

# The Position of Solid Carbon Dioxide in the Triboelectric Series

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## Abstract

The process of releasing liquid carbon dioxide from a fire extinguisher is accompanied by a strong static charging of the plastic material making up the extinguisher discharge horn. Firefighters are often reporting an electric shock when operating CO<sub>2</sub> extinguishers, but the origin of this electrostatic hazard is largely unknown. Here we begin to investigate this phenomenon, and test the hypothesis of plastic samples being tribocharged upon contact with rapidly flowing solid CO<sub>2</sub>. Using Faraday pail measurements we show that non-conductive polymers gain a net static charge when brought in and out of contact with dry ice (solid CO<sub>2</sub>). These measurements of charge sign and magnitude give indirect evidence helping to place for the first time solid CO<sub>2</sub> on the triboelectric series. PDMS, PTFE and PVC samples acquire a negative charge when rubbed against dry ice, while PMMA, glass and nylon surfaces become positive. Therefore we suggest the position of dry ice CO<sub>2</sub> in the triboelectric series to be close to that of materials with stable cations and unstable anions, possibly locating it between PMMA and PVC.

## Introduction

Contact electrification<sup>[1]</sup> is a process in which two materials that are brought in and out of contact acquire a net charge of opposite sign. Although contact electrification is exploited in several important technologies, such as photocopying and laser printing,<sup>[2]</sup> electrostatic painting,<sup>[3]</sup> industrial separations,<sup>[4]</sup> and new forms of alternating current generation,<sup>[5]</sup> when

1 uncontrolled it remains a detrimental, or even dangerous, phenomenon.<sup>[6]</sup> For examples, in  
2 industries such as textiles, manufacturing of explosives, storage of grains and flour, static  
3 electricity is a well-known hazard.<sup>[6b, 7]</sup> Contact charging is however not limited to contact  
4 between polymers, as the flow of water, liquid as well as gaseous hydrocarbons<sup>[8]</sup> is known to  
5 generate static charges.<sup>[7a, 9]</sup> Analogously, when a CO<sub>2</sub> extinguisher is operated, the liquefied  
6 gas expands and rapidly moves across the surface of the discharge horn, generating a large  
7 amount of electrostatic charges.<sup>[10]</sup> Major accidents have been associated to static charging  
8 created after the release of CO<sub>2</sub> extinguishers, such as an explosion in Germany in 1966.<sup>[11]</sup>  
9 Electrification induced by solid CO<sub>2</sub> has been studied by a number of groups,<sup>[12]</sup> and as early  
10 as in 1954 Heidelberg and co-workers investigated charge generation during release of CO<sub>2</sub>  
11 from a large fire-snuffing installation.<sup>[11]</sup> They reported a highly variable rate of charge  
12 generation, but to date, how different dielectrics respond to contact with solid CO<sub>2</sub> and how  
13 the environment influences CO<sub>2</sub>-related tribocharging events are still largely unexplored.  
14 Here we have begun to quantify the magnitude and sign of static electricity that develops on  
15 polydimethylsiloxane (PDMS), polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC),  
16 poly(methyl methacrylate) (PMMA), nylon and glass surfaces that were rubbed against dry ice  
17 under either an air or argon atmosphere, and tried for the first time to tentatively place CO<sub>2</sub> in  
18 triboelectric series.

## 19 **Results and Discussion**

20 We first consider experiments in which solid CO<sub>2</sub> is let sliding down an inclined plane made  
21 by a sheet of the polymer under test (Fig. 1a). This system is especially convenient in terms of  
22 reproducibly controlling the contact force. Solid CO<sub>2</sub> is not found in any available triboelectric  
23 series,<sup>[13]</sup> and therefore we performed experiments where dry ice was contacted against  
24 different polymers whose position in these charts is known.

