triboelectric series?

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ABSTRACT

Water flowing through tubes of different materials and collected in a Faraday cup contains net electric charge. Water charge is always positive but its magnitude depends on the material position in most triboelectric series. On the other hand, water acquires net negative electric charge when falling through air but its charge is modified after it passes through an electric field. Thus, water is located on the top of the triboelectric series and its charge is a robust and reliable way to organize materials within the triboelectric series, giving due attention to its surface properties.

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1. Introduction

The triboelectric series (TS) is an empirically determined list of materials ordered according to their tendency to acquire positive or negative charge when in contact and then separated [1]. The phenomenon is known as triboelectrification or contact electrification. Dozens of TSs exist in the literature and inconsistencies are often found among them [1,2]. Indeed, contact electrification is a hardly reproducible phenomenon [3] and setting up robust, repeatable experiments is challenging [4]. While the charging mechanism is well understood in the case of conductors, it is poorly understood in insulating materials and the charge-carrier type has been the center of enduring controversy. Evidence published during the last decade supports ions [5–7] and electrons [8,9] as the charge carrier, triggering a lively debate [10].

Water plays an important role in the electrification of materials, demonstrated by the participation of aqueous ions [11], including $[\text{H}(\text{H}_2\text{O})_n]^+$ and $[\text{OH}(\text{H}_2\text{O})_n]^-$. Accumulation of hydroxyl ions on hydrophobic interfaces [12,13] has been demonstrated, debated and criticized [14]. Also, recent work [15] has shown that pure water becomes electrified when under the influence of electric fields, contrary to the long-held assumption that pure substances should be electroneutral [16]. Moreover, water causes charge

buildup in hydrophilic particles [17] and in metals [18]; and it can store charge for long periods of time [19].

A particular kind of contact electrification, known as flow electrification [20–22] has been reported for insulating liquids over the years, in relation to petroleum pipeline hazards. In addition, it was discovered that ultrapure water used in the production process of semiconductor chips can electrify circuits causing serious problems such as breakdown of electronic components [23]. In fact, Yatsuzuka et al. [23,24] and others [25,26] have shown that when pure water flows through hydrophobic materials such as polytetrafluoroethylene (PTFE), it becomes positively charged. However, there is no systematic work on the flow electrification of water in contact with hydrophilic surfaces [27] and other hydrophobic materials. This paper addresses water ability to acquire excess electric charge when flowing through different materials, by using a simple apparatus with highly reproducible results.

2. Materials and methods

Deionized water was passed through tubes made of different materials and collected in a Faraday cup to measure the excess charge. The following materials were used in this study: PTFE (internal diameters $\varphi_i = 0.813$ mm and 1.321 mm); silicone ($\varphi_i = 1.600$ mm), from Cole Parmer; polystyrene ($\varphi_i = 1.325$ mm) from Plastruct; copper, stainless steel, and aluminum ($\varphi_i = 0.865$ mm), from KS Engineering; and glass ($\varphi_i = 0.885$ mm) from VWR. All tubes were 13 cm long.

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The experimental setup is illustrated in Fig. 1. A plastic container was used as a water reservoir. Water passed through a grounded metal valve that was connected to the plastic container with a metal needle between the valve and the tube. This was shielded by a grounded steel cylinder ($\phi_i = 4$ cm, length $L = 13$ cm) to prevent induction electrification or interference from external electrical fields [24]. The Faraday cup comprised two electrically isolated, concentric metal cups ($\phi_i = 12.5$ and 16 cm, $L = 16.5$ and 19.0 cm, respectively). The inner cup was connected to the input of an electrometer (Keithley, 6512) while the outer cup was connected to ground. The electrometer output was connected to a data-acquisition device (DAQ), manufactured by National Instruments (NI, USB-6009) and measurements were recorded with Labview Datalogger software. All experiments were carried out using deionized water (Barnstead Nanopure Diamond System, 18.2 M Ω cm), and a gravity line was used to avoid perturbations. During the experiments, temperature and relative humidity were maintained at 20 – 25 °C and 30 – 50% respectively.

Experiments were carried out according to the following protocol: 50 mL of deionized water were placed in the plastic container, signal recording was turned on and 30 s later the valve was opened. Water jet exiting the tube of the material under test was then collected within the Faraday cup. To verify the effect of external fields, the outer cylinder was connected to an external DC source, applying positive or negative potential. No tubes were used in these experiments. Water falls through the air at two different flow rates (5 and 50 mL/min).

