Tracking Down the Origin of Arc Plasma Science.

I. Early Pulsed and Oscillating Discharges

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ABSTRACT

The early development of arc plasma physics is closely related to the development of suitable sources of electrical energy. The harnessing of electrostatic charge in Leyden jars (early capacitors) enabled the controlled production of sparks and pulsed arcs. A contemporary introduction to sparks and arcs gives the foundation for critically assessing the early development, when observation and discovery of phenomena were still far from understanding. The modern development of discharge physics can be traced back to the 18th century. Notably, and generally unnoticed by the scientific community until today, Joseph Priestley observed cathode erosion and film deposition of cathode material as early as 1766.

"…As quick advances seem to have been made of late years, as in many equal period of time past whatever. Nay, it appears to me, that the progress is really accelerated."

Joseph Priestley, *History and Present State of Electricity*, 1767

I. INTRODUCTION

The early development of plasma physics, or more narrowly discharge physics, is intimately related to the development of suitable sources of electrical energy. As it will become obvious, each major advancement of generation and storage of electrical energy enabled the discovery of new phenomena, though, there was usually a large gap between initial observation and understanding.

It can be assumed that discharges due the frictional charge-up have been observed by the Greek philosophers. This knowledge was re-discovered and greatly expanded in the 17^{th} and 18^{th} century. The development of electricity has been the subject of numerous historical studies (e.g., [1-8]) and therefore there is no need to repeat the findings of these studies here. Instead, the historical work can be used to illuminate the development from a different perspective, namely, the discovery, development, understanding, control, and application of discharge plasmas. To add personal flavor and to narrow the subject, I chose to especially focus on arc plasmas at the beginning of the modern scientific area, and especially on cold-cathode (cathodic) arcs. Arcs can be produced in a pulsed or continuous mode. Because there have been two distinct developments of electrical energy sources, the capacitor and the electrochemical battery, the distinction of pulsed and oscillating and continuous arc discharges appeared quite natural.

II. THE STARTING POINT: A MODERN VIEW ON ARC DISCHARGES

The arc discharge can be defined as an electrical discharge of relatively high current at relatively low burning voltage characterized by a collective mechanism of electron emission from the cathode. The qualification "relatively" has to be understood with respect to other forms of electrical discharges. For orientation one may say that the current is generally greater than 1 Ampere and the burning voltage is less than 100 Volt. The crucial "ingredient" to the definition is the "collective mechanism" of electron emission, as opposed to individual mechanisms. Individual mechanisms are photo emission and secondary electron emission by particle (ion, atom, electron) impact. Collective electron emission includes thermionic emission, field emission, thermo-field emission, and explosive emission. While individual mechanisms are based on highly localized disturbance of the potential barrier, collective mechanisms are based on globally effecting the whole electron distribution function (heat) and potential barrier (electric field).

The fact that several mechanisms could lead to collective electron emission leads to the existence of several modes of cathode operation. For example, arc discharges on cathodes that are globally cold (i.e. near room temperature), are characterized by non-stationary cathode spots. Cathodes spots are locations of greatly enhanced local power density, enabling operation of the arc through sufficient emission of electrons and cathode material, i.e. production of charge carriers securing current between electrodes. The initially solid cathode material is transformed into the plasma state; this mode of operation is known as the cathodic arc mode. The cathodic arc mode occurs at any gas pressure but has been extensively studied in vacuum, where is it also known as the vacuum arc mode. The high power density at cathode spots leads to melting of the zone between dense plasma and solid cathode, and the formation of microscopic "droplets" or "macroparticles" is characteristic for this mode.

If the cathode becomes sufficiently hot, it can deliver electrons needed for the discharge via thermionic emission, and the cathode switches into the thermionic mode. This mode is characterized by a more-or-less stable and stationary broad cathode spot or hot zone of much lower current density than the current density of the non-stationary cathodic arc mode.

Regardless of the arc mode, a plasma is formed between anode and cathode, consisting of electrons and ions of the background gas and electrode material. In case of a cathodic arc, most ions originate from the cathode material. In some special cases, the anode can be very hot and evaporates, most ions may originate from the anode material (anodic arcs).

Arc discharges can be made in short or long pulses, or operated continuously (DC) if the arc power supply has the capability of supplying high current at voltages exceeding the arc burning voltage. At the initial, transient phase of an arc discharge, the voltage between the electrodes is much higher than the voltage at later times or at steady-state conditions. This very early phase is the *spark* phase of the arc discharge (Fig. 1). For very short electrode distances (less than 1 mm), the spark phase can be as short as a few nanoseconds; its duration is determined by the time the electrode material needs to bridge the gap distance [9]. For large gap distances, the duration of the transient spark phase depends on the electrical circuit, pressure, and other parameters, and it can be as long as some 10 μs.

With this background knowledge we may now go back more than two hundred years and try to track down the origin of arc plasma science.