1 Fig. 2a, b illustrates the experimental setup in which PDMS, PTFE, PVC, PMMA, nylon and  
2 glass plates were rested on an inclined plane made by a wood surface tilted 30° away from the  
3 horizontal plane (Fig. 1b). Wood was used as to hold the samples because it is known to gain  
4 a negligible charge after contact with any other polymer. The choices of the polymer materials  
5 were motivated by i) PDMS, PTFE, PVC and PMMA known to be close to the bottom (i.e.  
6 negative end) of the triboelectric series,<sup>[14]</sup> and ii) glass and nylon being towards the top (i.e.  
7 positive) end of the series. After contact with CO<sub>2</sub>, glass, PMMA and nylon gain a positive  
8 charge, while PDMS, PTFE and PVC become negative. Our Faraday pail data therefore suggest  
9 that solid CO<sub>2</sub> should be placed in a triboelectric series between PMMA and PVC (Fig. 1b).  
10 Furthermore, the magnitude of charging is strongly ambient-dependent: data comparing  
11 between tribocharging in air and argon are shown in Fig. 2a and Fig. 2b, respectively. In 2018,  
12 Grzybowski and co-workers observed the magnitude of charges developed by polymers upon  
13 contact-electrification to be depend not only on the material, but also on the nature of the  
14 atmosphere surrounding the polymers.<sup>[15]</sup> The dielectric strength of air (3 kV/mm)<sup>[16]</sup> is six  
15 times than that of argon (0.5 kV/mm),<sup>[17]</sup> and our data are consistent with an atmosphere of  
16 high dielectric strength favouring tribocharging. For tribocharging mechanism, as our recent  
17 work shows that charge carriers are anionic polymer fragments,<sup>[18]</sup> we suspect that  
18 triboelectrification between solid CO<sub>2</sub> and polymers is ascribed to materials transfer from  
19 polymers to CO<sub>2</sub> and will have potential guide to gas-solid fluidized reactors.<sup>[19]</sup>  
20 Our Faraday pail data show that for PDMS, PTFE and PVC samples in argon about 34%, 52%  
21 and 90% (respectively) of tribocharges have dissipated 20 s after the separation from a CO<sub>2</sub>  
22 surface (Fig. 3b). For these polymer samples a faster decay is observed in air, where about 85%,  
23 91% and 96% of the negative charges are lost over the same period of time (Fig. 3a). Charge  
24 dissipation, in both air and argon, is faster for PVC than for PTFE and PDMS (Fig. 3c), which  
25 is probably linked to the lower work function of the former.<sup>[18]</sup> We hypothesised that the

1 differences in charge magnitudes observed under argon and in the presence of atmospheric  
2 water could be due to the different abilities of these media to stabilise charge.<sup>[20]</sup> Under ambient  
3 conditions, polymers are known to harbor surface water layers, and charges can, potentially,  
4 be dissipated “laterally” through surface conductance. In contrast, under a dry and inert  
5 atmosphere, this mechanism of charge dissipation is likely to be inoperative or less efficient.

## 6 **Conclusion**

7 The conclusions of the present work are twofold. Firstly, solid CO<sub>2</sub> can be tentatively placed  
8 between PMMA and PVC in a triboelectric series. This is important, since this can guide the  
9 engineering and design of materials such to either maximise or minimise their static charging  
10 upon contact with solid CO<sub>2</sub>. For example, the Australian Standard concerning the  
11 manufacturing of CO<sub>2</sub> extinguishers (AS/NZS 1841.6:2007) states that “a discharge horn shall  
12 be constructed of electronically non-conductive material”. CO<sub>2</sub> extinguishers are primarily  
13 used on electrical fires, or on fires involving electrical equipment, hence the need of an  
14 insulating horn but here we have shown that not all insulators have the same tendency to build  
15 up static electricity after contact with dry ice. Secondly, we have shown that contact  
16 electrification between CO<sub>2</sub> and polymers is not just material-dependent, but also dependent  
17 on the environment: in atmosphere of high dielectric strength the density of surface charges  
18 generated upon contact is maximised. This work extends our growing understanding of static  
19 electricity and it may guide the development of the experimental platforms for the study of how  
20 charged groups can influence chemical bonding and reactivity, an area that is beginning to  
21 attract significant interest in chemical catalysis.<sup>[21]</sup>