3. Results and discussion

Every experimental run led to water electrification with excess positive charge but of different magnitudes. Typical results are presented in Fig. 2, where the acquired charge is plotted as a function of volume. The highest positive charge was obtained with PTFE tube that is consistent with appearing as a negative material in most TS, and considering data from previous reports [23–27] a net positive charge of water should be expected. In the cases investigated here, the cup charge change is linear with flow time. For example, we can fit the PTFE curve of Fig. 2 with time using the equation $Q(\text{nC}) = 0.083t(\text{s}) + 0.8419$, where Q is the charge of water and t is time. Current determined using the equation ($i = dQ/dt$) is

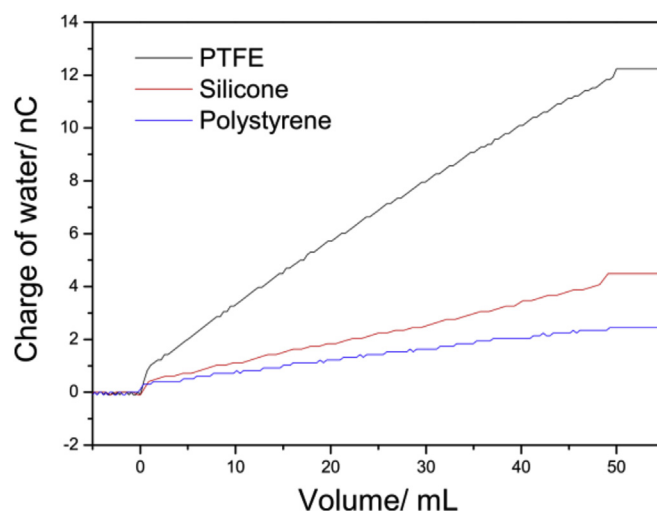


Fig. 2. Representative plots showing electrical charge acquired by 50 mL of deionized water after flowing through various hydrophobic materials.

83 pA. Other authors [22] used different setup with PTFE obtaining current ca. 35 pA, in the same order of magnitude. On the other hand, the aqueous ions imbalance is very low: for example, the charge concentration of 10 nC in 50 mL of water corresponds to approximately 2×10^{-12} mol L^{-1} , which implies that the charge species are hardly detected using standard analytical methods like pH or conductivity measurements.

The summary of all results is presented in Table 1. The table includes values of charge per mass of water after having flowed through various material types, including air. The materials in Table 1 are purposely ordered as they usually appear in most TS. With the exception of air, water always acquires a net positive charge, against all materials tested and its magnitude follows the standard TS. Water acquires higher positive charge when flow-electrified with hydrophobic materials (PTFE, silicone, and polystyrene). Charge accumulated against copper and stainless steel is the same within measurement in certainty, but aluminum electrifies water only one fifth as the other metals. Glass imparts to water a little positive charge and finally in air the charge is negative. Electric charge generated by flow is very stable and remains without appreciable change for more than 24 h.

Table 1 shows that there is a little difference in water charging considering flow ratio in air (5 or 50 mL min^{-1}) or tube diameter for PTFE (0.813 or 1.321 mm). In fact, previous reports [27,28] describe differences between flow velocities and this must be associated with our findings here where as faster water flows more charge it acquires. Moreover, besides flow rate there are many complicating factors that may influence charge in water: solid-water contact area, oxide layers in metals, temperature, laminar and turbulent flow, among others. These variables and others will be subject of future work.

These results show a correlation between water flow electrification and position in the TS. To understand the basis of flow electrification of water, we recall that ion partitioning [11,17] near solid-liquid interfaces, and particularly hydroxyl adsorption [12,13] at water-hydrophobic interfaces, is decisive in material electrification. At hydrophobic interfaces, hydroxyl ions are predominantly adsorbed at the Stern layer causing negative electrification. The hydroxyl adsorption is not only responsible for charge buildup in hydrophobic materials, but it is also associated with charge buildup due to adsorption [29] in metals. Also, the exclusion-zone (EZ) formed on the vicinity of various hydrophilic

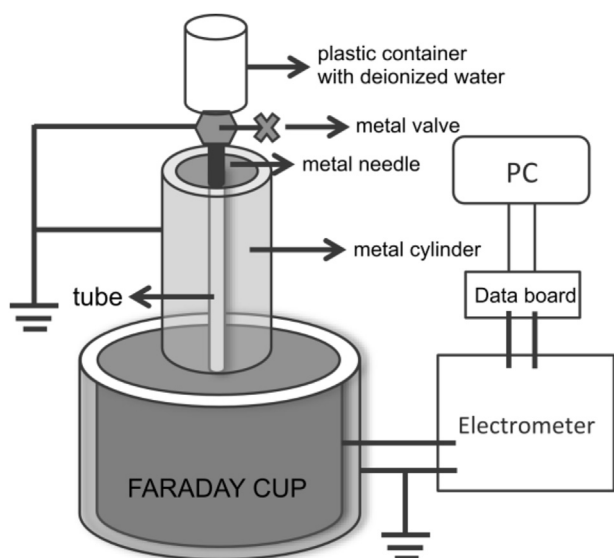


Fig. 1. Experimental setup used to measure electrical charge of water.

