Historical Introduction to Capacitor Technology

Key words: capacitor, capacitor history, ceramic capacitor, film capacitor, double layer capacitor, electrochemical capacitor

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Introduction to the Series

Over the next several years, this magazine will publish a series of papers, hopefully one per issue, on the subject of capacitor technology. The intention is to cover all important areas of the technology in some detail, including film, ceramic, electrolytic, and double-layer capacitors. One of the authors (S. B.) will edit the series.

Early History

Invention of the Capacitor

Capacitors are a good example of the fact that even the simplest device, in this case nothing more than an insulator between 2 conductors, can become complex given 250 years of technical evolution. The beginning of capacitor technology is generally attributed to the invention in October 1745 of the Leyden jar by the German Ewald Georg von Kleist. Independently, Pieter van Musschenbroek, a Dutch physicist at the University of Leyden, discovered the Leyden jar in 1746 [1]. As originally constructed, the Leyden jar consisted of a narrow-neck jar partially filled with water with an electrical lead brought through a cork in the neck of the bottle to the water. In von Kleist's implementation, his hands holding the jar formed the outer electrode. After charging the jar with an electrostatic generator connected to the water, von Kleist was able to give himself a painful shock by touching the lead to the water while still holding the jar, something he apparently did only once! The Dutch Leyden jar employed a foil electrode over the outside surface of the jar to form a true capacitor. The American journalist, statesmen, and inventor Benjamin Franklin showed that the water in the jar was not an essential element as had been thought by the inventors; as a result, he was able to make flat capacitors consisting of a sheet of glass between foil electrodes [2]. Faraday made major contributions to capacitor technology, including the concept of dielectric constant as well as the invention of the first practical fixed and variable capacitors. His contributions to capacitor technology are recognized in the unit for capacitance.

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Early Sources of Commercial Demand

Capacitor technology did not evolve rapidly until the invention of the vacuum tube (De Forest, 1907; Langmuir, 1916), which facilitated electronic amplifiers required for long-distance telephone (coast-to-coast, 1915) and practical radio technology first licensed commercially in 1920; however, the first AC line-powered radio was not introduced until 1927 (RCA Radiola 17). The rapid evolution of line-operated radio receivers created a large consumer product market for capacitors.

Early Capacitors

A wax-impregnated paper dielectric capacitor with foil electrodes was invented by Fitzgerald in 1876 [3]. The earliest capacitors used in radio receivers employed foil and wax-impregnated paper (Figure 1) for power supply filtering and mica dielectric capacitors for RF circuits (Figure 2). As wax-impregnated paper and foil capacitors are quite bulky, the power supplies of these radios normally employed filter chokes, i.e., inductors, in combination with the rectifier and capacitors to reduce power supply ripple. For example, the first line-powered RCA radio employed two 1-μF capacitors and three filter chokes. Higher voltage capacitors of the time were based on oil-impregnated paper and metal foil.

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Figure 1. Examples of early waxed paper and foil capacitors taken from antique radios. Such capacitors tend to be unreliable and are usually replaced with metalized polymer film capacitors when restoring a radio. Photo courtesy of P. I. Nelson, www.antiqueradio.org, and used with permission.