## 22 **Experimental**

23 **Materials.** Redistilled solvents and Milli-Q<sup>TM</sup> water (>18 MΩ cm) were used for substrate  
24 cleaning. Samples of polytetrafluoroethylene (PTFE, from McMaster-Carr, part n. 8545K26),

1 poly(dimethylsiloxane) (PDMS, from McMaster-Carr, part n. 87315K65), polyvinyl chloride  
2 (PVC, from McMaster-Carr, part n. 87545K521), poly(methyl methacrylate) (PMMA, from  
3 McMaster-Carr, part n. 8536K141) nylon (nylon-66, part n. 514-607, RS Components  
4 Australia®) and glass (slide from Qorpak®) were cut to sheets of 2 × 2 cm and were  
5 approximately 0.3 cm thick. Solid CO<sub>2</sub> was purchased from BOC Australia.

6 **Methods.** Prior to being tribocharged, polymers were washed with water, methanol,  
7 dichloromethane and then dried under a flow of nitrogen gas. The charge on the polymer was  
8 measured using a Faraday cup connected to an electrometer (JCI 140 static monitor and JCI  
9 147 charge measurement units) operating on the 10<sup>-9</sup> Coulomb scale. Charging data are  
10 reported as charge-to-geometric area ratios. A solid timber wedge was used to hold plastic  
11 (nylon, PMMA, PVC, PTFE and PDMS) and glass sheets at 30° from the horizontal. A small  
12 sample of dry ice (generally 3.5 g, rod shaped) was rubbed against the inclined plane made  
13 by the plastic and glass samples by means of letting it slide, assisted by gravity, from top to  
14 bottom of the inclined plane (Fig. 1a). This operation of contacting and then separating the dry  
15 ice sample from the dielectric sheet was repeated a discrete number of times. After the last  
16 contact-separation cycle, the plastic or glass sample was transferred to the Faraday pail to  
17 measure the magnitude and sign of its tribocharging. The number of contact-separation cycles  
18 (with one cycle defined as one slide down the tilted plane) was varied between one and 50 and  
19 the time that elapsed between the last cycle and the charge measurement was generally between  
20 3 and 5 s. Experiments and charge measurements under argon atmosphere were conducted  
21 using a glove box (Innovative technology, PL-HE-2GB with PL-HE-GP1 inert gas purifier)  
22 with water and oxygen levels being less than 1 ppm.