Table 1

Charge per mass acquired by flow electrification of water contacting with various materials, and charge per mass normalized by dividing by tubing internal area. Combined standard deviations are results from five independent experiments.

Material	Q/M (nC g ⁻¹)	(Q/M)/internal area (nC g ⁻¹ cm ⁻²)	Sign
Air (50 mL min ⁻¹)	-0.0159 ± 0.0009	N/A	-
Air (5 mL min ⁻¹)	-0.0131 ± 0.0004	N/A	-
Glass	+0.0034 ± 0.0002	+0.0010	+
Aluminum	+0.0057 ± 0.0007	+0.0016	+
Stainless steel	+0.0279 ± 0.0017	+0.0079	+
Copper	+0.0261 ± 0.0011	+0.0074	+
Polystyrene	+0.0503 ± 0.0099	+0.0093	+
Silicone	+0.0645 ± 0.0018	+0.0099	+
PTFE ($\phi_i = 0.813$ mm)	+0.1364 ± 0.0036	+0.0411	+
PTFE ($\phi_i = 1.321$ mm)	+0.1988 ± 0.0098	+0.0369	+

surfaces [30] displays a negative net charge while balanced by complementary positive charge beyond the EZ, formed by protons or hydronium ions in the bulk of water [31]. Thus, the present results are understood considering both hydroxyl ion partitioning and EZ. The difference of magnitude between materials tested must be due to the ability of each material to adsorb $[\text{OH}(\text{H}_2\text{O})_n]^-$ ions or to produce larger or thinner EZ charged interfaces.

The electrification of dropping water is well known since the classical Kelvin experiment, called the water-dropper condenser [32] and, as in the Kelvin experiment, water is spontaneously charged as it falls through air. In fact, as seen in Table 1, a negative net of charge is found when no tube is used and water falls only through air. Moreover, using our base setup shown in Fig. 1, water can fall in the air through a biased noncontacting metal cylinder, previously used to prevent our system from external electrostatic fields. The results are presented in Fig. 3 and show that the charge acquired by water can be controlled in the presence of an external DC source, when a surrounding negative electric potential builds positive charge on water while a positive potential builds negative excess charge, reproducibly. This charging behavior was recently [15] described and interpreted using the electrochemical potential definition [33] where charging is due the loss of ions according to the applied potential. The electrochemical potential ($\mu_i = \mu_i^0 + RT \ln a_i + zVF$, where μ_i is the electrochemical potential, R is the gas constant, T is the temperature, a_i is the activity, z is the valence, F is the Faraday constant and V is the electric potential) of ions under a given electric potential requires an excess cation concentration under negative potential (V) and excess anion concentration under positive V . This information is relevant to control water charging

and preventing electrostatic discharge (ESD) in industrial environments, e.g. on the processing of semiconductors and other situations when liquids are handled.

4. Conclusions

Water flowing through tubes of different materials acquires positive charge whose magnitude is correlated with the materials' position in the triboelectric series. However, water acquires negative charge when flowing through air but its charge is modified by applying an external electric field. Water is thus located at the top of the TS, between air and glass. Water flow charge can be used to construct robust and reliable triboelectric series, exempt of the mechanochemical effects that have been described in the literature.