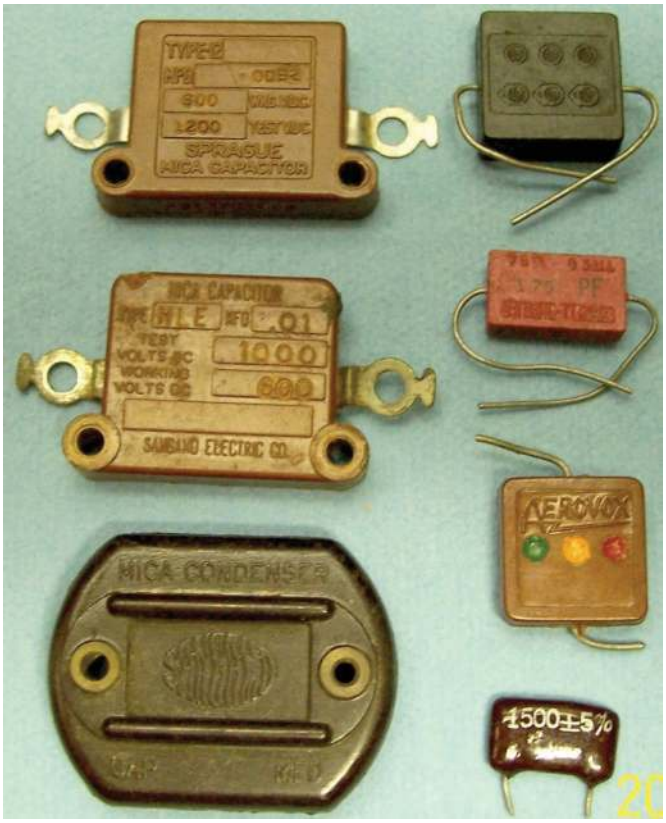

Figure 2. Selection of early mica capacitors. From the beginning, mica capacitors were very reliable, as they are today. Their expense precludes widespread use today, although they are still available. Photo courtesy of William Harris, nbcblue@hotmail.com.

Mica dielectric capacitors (Figure 2) were invented in 1909 by William Dubilier, with principal application in the area of radio transmission. In 1915, Dubilier founded the Dubilier Condenser Company in New York, and in 1933, the company merged with Cornell Radio to form Cornell-Dubilier Electric. From the beginning, mica capacitors, typically silver mica, have been highly reliable because mica is an excellent dielectric with outstanding discharge resistance.

Patents on the electrolytic capacitor (Figure 3) technology date back to 1897 when Charles Pollak was granted a patent for a borax electrolyte aluminum (Al) electrolytic capacitor, and the first wet electrolytic capacitors appeared in radios in the late 1920s. These had a very limited lifespan, and the company that introduced them went bankrupt. In 1936, Cornell-Dubilier opened a factory in Plainfield, NJ, and introduced a line of commercial Al electrolytic capacitors. This might have been the first commercial production of electrolytic capacitors since failure of the technology in the late 1920s. Electrolytic capacitors did not become highly reliable until World War II when sufficient resources were devoted to identify and eliminate the causes of early failure [4].

Ceramics have been used as electrical insulation since the earliest studies of electricity. As noted earlier, the first capacitor, the Leyden jar, was a ceramic capacitor. Prior to World War II, mica was the most common ceramic dielectric for capacitors, although porcelain, steatite, cordierite, and rutile were also used. Capacitors based on titanium dioxide (rutile) were available commercially around 1926. The 1941 discovery of barium titanate [5] with a dielectric constant in the range of 1,000, about 10 times greater than any dielectrics known at the time, focused attention on the barium titanate family of materials for a range of wartime applications, including capacitors (Figure 4). In the following decades, a great deal of effort was devoted to understanding the crystallography, phase transitions, and the optimization of this family of materials [6]. The development of multilayer ceramic capacitor (MLCC) fabrication using the tape casting and ceramic-electrode cofiring processes during the 1970s and 1980s expanded the range of ceramic capacitor application to larger capacitances and higher voltages depending on whether the layers were arranged in series or parallel. At present, more than 10^{12} barium titanate–based MLCC are manufactured each year. Ceramic capacitors are not limited to barium titanate MLCC. A wide range of ceramic formulations has been developed, some with very high dielectric constants but usually with large temperature/voltage coefficients, and others with lower dielectric constants but lower, and in some cases near zero, temperature/voltage coefficients.

A metalized, self-clearing paper capacitor was patented by Mansbridge in 1900 [5], [6] and was based on metalizing with a metal particle-filled binder, which resulted in frequent shorts through the paper. Metalized paper capacitors reached maturity during World War II, with Bosch manufacturing metalized paper capacitors using lacquer-coated paper and vacuum-deposited metal [7]. The lacquer reduced electrolytic corrosion of the metal and increased insulation resistance. Further attention was given to metalized paper capacitors around 1950 when they were in-

Figure 3. Examples of early electrolytic capacitors taken from antique radios. These capacitors are also unreliable and are replaced when restoring such a radio. Photo courtesy of P. I. Nelson, www.antiqueradio.org, and used with permission.

troduced into the telephone system. Metalized paper capacitors were very reliable as long as they were dried carefully and sealed into a dry environment. Around 1954, Bell Labs took this system a step further by separating the lacquer from the paper and making capacitors based on 2.5-μm-thick metalized lacquer film that were substantially smaller than metalized paper capacitors [8]. This could be the first metalized polymer film capacitor.