### 23 **Conflicts of Interest**

24 The authors declare no conflicts of interest.

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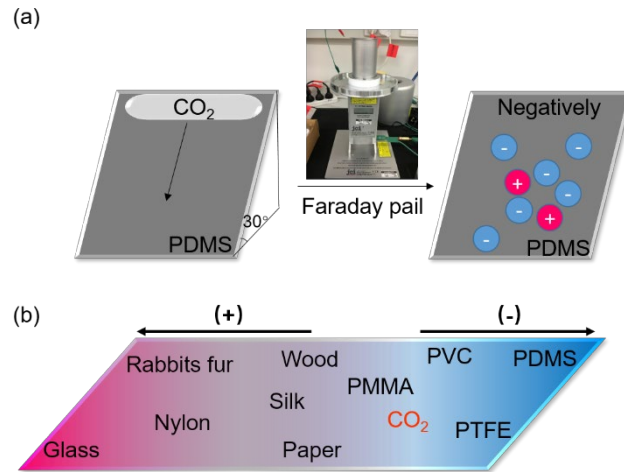
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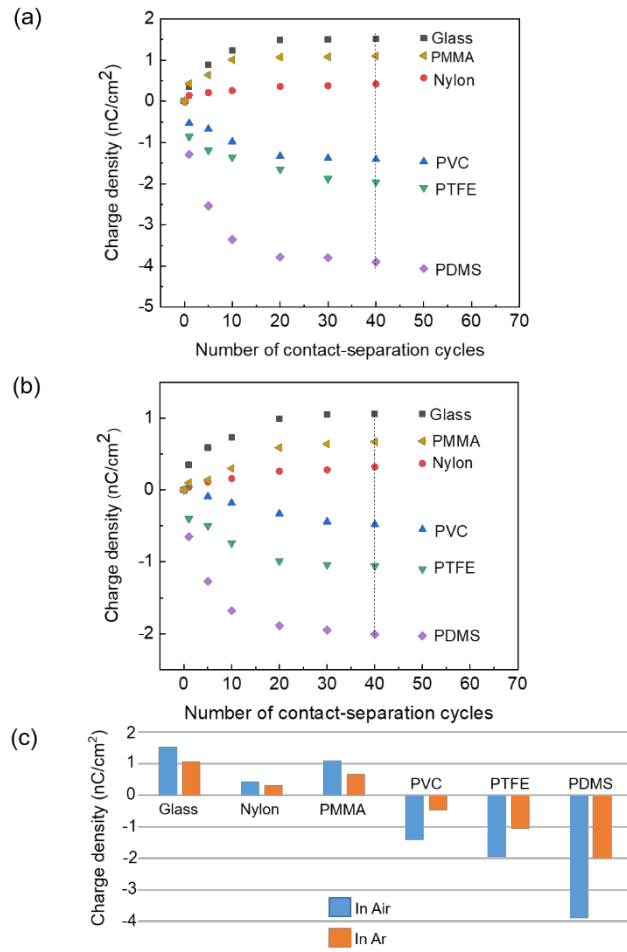
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**Fig. 1.** (a) Illustration of the experimental setup in which dry ice samples are rubbed (slid down) against a polymer surface. The amount and sign of the net charge gained by the plastic sample is measured by inserting it into a Faraday pail connected to a high-precision electrometer. (b) Relative position of various dielectric materials in a triboelectric series<sup>[22]</sup>: materials located toward the right (−) tend to acquire a net negative charge upon contact with materials located to their left (+). The tentative position of CO<sub>2</sub> in the series (red ink in (b)) is based on the Faraday pail data presented in Figs. 2 and 3.

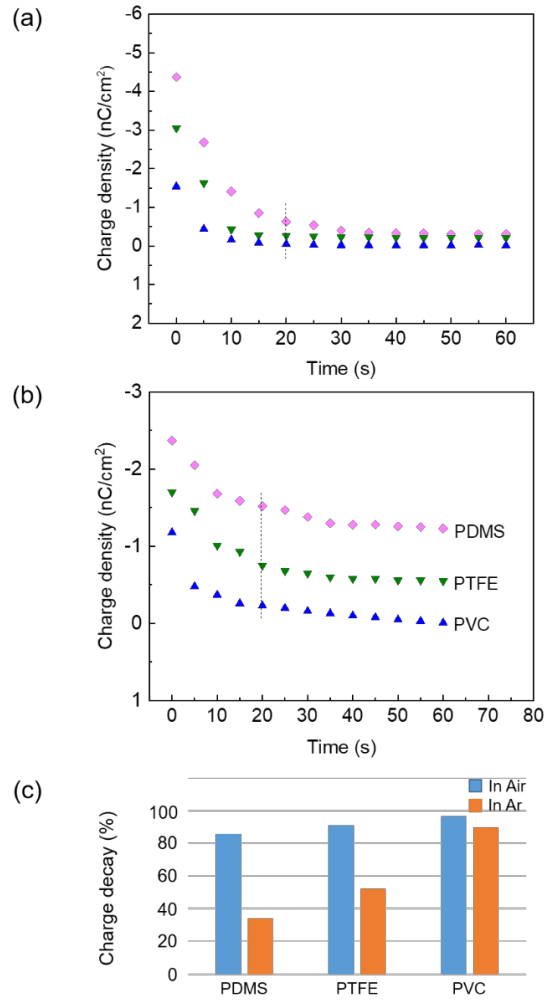
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**Fig. 2.** Tribocharging of polymer samples against dry ice. (a) Faraday pail data for samples charged by cyclically sliding solid CO<sub>2</sub> across an inclined surface. Data were acquired under ambient air: glass, nylon and PMMA samples gained a net positive charge, while PVC, PTFE and PDMS become negatively charged. (b) Tribocharging data for experiments performed under argon; for all the polymers their net charge is smaller in argon than in air. (c) Difference in the tribocharging – air vs argon – for samples that were subject to 40 contact-separation cycles.