III. DISCHARGES BASED ON FRICTIONAL ELECTRICITY

One could go straight to the time of the first capacitors and describe discharge plasmas but the development appears much more logical when put in the context of many steps of development preceding "true" arc discharges.

In practically all histories of electricity, the modern area is generally considered to have emerged with a book publication [10] by William Gilbert (1544-1603) in the year 1600, in which Gilbert summarized the knowledge about electricity and magnetism of his time. Usually, Otto von Guericke's (1602-1686), mayor of Magdeburg in Germany, is mentioned as the next important experimenter in static and friction-induced electricity. Guericke is best known for his 1650 invention of the vacuum pump and his famous half-sphere experiments. He was also the inventor of the first static electric machine, the earliest record goes back to 1663. He found that a sulfur globe "the size of a child's head" is charged by turning it and rubbing it with a dry hand. The charged globe first attracted, and after contact repelled, light objects such as feathers. It is said in some sources of literature that the sphere was able to generate sparks but Guericke did not describe his experiments in electrical terms. In fact, Guericke seemed to have not recognized the electric nature of his experiments (p.xvi, [11]).

In 1675, the French astronomer Jean Picard (1620-1682) studied air pressure at different elevations using a mercury barometer, which was invented by Evangelista Torricelli (1608-1647) of Italy in 1643. When it was dark Picard noticed a glow in the "empty" glass tube above the mercury column, which was strongest when the mercury was moving up and down in the tube.

Francis Hauksbee the Elder (c.1666-1713), Chief Curator of the Royal Society in London, performed experiments on capillary phenomena, propagation of sound in compressed and rarefied air, on freezing of water, specific gravity and refractive index. He was the first who extensively experimented with static electricity and air pumps and who could reproducibly generate what we would call today discharge plasma. He had knowledge about Picard's observations as well as Otto von Guericke's sulfur globe experiments. In October of 1705, Hauksbee tried rubbing substances other than mercury inside evacuated jars. He eventually decided to see what would happen if he simply rubbed an evacuated glass globe. He built a machine in which a glass sphere could be rapidly spun on an axle by a "great wheel". The axle was hollow and connected to the globe through a valve and on the other end to a vacuum pump. A glow appeared when he spun the sphere in the dark, rubbing it with his bare hand (Fig. 2).

At about the same time, in 1708, Samuel Wall (?-1710(?); not William Wall, as sometimes mentioned), a London physician and "promoter of the spagyric art," suspected a connection between frictional electricity and lightning:

> *"I found by gently rubbing a well polished piece of amber with my hand, in the dark, that is produced a light: whereupon I got a pretty large piece of amber,…being very dry, it afforded a considerable light. ….upon drawing the piece of amber swiftly through the woollen cloth, and squeezing it pretty hard with my hand, a prodigious number of little cracklings were heard, and every one of these produced a little flash of light. …This light and crackling seems, in some degree, to represent thunder and lightning."* ([12]; cf. also [1], vol. I, p. 14, and [8] p.236)

Two generations later, around 1752, this suspicion was convincingly confirmed by kite and lightning rod experiments proposed by Benjamin Franklin – but much happened before that.

Static electricity and discharge phenomena became a subject of science as well as amusement for the growing class of "enlightened" people in the 18th century. Stephen Gray (1695-1736, also spelled Grey), who should become famous far beyond London, introduced a popular experiment suspending a boy using insulating strings. The boy could be electrified (i.e. charged by contact with a frictional machine) and was able to electrostatically attract light objects. On the other side of the channel, in France of 1733, Charles-François de Cisternay du Fay (1698-1739) suspended himself and other people from the ceiling of a room with silk lines. He demonstrated effects of electrification through *"pricking shoots attended with a crackling noise"* when *"another person approached him, and brought his hand within an inch, or thereabouts, of his face, legs, hands, or cloths."* ([1], vol. I, p. 58). Du Fay is best known for his discovery of two kinds of electricity. Stephen Gray experimented with a large number of materials and introduced the distinction between conductors and insulators ("electrics"). In 1734 he described a "pencil of electric light," (p.71 [1]) today known as corona discharge. He also experimented with water in charged glass tubes and came very close to inventing the capacitor (see below), in fact, he anticipated it:

> *"And although these effects are at present but in minimis, it is probable, in time, there may be found out a way to collect a greater quantity of the electric fire, and consequently to increase the force of that power, which...seems to be of the same nature with that of thunder and lightning."* [13]

In the desire to increase the effects of electricity, a number of improvements to frictional machines were made. For example, in 1734, Johann Heinrich Winckler (1703-1770), a professor of languages at the university in Leipzig, Germany, installed a cushion in his frictional machine and increased the rotational speed of the glass globe to 680 turns per minute (p.89 [1]). Many more details about frictional machines can be found in the literature [14]. Despite these efforts, the amount of charge available for experiments was limited, and the effects were modest until storage of charge in a capacitor was invented.