Polyethylene terephthalate (PET) was patented by Whinfield and Dickson in 1941. A very strong PET, trademarked Mylar by Dupont (1952), evolved from work on Dacron in the early 1950s and was produced as 12-μm metalized capacitor film by 1954 [8]. Semicrystalline polypropylene was discovered around 1951 by multiple investigators, which resulted in patent litigation that continued into the late 1980s! A 1959 paper [9] discusses "Development of Plastic Dielectric Capacitors" made from polyethylene, polystyrene, polytetrafluoroethylene, PET, and polycarbonate, i.e., the most common capacitor films other than polypropylene. By 1970, film-foil capacitors (without paper) were being manufactured for electric utility applications.

Figure 4. Examples of early ceramic capacitors taken from antique radios. Early ceramic capacitors looked very much like modern examples, although somewhat larger for a given capacitance. Then, as now, ceramic capacitors were very reliable. Photo courtesy of P. I. Nelson, www.antiqueradio.org, and used with permission.

Capacitors based on electric double-layer charge storage were first patented by General Electric in 1957 but were never commercialized. Subsequent double-layer capacitor designs patented by Standard Oil of Ohio did lead to commercial product introduction in 1978 by Nippon Electric Corporation. Their Supercapacitor trademarked product was rated at 5.5 V and had capacitance values up to 1 F. These 5-cm^3-size or smaller capacitors were used as battery substitutes to provide backup power for volatile CMOS computer memory. Products available today from about 2 dozen manufacturers around the world range in sizes up to 9 kF (9,000 F) at 2.7 V, with this largest-size device being easily held in one hand.

Figure 5 presents a time line for the development of capacitor technology along with a corresponding cultural (musical) time line that may help relate technological and cultural/historical development.

Present Challenges and Limitations

At present, the important capacitor technologies are impregnated foil-polymer film (for high voltage, high current), metalized film, ceramic, electrolytic, and electric double layer, although metalized paper is still used occasionally in "soggy foil" designs, i.e., self-clearing, fluid-impregnated, high-voltage capacitors. Each of these major technologies faces challenges as they compete with each other for market share.

Ceramic capacitor dielectrics exhibit high dielectric constant but low breakdown field. As a result ceramic capacitors provide very high capacitance but typically exhibit a low breakdown field as a result of porosity in the ceramic structure, which arises from incomplete consolidation of the ceramic particles during the manufacturing process. In addition, a higher dielectric constant material tends to have a lower breakdown field than a lower dielectric constant material simply because, at a given electric field, it stores more energy, which can precipitate breakdown. Thus, a major challenge in ceramic capacitor technology is to improve density and breakdown strength through techniques such as the use of nanoceramic powders, various forms of impregnation to reduce porosity, etc. The relatively low breakdown strength combined with very high dielectric constant of ceramic capacitors makes them well suited to low-voltage applications because the thickness can be matched well to the voltage. They are less well suited to high-voltage applications as a result of the low breakdown strength, although doorknob ceramic capacitors are manufactured to at least 50 kV, which is achieved by incorporating a large safety margin at the expense of a low capacitance on the order of 1 nF.

The failure mode of ceramic capacitors also presents a challenge. Unlike polymer capacitors, which fail gracefully by oxi-

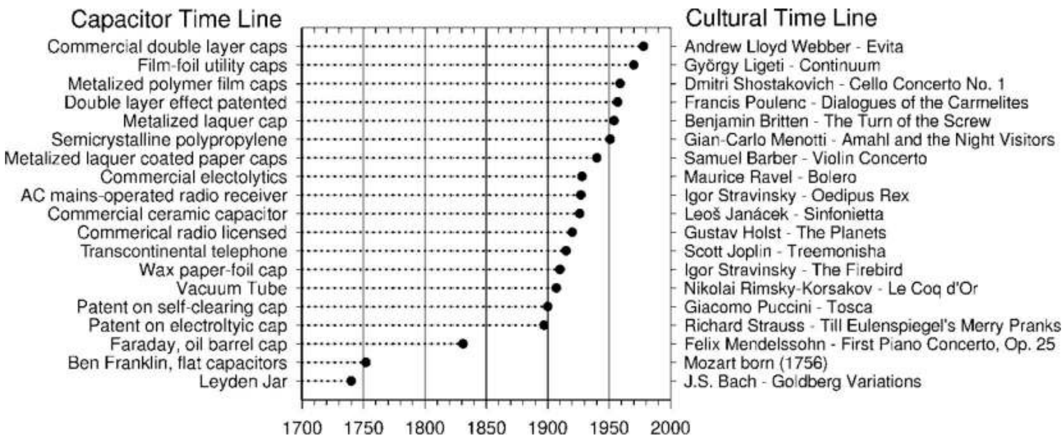

Figure 5. Capacitor time line with corresponding cultural time line for reference.