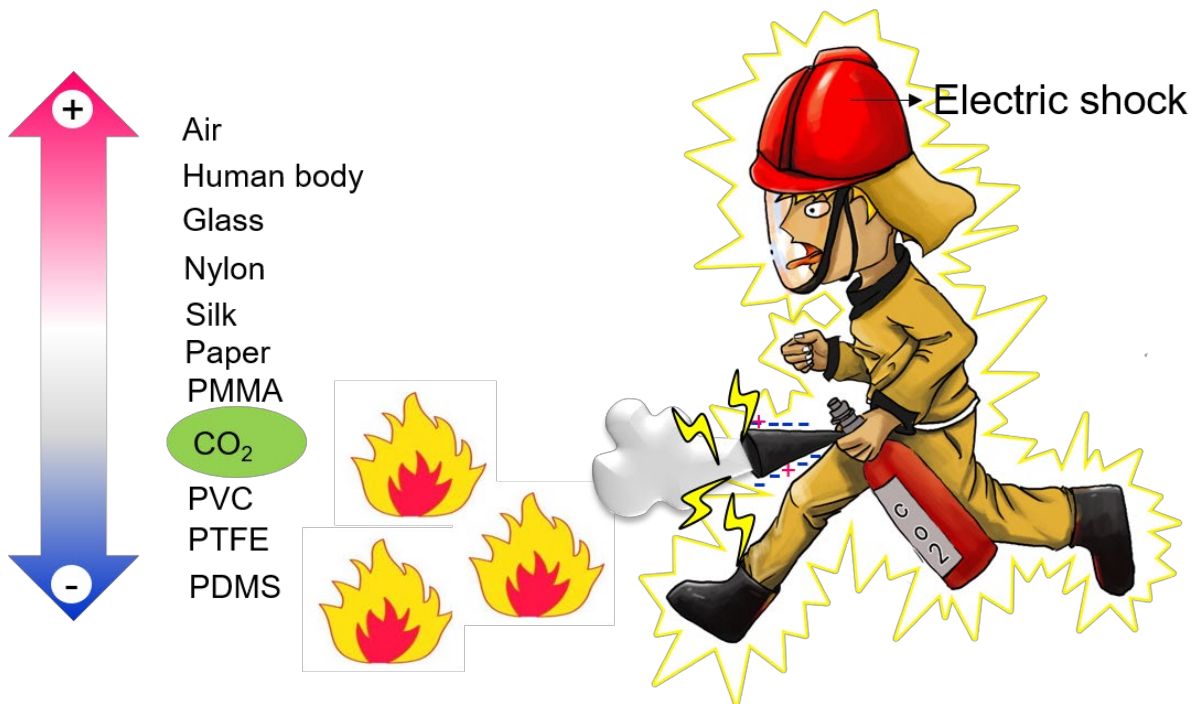
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**Fig. 3.** Decay in (a) air and (b) argon of the static charging (Faraday pail measurements) of tribocharged PDMS, PTFE and PVC samples against with CO<sub>2</sub>. In air, charge on samples about 85%, 91% and 96% of their tribocharges have dissipated after 20 s. For experiment in argon, the decay of samples are slower and these samples lose about 34%, 52% and 90% of their net charging over the same time scale. The faster charge decay in air is probably due to reaction with water molecules adsorbed on the polymer surface. For PVC samples the decay is more rapid than PTFE and PDMS both in air and argon, the faster charge decay in PVC is ascribed to its lower work function and larger electron affinity.<sup>[18]</sup>

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- 1 **TOC. Static electricity: where is dry ice in the triboelectric series?** Using Faraday pail measurements we show
- 2 that PDMS, PTFE and PVC samples acquire a negative charged when rubbed against dry ice, while PMMA, glass
- 3 and nylon surfaces become positive. We therefore suggest the position of dry ice CO<sub>2</sub> in the triboelectric series to
- 4 be close to that of materials with stable cations and unstable anions, possibly locating it between PMMA and PVC.