IV. THE CAPACITOR AS AN ENERGY SOURCE FOR SPARKS AND PULSED ARC DISCHARGES

A seminal event in the early history of discharges was the invention of the capacitor. A detailed account of the history is far beyond the scope here, but a summary could read as follows. The invention was made independently, and practically simultaneously, by Ewald Jürgen von Kleist (1715-1759), dean of the cathedral at Cammin in Pomerania (Germany), and by Andreas Cunaeus (1712-1788), a frequent visitor to professor Pieter van Musschenbroek (1692-1761) at the University of Leiden (spelled Leyden in the 18th century) in the Netherlands. Von Kleist reports in a letter, dated November 4th, 1745, to Johannes Nathaniel Lieberkühn (1711-1756), member of the Academy of Sciences in Berlin:

> *"When a nail or thick wire etc. is put into a small apothecary's phial and electrified, remarkable effects follow; the phial must be well dried and warm. If a little mercury or a few drops of spirit of wine were put into it, the experiment succeeds better. As soon as the phial is removed from the electrifying machine, it throws a pencil of flame, and, with this little burning machine in my hand, I have been able to walk more than 60 steps in the illuminated room."* ([15] p.178)

About at the same time, Musschenbroek tried to draw "electrical fire" from glass vessels filled with water, an idea proposed by Georg Matthias Bose (1710-1761), professor at the university of Wittenberg, Germany. Electrification of water was previously described by Andreas Gordon (1712-1751), a Scottish-born professor in Erfurt, Germany [16]. Cunaeous, a layer who occasionally assisted Musschenbroek, tried to arrange Bose's experiment by himself, holding the bottle in one hand and drawing the spark with the other, giving himself a terrible shock. He reported this to Musschenbroek and his colleague Jean Nicolas Sébastien Allamand (1713-1787). Musschenbroek repeated the experiment and described it as follows in a letter to René Antoine Ferchault de Réaumur (1783-1757), correspondent at the Paris Academy:

> *"…I would like to tell you about a new terrible experiment, which I advise you never to try your self, nor would I, who have experienced it and survived by the grace of God, do it again for all the kingdom of France. I was engaged in displaying the powers of electricity. An iron tube AB was suspended from blue-silk lines; a globe, rapidly spun and rubbed, was located near A, and communicated its electrical power to AB. From a point near the other end B a brass wire hung, in my right hand I held the globe D, partly filled with water, into which the wire dipped, with my left hand E I tried to draw the snapping sparks that jump from the iron tube to the finger, thereupon my right hand F was struck with such force that my hole body quivered just like someone hit by lightning…."* [17]

The news of the greatly enhanced power of electricity spread quickly and the conditions for the correct operation were determined, allowing others to improved Leyden jars, as they were named. Most noticeably, Sir William Watson (1715-1787) and Dr. John Bevis (1693-1771) improved the jar by coating the inside and outside with tin foil. The Leyden jar became the standard device for storing electric energy in the second half of the 18th century.

The size and storage capacity was constantly increased. John Cuthbertson (1743-1821), an English instrument maker who was living in Amsterdam from 1768 to circa 1796, built perhaps the most powerful batteries of Leyden jars and electrostatic charge generators. The term "battery" was used in the 18th century to a number of capacitors connected electrically in parallel (Fig. 3), while a "battery" in the 19th century and later implied a number of electrochemical cells electrically in series. Cuthbertson's largest and most famous frictional generator was made for the Teyler's Foundation in Haarlem, with glass discs 1.65 m in diameter, coupled to one hundred Leyden jars. The jars were connected in parallel by being set on lead foil, with brass rods connecting their central terminals [18]. This system could produce a powerful spark bridging about 60 cm of electrode distance in air. In the 18th century, the energy of electrical machines was rated by the amount of standard iron wire that the machine could melt. This particularly enormous machine could melt 16.6 m of wire, 169 μm (1/150 inch) in diameter. Bern Dibner, a distinguished historian, found out that "In 1789, Cuthbertson completed another battery of 25 giant Leyden jars each 50 cm (20 inches) high. All the inner leads were connected through brass rods to a large raised central sphere and this was topped by a Henley quadrant electrometer [named after William Henley (?-1779)]. There was an additional battery consisting of nine units of 15 jars each, forming an assembly of 135 jars, connected in multiple and providing a condenser surface of 103 square feet (9.57 m^2)." [14].