dizing/vaporizing the dielectric and aluminum electrode, ceramic dielectrics tend to crack during breakdown, rendering the entire device useless. In addition, the internal electrode, typically 0.5 to 1 μm in thickness, cannot be vaporized readily to isolate the breakdown region electrically. The catastrophic failure mode of ceramic capacitors is an obstacle to their acceptance for critical applications in which a disruption of operation is not acceptable or in which the energy stored is so large as to render the capacitor dangerous upon shorting. Efforts have been made to address this issue, such as integrating fuses at MLCC terminations and parylene coating on monolithic ceramic capacitors, but success has been very limited.

The abundance of ceramic compounds and the diverse properties thereof has resulted in a wide range of materials suited to specific applications, a good example of which is the recent development of a class of antiferroelectric ceramics with a field-dependent phase transition to ferroelectric, as a result of which they achieve an energy density greater than 10 J/cc. Some such materials have a meta-stable antiferroelectric to ferroelectric transition that results in a large dielectric constant under DC bias, which makes them an excellent candidate for DC link capacitors. Recently, glass-based dielectrics have become a popular candidate for high breakdown strength materials. Porosity-free ferroelectric glass-ceramics in which ferroelectric particles are precipitated from an engineered glass have achieved a breakdown strength near 100 V/μm, an order of magnitude greater than conventional ceramics. As a result of their inorganic nature, ceramic capacitors can be formulated to operate at much higher temperatures than organic polymer-based dielectrics, which is important for applications such as filter capacitors in power electronics based on wide band gap semiconductors.

Polymer films can have Weibull characteristic breakdown fields >700 V/μm for test areas of a few square centimeters with a Weibull slope parameter in the range of 15, which is very good. However, they have low dielectric constants, in the range of 2.2 for near-perfect dielectrics such as polypropylene and polystyrene and up to 12 for ferroelectric polymers such as polyvinylidene fluoride (PVDF), which are far from perfect with tan(δ) in the range of 1%. Thus, the emphasis in this technology is greater dielectric constant and, if possible, greater dielectric strength. Promising developments have been reported based on copolymers of PVDF that are ferroelectric relaxors. Of polymer films, only PET is well suited to low-voltage capacitors because it can be made to less than 0.5 μm in thickness. Polypropylene, which along with PET dominates film capacitors, cannot be made thinner than about 3 μm, which, given its breakdown field in the range of 700 V/μm, means it is not well matched to low-voltage applications. The other major advantage of metalized polymer film capacitors is graceful failure that results from self-clearing. This allows operation at increased field because breakdown of the polymer film results in only a minute reduction in capacitance rather than catastrophic failure of the capacitor as is the case with foil-based or ceramic-based designs. Self-clearing comes at the cost of a number of complications, including a wire arc metal spray end connection that has limited current-carrying capability, the improvement of which is an area of active investigation.

For very high-voltage applications, metalized film capacitors can be made with multiple sections in series across the film. This facilitates fairly compact, high-voltage capacitors; however, a great deal of volume is wasted as a result of the margins required between the sections so that high energy density in such designs is unlikely. For fast pulse discharge applications, the end connections of such designs often limit the peak current output.

Foil-film designs dominate capacitors used for reactive compensation in utility power systems, although designs based on metalized film capacitors are available. Foil-film capacitors can achieve very high power density, i.e., very large current discharge over very short times, because they can be designed with low equivalent series inductance, very low equivalent series resistance (ESR), and unlimited end-connection current density. The energy density is limited by the need for conservative operating fields because the system is not self-clearing. Foil-film technology can be used to make extremely compact, high-voltage capacitors through the use of multiple sections in series within the winding. Unlike the case of metalized film capacitors, this can be done with very little wasted volume because the margin between sections runs across the film in the longitudinal direction (film width) rather than in the winding direction (film length) as for metalized film capacitors. In such a multiple-sections foil design, the winding connections must be made at the center (to the first foil) and at the outer radius (to the last foil), which means that the current spirals between the 2 connections, which creates substantial inductance. Thus, the self-resonant frequency of such capacitors can be very low (100s of kHz) relative to other designs.