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References

- [1] A.F. Diaz, R.M. Felix-Navarro, *J. Electrostat.* 62 (2004) 277–290.
- [2] J. Henniker, *Nature* 196 (1962) 474.
- [3] J.H. Dessauer, A.E. Clark, *Xerography and Related Process*, Focal Press, New York, 1965.
- [4] L.B. Schein, *Science* 316 (2007) 1572–1573.
- [5] A.F. Diaz, Diaz, Guay, *J. IBM J. Res. Dev.* 37 (1993) 249–259.
- [6] L.S. McCarty, A. Winkleman, G.M. Whitesides, *J. Am. Chem. Soc.* 129 (2007) 4075–4088.
- [7] R.F. Gouveia, C.A.R. Costa, F. Galembeck, *J. Phys. Chem. C* 112 (2008) 17193–17199.
- [8] C.Y. Liu, A. Bard, *J. Nat. Mater.* 7 (2008) 505–509.
- [9] C.Y. Liu, A.J. Bard, *J. Am. Chem. Soc.* 131 (2009) 6397–6401.
- [10] S. Piperno, H. Cohen, T. Bendikov, M. Lahav, I. Lubomirsky, *Angew. Chem. Int. Ed.* 50 (2011) 5654–5657.
- [11] T.A.L. Burgo, C.A. Rezende, S. Bertazzo, A. Galembeck, F. Galembeck, *J. Electrostat.* 69 (2011) 401–409.
- [12] T.W. Healy, D.W. Fuerstenau, *J. Colloid Interf. Sci.* 309 (2007) 183–188.
- [13] K.N. Kudin, R. Car, *J. Am. Chem. Soc.* 130 (2008) 3915–3919.
- [14] R. Zimmermann, U. Freudenberg, R. Schweiß, D. Küttner, C. Werner, *Curr. Opin. Colloid Interf. Sci.* 15 (2010) 196–202.
- [15] L.P. Santos, T.R.D. Ducati, L.B.S. Balestrin, F. Galembeck, *J. Phys. Chem. C* 115 (2011) 11226–11232.
- [16] IUPAC. *Gold Book*, <http://goldbook.iupac.org/E01992.html>.
- [17] R.F. Gouveia, F. Galembeck, *J. Am. Chem. Soc.* 131 (2009) 11381–11386.
- [18] T.R.D. Ducati, L.H. Simões, F. Galembeck, *Langmuir* 26 (2010) 13763–13766.
- [19] K. Ovchinnikova, G.H. Pollack, *Langmuir* 25 (2009) 542–547.
- [20] A. Klinkenberg, J.L. van der Minne, *Electrostatics in the Petroleum Industry*, Elsevier, Amsterdam, 1958.
- [21] G. Touchard, *J. Electrostat.* 51–52 (2001) 440–447.
- [22] M. EL-Adawy, T. Paillat, G. Touchard, J.M. Cabaleiro, *IEEE Trans. Ind. Appl.* 18 (5) (2011) 1463–1475.
- [23] K. Yatsuzuka, Y. Mizuno, K. Asano, *J. Electrostat.* 32 (1994) 157–171.
- [24] K. Yatsuzuka, Y. Higashiyama, K. Asano, *IEEE Trans. Ind. Appl.* 32 (1996) 825–831.
- [25] M. Matsui, N. Murasaki, K. Fujibayashi, P.Y. Bao, Y. Kishimoto, *J. Electrostat.* 31

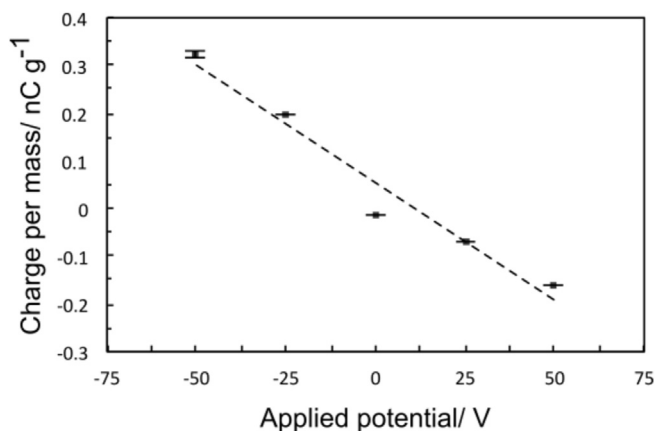


Fig. 3. Charge density on collected water after falling (50 mL/min) through air and exposed to different external potentials. Combined standard deviations are results from five independent experiments.

- (1993) 1–10.
- [26] B. Ravelo, F. Duval, S. Kane, B. Nsom, J. Electrostat. 69 (2011) 473–478.
- [27] T. Paillat, E. Moreau, G. Touchard, Ind. Appl. Conf. 2000. Conf. Rec. 2000 IEEE 2 (2000) 743–748.
- [28] G. Gibbings, J. Electroanal. Chem. 25 (1970) 497–504.
- [29] S. Yamamoto, H. Bluhm, K. Andersson, G. Ketteler, H. Ogasawara, et al., J. Phys. Condens. Matter 20 (2008) 184025.
- [30] J.-M. Zheng, G.H. Pollack, Phys. Rev. E 68 (2003) 031408.
- [31] J.-M. Zheng, W.-C. Chin, E. Khijniak, E. Khijniak Jr., G.H. Pollack, Adv. Colloid Interface Sci. 127 (2006) 19–27.
- [32] W. Thomson, Proc. R. Soc. Lond. 16 (1867) 67–72.
- [33] A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, sixth ed., John Wiley & Sons, New York, 1997.