Quickly after the discovery of the charge storage capabilities of the Leyden jar, it was recognized that capacity increases with larger area and thinner glass wall. For example, Benjamin Wilson (1721-1788), a leading English "electrician" (as they called themselves), writes on October 6, 1746, in a letter to John Smeaton (1724-1792) that "*the electrical matter in the Leyden bottle…was always in proportion to the thinness of the glass,* [and] *the surface* [area] *of the glass….*" ([1] p.119) Ignoring these findings, 18th century publications usually give the surface area but are silent about the glass thickness. Measurements on historic Leyden jars show that the glass thickness of most Leyden jars was 1-3 mm depending on the size of the jar. The wall thickness was thicker on the bottom and around the neck because these areas must withstand stress. Some of the less advanced Leyden jars were made from wine bottles and have thus greater wall thickness with less capacity [18]. For the purpose of an estimate, neglecting edge and curvature effects, one may use the formula

$$C = \varepsilon\varepsilon_0 \frac{A}{d} \qquad (1)$$

for the capacity, where $\varepsilon \approx 4$ is the relative permittivity of glass, ε_0 is the permittivity of free space, A and d are the area and distance of the capacitor electrodes separated by the glass. Cuthbertson's very large battery of almost 10 m^2 had therefor a capacity between 0.1 μF and 0.4 μF. The stored energy

$$E_C = \frac{1}{2} C V^2 \qquad (2)$$

is therefore between 125 J and 500 J if a charging voltage of 50 kV is assumed! For comparison, 40 J of stored electrical energy are considered dangerous by today's safety standards [19].

Returning to the earlier, much smaller Leyden jars of 1746, Watson experienced the stored energy when short-circuiting a jar with a wire: "the charged phial will explode with equal violence, if the hoop of the wire be bent, so as to come near the coating of the phial…" ([1] p.117). Figure 4 shows a similar experiment as described by the still young Alessandro Volta. With today's knowledge we can estimate that the discharge current must have been high, the peak limited by the inductance of the circuit, and decaying exponentially or, more likely, oscillating in the LC-circuit. Using the above formula one can estimate $C \approx 1\,\mathrm{nF}$ and $E_C \approx 1\,\mathrm{J}$ for early Leyden jars. The stored energy is still clearly below the hazardous level, and some of the early reports on "terrible" experiences appear exaggerated but understandable because the physiological effects were not anticipated.

In France, Jean Antoine Nollet (1700-1770), also known as Abbé Nollet, one of the most famous and influential electricians, also experimented with Leyden jars, investigating the effects of electric shocks on animals. Just months after Musschenbroeck's letter, he charged his jars to the limits of the dielectric strength of the glass finding "bursting of the glass vessels by electric explosions. They [the glass vessels] were pierced with round holes, three of four lines in diameter" (p. 126 [1]) (a line is the 12th part of an inch, or 2.1 mm). Today's glass has breakdown strength of about 45 kV/mm. It can be assumed that glass of the time contained more defects, which actually determine the breakdown strength. Timonthy Lane (1733/34-1807), instrument maker at Knightsbridge near London, found that

> *"The quantity of electricity necessary to burst the phial, appears to vary more in proportion to its thickness than its size; many phils of various sizes may be broken at 10 of the electrometer, while others, nearly of thr same size, remain sound, with a stroke at 30, or even more. I generally found green glass more difficult to break than white."* [20]

A breakdown field strength of 10-20 kV/mm may be a good estimate, leading to 20-60 kV as the maximum charging voltage of early Leyden jars.

Shortly after the discovery of the Leyden jar, many electricians used the discovery to perform experiments on humans, animals, and the nature of electricity itself. Among them, besides Musschenbroeck, Wilson, and Watson, were John Canton (1712-1772), Lord Charles Cavendish (son of the second Duke of Devonshire; his oldest son was the famous Henry Cavendish, 1731-1810) and Benjamin Franklin (1706-1790). Franklin became the first electrical experimenter to develop a certain level of understanding based on observations that electricity involves positive and negative charges. Watson went back to Hauksbee's experiment (Fig. 2) but incorporated the newly invented Leyden phial to enhance the light effects seen in low-pressure gas vessels.

> *"He* [Watson] *made this vacuum part of a circuit necessary to make the discharge of a phial; and, at the instant of the explosion, there was seen a mass of very bright embodied fire, jumping from one of the brass plates in the tube to the other."* (*[1]* vol. I p.349)

Most likely, no significant resistance was in the circuit, and thus the discharge appears to have transitioned into a high-current discharge with explosive emission at the cathode, such as one would find in a short pulsed arc discharge. The *very bright embodied fire, jumping from one of the brass plates* may refer to incandescently glowing macroparticles. Other researchers, depending on their circuit and setup, appear to have observed variations of glow-discharges rather than arcs and sparks. In 1759 however, when Wilson repeated experiments "first contrived by Lord Charles Cavendish," he observed a "singular appearance of light upon one of the surfaces of the quicksilver," ([1] vol. I, p. 355). The quicksilver (mercury) was part of the evacuation scheme, and it is not clear, but possible, that Wilson was referring to a cathode spot on mercury.

