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Mass spectrometry of atmospheric-pressure ball plasmoids

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ABSTRACT

Ball lightning is a naturally occurring atmospheric event that has perplexed researchers for centuries, and there is to date no complete explanation (chemical, physical, or otherwise) as to why ball lightning behaves the way that it does. There has been considerable effort to try to both produce and measure the properties of ball lightning type discharges over recent years, and this collected work has begun to reveal some interesting physical and chemical phenomena. We are able to produce water-based plasma ball discharges using high-voltage equipment, and these self-contained plasmoids are considered to be similar to natural ball lightning. In this article we present the first mass spectrometric analysis of water-based ambient ball plasmoids. Using an extremely simple sampling technique, we were able to detect several chemical species within the interior of the plasmoid. Several molecules that are common to plasmas generated in air were observed in the mass spectra, such as $[NO_2]^+$ and $[NO_3]^+$. More interestingly, we observed the protonated water clusters $[(H_2O)_2H]^+$ and $[(H_2O)_3H]^+$, ammonia (NH_3) as a component of a copper cluster, and several anions. Furthermore, many species observed in the mass spectra are in the form of hydrated clusters.

1. Introduction

Ball lightning is a one-in-a-million [1] atmospheric phenomenon that is poorly understood due to its rarity and unpredictability. Eyewitness accounts across several centuries describe large balls of light moving across the sky for several seconds during thunderstorms, with some reports detailing powerful explosions occurring when the ball of light dissipates. Images and video recordings of ball lightning phenomena have been captured by amateurs and are readily available via an internet search, however it was only last year that the first scientific measurements and analysis of naturally-occurring ball lightning were reported [2]. Cen et al. set out to observe cloud-to-ground lightning strikes during a thunderstorm in China's Qinghai Plateau, and by a brilliant stroke of luck ball lighting was observed immediately after a cloud-to-ground lightning strike. Their observation site was 0.9 km from the site of the ball lightning, which had a reported lifetime of 1.64 s and a diameter of approximately 1.1 m. The ball lightning event was characterized using emission spectroscopy, and emission lines from components of soil (iron, silicon, calcium, nitrogen) were observed in the spectra [2].

There is some debate in the literature regarding plausible theories that explain the properties of ball lightning [3–8], and to date there is no concrete physical or chemical explanation as to how ball lightning is formed and how these spheres of plasma can last for an extended period of time without energy input from an external power source. Perhaps the most fascinating aspect of ball lightning is this extended lifetime. It is remarkable that at atmospheric pressure and temperature, self-sustaining plasmas can last for more than a second. Simulations which model upwards of 600 chemical processes that could occur in ambient plasma discharges show that most reactions within this type of plasma should be complete in a millisecond or less [9,10], however ball lightning seems to defy the current understanding of atmospheric-pressure plasmas. Given the complexity of the system in question, a true phenomenological explanation of the formation mechanism and lifetime of ball lightning will most likely be a combination of several different physical and chemical processes.

In order to truly answer the fundamental questions surrounding the long lifetime of ball lightning, it is essential to generate plasmas that are at the very least semi-analogous to natural ball lightning. Tesla was the first to observe a "fireball" type discharge [11], and efforts to reproduce his experiments have led to direct current (DC) electrical discharges that can produce plasmas similar to ball lightning. Traditionally, DC plasma generating apparatus produce arc, corona, glow, or dielectric barrier discharges between

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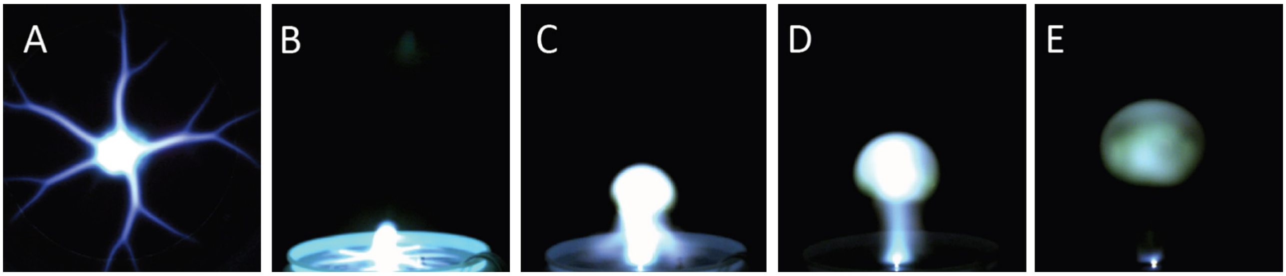

Fig. 1. Images of a plasmoid discharge from start to finish. (A and B) Pre-initiation phase, (C and D) buildup phase, (E) detachment phase. (B–E) were obtained from a single discharge via high-speed videography (Pixelink® PL-B&42U. (A) was obtained from a separate discharge under identical conditions, top–down camera setup.

two electrodes at atmospheric pressure [12]. These discharges are usually well behaved and are easily characterized with a variety of diagnostic techniques [13,14].