V. PRIESTLEY'S ORIGINAL EXPERIMENTS – THE DISCOVERY OF CATHODE EROSION AND CATHODIC ARC DEPOSITION

Joseph Priestley (1733-1804), an English theologian and chemist, is best known for the identification of ammonia, nitrous oxide and oxygen [21] (although oxygen was also isolated, at least two years prior to Priestley, by the Swedish chemist Carol Wilhelm Scheele (1742-1786) [22]). The young Priestley became interested in electricity in the early 1760s and he collected all information on electricity accessible to him, and even repeated all of the important electrical experiments he was going to describe. Supported by Richard Rice, John Canton (1712-1772), William Watson (1715-1787) and Benjamin Franklin (1706-1790), all leading electricians of the time, Priestley wrote *The History and Present State of Electricit*y [1], which became the most comprehensive textbook on electricity of the time. It was standard for at least a generation of scientists and remained influential for the rest of the 18th century [11]. The first edition appeared in 1767 in London; translations into French [23] and German [24] became available soon after. The third edition of 1775 [1] was reprinted in 1966 with a detailed introduction by Schofield [11]).

Priestley's life and work is well documented [25, 26], and therefore I can quickly proceeded to his original contributions to discharge physics. Having completed his historical "chore," Priestley went on performing his own experiments on electrical phenomena. He included some of them in later editions of his *History* as "original experiments." Most importantly for the current historical study, some of these original experiments contain a number of first observations regarding arc discharges. Priestley discovered erosion craters left by cathode spots:

> *"June the 13th, 1766. After discharging a battery, of about forty square feet, with a smooth brass knob, I accidentally observed upon it a pretty large circular spot, the center of which seemed to be superficially melted…after an interruption of melted places, there was an intrie and exact circle of shining dots, consisting of places superficially melted, like those at the center, Plate 1, fig.5, No.1"* (here Fig. 5).
>
> *June the 14th. I took the spot upon smooth pieces of lead and silver. It was, in both cases, like that on the brass knob, only the silver consisted of dots disposed with the utmost exactness, like radii from the center of the circle, each or which terminated a little short of the external circle. Examining the spots with a microscope, both the shining dots that formed the central spot, and those which formed the external circle, appeared evidently to consist of cavities, resembling those on the moon, as they appear through a telescope, the edges projecting shadows into them, when they were held in the sun."* ([27], pp. 261, 262)

The formation of circles of craters may be associated with damped oscillations of the electrical circuit. Figure 6 shows similar "cavities, resembling those on the moon," which are images of erosion craters of cathodic arcs taken by a modern scanning electron microscope. Priestley even found that the size of erosion craters depend on the electrode material:

> *"I took the circular spot upon polished pieces of several metals, with the charge of the same battery, and observed that the cavities in them were some of them deeper than others, as I thought, in the following order, beginning with the deepest, tin, lead, brass, gold, steel, iron,*

copper, silver…The semi-metals bismuth and zink received the same impression as the proper metals; being melted about as much as iron." [27]

Today we know that a higher discharge current causes the number of arc spots operating simultaneously to increase rather than a change in the character of individual spots. The number of spots, or the current per spot, also depends on the material and its surface conditions. Priestley observes:

"When the battery was charged very high, the central spot was the most irregular, many of the dots which composed it spreading into the outer circle, and some dots appearing beyond the outer circle…I imagined that...two or more concentric circles might be produced, if a greater quantity of coated glass was used, or perhaps if the explosion was received upon metals that were more easily fused than brass…upon tin, I first observed a second outer circle…it consisted of very fine points hardly visible, except when held in an advantageous light…(Plate I, fig. 5, No. 2)" [27], cf. Fig. 5.

Formation of arc craters is associated with formation of macroparticles. Referring to his experiment with a brass electrode, Priestley continues [27]:

"Beyond this central spot was a circle of black dust, which was easily wiped off." Using gold, "there were…hollow bubbles of the metal, which must have been raised when it was in a state of fusion. These looked very beautiful when examined with a microscope in the sun, and where easily distinguished from the cavities…The hole progress seems to have been first a fusion, then an attraction of the liquid metal, which help to form the bubbles; and lastly the bursting of the bubbles, which left the cavities."

He investigated the nature of the black dust from brass in another contribution [28]. He discharged a bank of parallel capacitors, a "battery of thirty-two square feet," through a brass chain.

"I had before observed that the electric sparks betwixt each link to be most intensely bright, so as, sometimes, to make the whole chain appear like one flame in the dark; but the appearance of the chain in the instant of the shock, as it hung freely in the air, was exceedingly beautiful; the sparks being largest and brightest at the bottom, and smaller by degrees, towards the top, where they were scarcely visible; the weight of the lower links having brought them so much nearer together." ([28] pp.281-282)

The electrical contacts between the links for the brass chain were insufficient to carry the high short-circuit current, and thus short arcs in air formed – today a well-known phenomenon on electrical contacts of switches. That weight pulling on the chain would improve the electrical contacts between the chain's links was not new, in fact, in his *History* (but not in the *Original Experiments*), Priestley refers to a letter of 1746, written by Wilson to Benjamin Hoadley (1706-1756),

> *"When he* [Wilson] *made the discharge with one wire only, he found the resistance to be less than when a chain was used…. He caused the chain to be stretched with a weight, that the links might be brought nearer in contact, and the event was the same as when a single wire had been used."* ([1] p.120)

Furthermore, also Watson, in 1747, made

> *"…use of wires, in preference to chains"* because *"the electricity conducted by chains was not so strong as that conducted by wires. This was occasioned by the junctures of the links not being sufficiently close, as appeared by the snapping and slashing at every juncture…"* (*[1]* p.132).

The use of wires versus chains was also mentioned by Lane:

> *"A wire in general is better than a chain, unless the chain is held very tight;…the electric fluid will be lost in passing from link to link of the chain."* ([20] p.454)

Using white paper on and under the brass chain, Priestley tried to determine the origin, composition, and amount of material eroded from each link by the passage of the electric fluid:

> *"To ascertain whether this appearance depend upon the discontinuity of the metallic circuit, on the 13th of the same month* [June 1766]*, I stretched the chain with a considerable weight and found the paper, on which it lay as the shock passed through it, hardly marked at all. Finding that it depend upon the discontinuity, I laid the chain upon white paper, making each extremity fast with pins struck through the links…September the 18th* [1766]. *Observing that a pretty considerable quantity of black matter was left upon the paper, on every discharge with the same chain; I imagined it must have lost weight by the operation…I found it had lost exactly half a grain of its weight."* ([28] pp. 278-279)

A grain is the smallest unit of the English weight system, equal to 65 mg. One could make a quick estimate about the erosion. From Fig. 4 of Plate I we know that his chain had about 24 links. In the average, each link lost about 1.35 mg. Assuming a typical erosion rate of 100 μg/As, the total charge that caused the erosion per link was about 13.5 As. That could be compared to the charge stored in the capacitor. The Leyden jar battery had a total area of 32 ft^2 = 2.97 m^2. Priestley did not bother to give the glass thickness (although he earlier quoted Watson saying that "the experiment succeeded best when the phial…was of the thinnest glass" [1] p.111). If we assume again a typical thickness of 1-2 mm, the capacity was 50-100 nF, much too small to store the above-estimated charge at a reasonable voltage. The solution may be related to the oscillating nature of the discharge current. The inductance of the circuit and the capacitance of the Leyden jars formed an LC-oscillator, and the charge stored in the Leyden jars passed through the contacts many times, eroding material from both sides of the link contacts with every oscillation until energy dissipation stopped the oscillation.

Since the discharge occurred in air, metal ions upon condensation on a surface, as well as the hot macroparticles, must have reacted readily with the oxygen and formed an oxide. Cathodic arc deposition can be used to deposit oxides such as black copper oxide [29], and it is safe to assume that the "black dust" from brass contained this oxide. Priestley's description agrees with this supposition:

> *"*[The black dust] *was so extremely light as to rise like a cloud in the air, so as sometimes to be visible near the top of the room; I concluded that it could not be the metal itself, but probably the calx* [oxide]*, or the calx and phlogiston, in another kind of union than that which constitutes the metal; and that the electric explosion reduced metals to their constituent principles as effectually as any operation by fire do it, and in much less time. I was confirmed in this opinion by finding…that this black dust collected from a brass chain would not conduct electricity."* ([28] p. 289)

One of the "Original Experiments" [28] contains also a record on what we call today cathodic arc coating:

> *"I next laid the chain upon a piece of glass;…the glass was marked in the most beautiful manner, wherever the chain had touched it; every spot the width and colour of the link. The metal might be scraped off the glass at the outside of the marks; but in the middle part it was forced within the*

pores of the glass; at least nothing I could do would force it off. On the outside of the metallic tinge was the black dust, which was easily wiped off." ([28] p.285)

Remarkably, one of the advantages of cathodic arc coating is superior adhesion due to the energetic condensation of the metal plasma on the substrate, and this feature has been noticed even at this early stage. In recent years, cathodic arc coating of metals and metal oxides on glass is considered an "emerging technology." Priestley did not only use brass on glass:

"I have since given the same tinge to glass with a silver chain, and small pieces of other metals" ([28] p.285).

He continued the deposition and observed that the coatings show interference colors. Since his experiments were done in air, a freshly deposited metal film tends to oxidize and form a more or less transparent compound. He correctly associates his observations with Sir Isaac Newton's discovery

"that the color of bodies depends upon the thickness of the fine plates which compose their surfaces" ([30] p. 329).