Additionally, ambient DC plasmas have been thoroughly characterized by mass spectrometry (MS) due to their use as ionization sources [15,16]. If the electrode configuration is such that it allows for the plasma to form and grow in one place, a free-floating and self-sustaining plasma can be produced. Since these self-contained plasmas last for an extended period of time with no external source of energy they are referred to as "plasmoids."

Using a water-based technique, Egorov and Stepanov were the first to produce a plasmoid discharge of this type in a laboratory [17], and several other groups have produced discharges similar to what they described [18–20]. To summarize this work, a bank of large capacitors was charged to several kV, and using high-voltage switches a short pulse of current was applied across two electrodes, one of which was fully submerged in a container full of water. The other electrode (the cathode in this case) was positioned such that just the tip slightly protruded from the surface of the water in the bucket. A plasmoid began to form, and buoyant forces generated from local heating of the ambient air around the tip of the cathode caused the plasmoid to rise upward and away from the tip of the cathode.

There are three distinct phases to this type of plasmoid formation (Fig. 1): the pre-initiation, buildup, and detachment phases [21]. First, current begins to flow from one electrode to the other, and "streamers" or "spider legs" begin to form and extend over the surface of the water rather than through the bulk electrolyte solution. In the center, above the cathode, a small ball of plasma begins to form. Next, the ball of plasma begins to grow in size and rise due to buoyant forces while still receiving continuous current from the cathode. Finally, when the capacitor has discharged a sufficient amount of energy, no additional plasma is formed, and a self-sustaining plasmoid remains for an extended period of time. In other words, the energy stored in the capacitor at the end of a discharge event is not sufficient to allow for additional plasmoid formation. Using our experimental setup, the detachment phase can last up to 200 ms, with an entire discharge event (pre-initiation, buildup, and detachment phases) lasting up to 400 ms.

Versteegh et al. have provided the most detailed insight into the underlying chemistry and physics of water-based plasmoid discharges using emission spectroscopy and probe measurements [19]. In this work, emission lines from H, Na(I), Ca(I), Ca(II), Cu(I), OH radical, and CaOH were observed in the ultraviolet/visible. Along with qualitative identification of chemical species present within the plasmoid, these specific emission lines reveal that the electron temperature of the discharge cannot be very high (< 1 eV), otherwise emission lines from more highly energetic atoms and molecules would have been observed. Furthermore, intensity ratios of a pair of Ca(I) lines were used to estimate the electron temperature to be 5000 K (0.43 eV) at the time of the initial pulse and 2500 K (0.22 eV) after 225 ms. Further investigation into the rotational temperature of the hydroxyl radical showed a non-thermal distribution of temperatures, leading to the hypothesis that the products of water dissociation contain the necessary energy to sustain visible emission for an extended period of time. Additionally, Stark broadening of Cu(I) lines in the pre-initiation phase of the discharge was used to estimate electron densities in the plasma to be on the order of 10^{16} cm^{-3} at 10 ms and 10^{14} cm^{-3} at 75 ms.

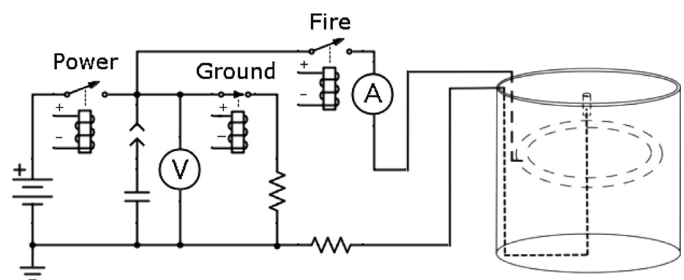

Fig. 2. Circuit diagram of plasmoid generating apparatus. *V* is a voltage divider across which voltage measurements are taken, *A* is a Hall effect current sensor.

2. Experimental

2.1. Plasmoid generator

The equipment that we use in our laboratory has been described previously [22], but some of the key components will be highlighted here for the sake of clarity and understanding. Our power supply can produce up to ±10 kV DC and wiring our capacitors in parallel can generate greater than mF capacitances, thereby generating several kJ of energy. A schematic of the hardware and circuitry is shown in Fig. 2. The following description of the experimental setup was the same for every trial unless specifically noted otherwise. Voltage and capacitance parameters were chosen in part because of safety concerns, but discharges under these conditions are typically well behaved. It is also important to mention that, much like natural lightning strikes, no two plasmoid discharges are exactly alike. In other words, under identical conditions the lifetime, shape, rise velocity, and electrical behavior of plasmoid discharges can vary.

An 873 μF parallel-plate, oil-filled capacitor (Maxwell) was charged to +4000 V DC using a Glassman EK Series high-voltage power supply. The current being transferred from the capacitor to the plasmoid generator and eventually to ground was regulated by a series of three Ross Engineering high-voltage E Series relays. An Arduino® Uno microcontroller controlled the timing of these relays and recorded current and voltage measurements. Current pulses were applied across two electrodes, one of which was fully submerged in a very dilute solution of hydrochloric acid in water, a more detailed description of which is given in the next section. One full plasmoid discharge will also be referred to as a "shot" at other points in this article.