"Having occation to take a great number of explosions,…I observed that a piece of brass, through which they were transmitted, was not only melted, and marked with a circle by a fusion round the central spot, but likewise tinged beyond the circular with a greenish colour, which I could not easily wipe out with my finger. …I continued the explosions till, examining with a microscope, I plainly perceived all the prismatic colours, in the order of the rainbow." ([30] pp. 330-331)

Today, a straightforward approach to improve uniformity of coatings is to increase the distance between the arc plasma source and the substrate. Greater distance allows the plasma to expand, increasing the coated area, improving film uniformity but reducing deposition rate. The idea is not new, as one can see from the following:

"1. When a pointed body is fixed opposite to a plain surface, the nearer it is placed, the sooner the colours appear, the closer do they succeed one another, and the less space they occupy. It seems, however, that when the point is at such distance that the electric matter has room to expand, and form as large a circular spot as the battery will admit, this coloured space is as large as it is capable of being made; but still the colors appear later, in proportion to the distance beyond that. …2. The more accutely pointed is the wire, from which the electric fire issues, or at which it

enters, the greater is the number of [interference] *rings. A blunt point makes the rings larger but fewer…5. All the colours make their first appearance about the edge of the circular spot. More explosions make them expand towards the extremity of the space first marked out; while others succeed in their places; till, after thirty of forty explosions, three distinct rings appear, each consisting of all colours.”* ([30] pp. 331-333)

VI. EPILOG TO PART I

The limitation of energy storage in batteries of Leyden jars allowed only pulsed and oscillating discharges to exist – no continuous discharge was yet possible. Therefore, cathodes could not heat up to operate in the thermionic mode, and early discharges utilize electrode emission mechanisms characteristic for globally cold cathodes. As a consequence, these discharges show characteristics today associated with cathodic arc discharges: explosive emission processes, formation of erosion craters, macroparticles, and well-adhering coatings on surfaces placed in the plasma stream.

Because Priestley's "original experiments" were included in his widely distributed *History*, electricians of the 18th century were well aware of them, however, no practical application could be derived at that time. His observations remained a laboratory curiosity, and they were largely forgotten when cathodic arc research was revived in the 1880s by the work of Thomas Alva Edison.

I would like to conclude Part I of this publication with a final quote:

"Speculation is only of use as it leads to practice, that the immediate use of natural science is the power it gives us over nature, by means of the knowledge we acquire of its laws; whereby human life is…made more comfortable and happy."

Joseph Priestley, *History and Present State of Electricity*, 1767

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Figure Captions

Fig. 1. Schematic voltage-current characteristics of electrical discharges. Top: atmospheric pressure, bottom: low-pressure. Regions of $dV/dI < 0$ are not stable: Townsend-to-glow, glow-to-arc and spark-to-arc transitions are indicated by arrows. The spark is a transient discharge form, the other forms can be stationary. The scales are logarithmic: The voltage scale includes about 5 orders of magnitude, with the highest values in the 10s of kV-region, and the current scale about 12 orders of magnitude, with the highest values in the 10's of kA-region. This diagram is for general illustration only.

Fig. 2. Hauksbee's frictional machine, which became a prototype in the early 18^{th} century, here with two glass tubes, the inner being evacuated [with significant residual pressure!], producing light when the outer was turned and rubbed (from [31] plate III, cf. also [1] plate IV, [8] Fig. 8.2, and [32] Fig. 10.1).

Fig. 3. A battery of Leyden jars (from [1] plate III).

Fig. 4. Short-circuit discharge of a Leyden jar, producing a "spark" or oscillating discharge (segment of an engraved plate from Alessandro Volta to Joseph Priestley, 1775, [4] p.31).

Fig. 5. Cathode erosion crates or "Circle of shining dots, consisting of places superficially melted," from Plate 1, Fig.5 of [27].

Fig. 6. Erosion craters (here caused by a cathodic arc discharge on copper), similar to "cavities, resembling those on the moon" This image was obtained using a scanning electron microscope; courtesy of Burkhard Jüttner, Berlin.

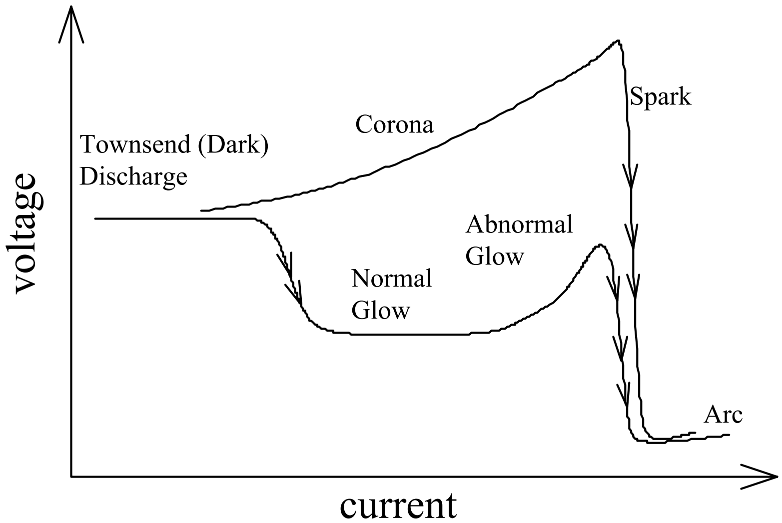
Townsend (Dark)
Discharge
Corona
Spark
Abnormal
Glow
Normal
Glow
Arc
voltage
current

Fig. 1

Fig. 2

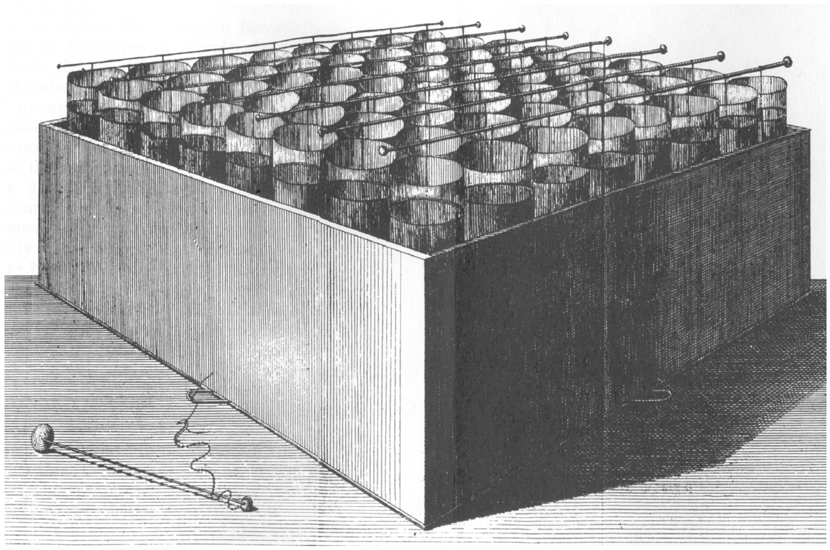

Fig. 3

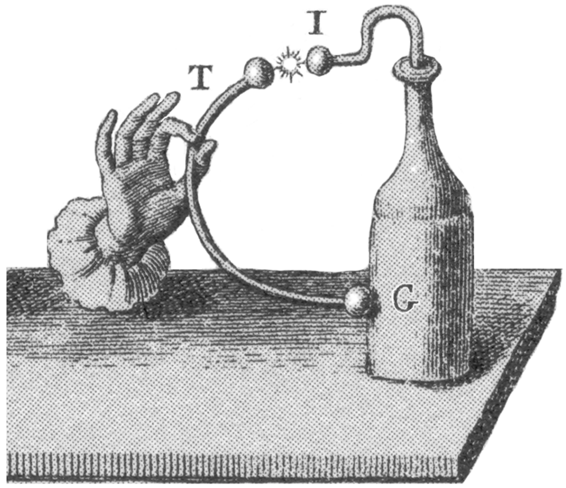

Fig. 4

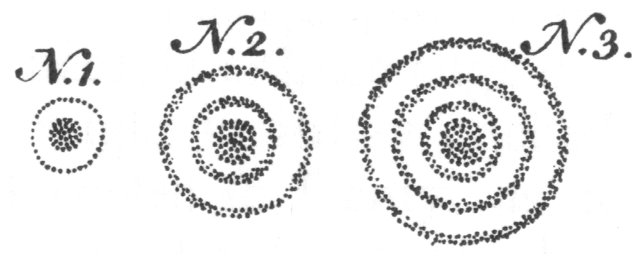

Fig. 5

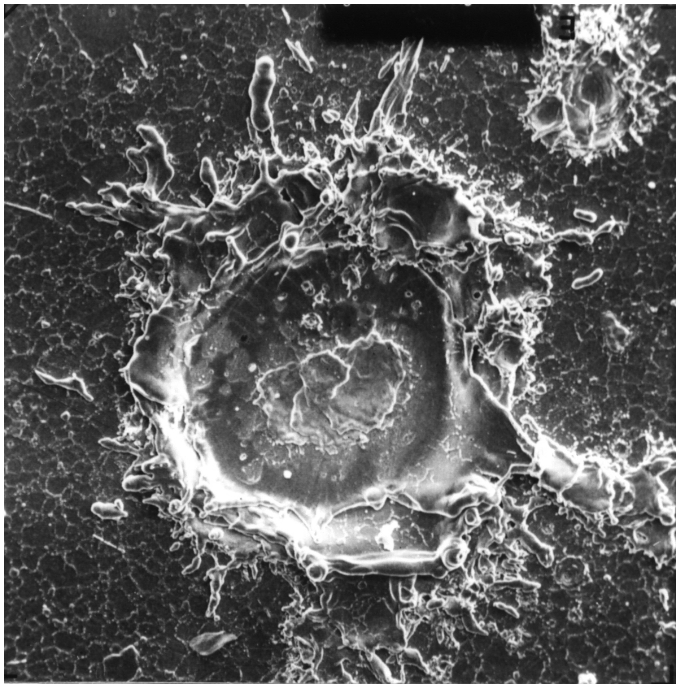

Fig. 6