Aluminum electrolytic capacitor technology tends to be fairly mature, although the size of electrolytic capacitors has dropped substantially over the years, especially for the lower voltages. The maximum voltage rating of Al electrolytic capacitors has also increased slightly. Aluminum electrolytic capacitors have several limitations other than the obvious one of being unipolar unless operated in series. They have substantial leakage current, as a result of which they are rarely used in series to achieve higher voltage. The maximum operating voltage is limited to below 1 kV by the inability to grow the aluminum oxide coating sufficiently thick.

Solid tantalum electrolytic capacitor technology is less mature, which has resulted in greater changes, including reduced ESR and the use of conducting polymer electrolyte in some designs. Nevertheless, solid tantalum capacitors tend to have high ESR as a result of the solid electrolyte that makes contact with the tantalum oxide dielectric and replaces the liquid in the aluminum electrolytic capacitor. Solid electrolytes generally have lower conductivity than liquids.

In the past, double-layer or electrochemical capacitors tended to live in a world of their own because their electrical properties differ greatly from traditional capacitors. Electrochemical capacitors are based on the electric double-layer capacitance formed between ionic and electronic conductors, which results in capacitance per unit volume or weight that is unmatched by any other technology; yet, they are unsuitable for ac filtering because they cannot charge and discharge at 60 Hz. However, they can charge and discharge more rapidly than batteries. As a result, double-layer capacitors are often used to complement batteries in applications that have rapidly varying loads such as those encountered in electric and hybrid electric vehicles. Double-layer capacitors can also be used as a battery replacement in some applications. Compared with conventional capacitors, double-layer capacitors have limited life at elevated temperature, which is often as low as 1,000 hours at 70 or 85°C. Nevertheless, their life at elevated temperature exceeds that offered by alternative technologies having comparable or greater energy density, such as secondary batteries. Thus, double-layer capacitors have their own spectrum of optimal applications that component engineers are only beginning to exploit.

Outlook

Electrostatic capacitor technology has evolved substantially in terms of materials and quality of those materials. The widespread commercialization of self-clearing, metalized film capacitors was a major advance, although as discussed earlier, the concept of self-clearing goes back to around 1900. The energy density of millisecond time scale pulse discharge capacitors based on metalized film is over 2 J/cm^3 for capacitors that can sustain very large numbers of discharges, and somewhat more for capacitors with limited time at charge and numbers of discharges. The importance of self-clearing and the resulting graceful failure is sometimes not appreciated fully. Graceful failure is essential for any capacitor that stores large amounts of energy because the alternative is explosive failure, which is hazardous. In addition to the improvements brought by metalized film, high-temperature film dielectrics have been developed that facilitate wave soldering of circuit boards, down-hole applications in the oil industry, etc.

Ceramic capacitors have come a long way from their beginning, with a wide range of formulations varying from very high dielectric constant, but typically with large field and temperature dependence, to formulations for precision capacitors with a very low temperature coefficient. At present, barium titanate–based MLCC are the mainstay in microelectronics, while specialty ceramic capacitors with high temperature stability, high voltage, and/or ultra-high capacitance are being used throughout the electronics industry. Innovations in materials technology continue to move the ceramic capacitor technology forward. Ceramic compositions and processing that yield improved breakdown strength, energy density, and operating temperature range will be the focus for the foreseeable future. Research to incorporate graceful failure into ceramic capacitor technology is also underway.

Electrolytic capacitors have become the mainstay of power supply filtering; however, their limited operating temperature range poses a problem for future high power density electronics based on wide band gap semiconductors. As a result, research is ongoing to develop alternatives for such applications.

Double-layer capacitors were originally a solution looking for a problem because they do not filter and, thus, are un-capacitor-like and because they store little energy and, thus, are un-battery-like. With increasing electrification of technology, for example in transportation, double-layer capacitors have become a widely used capacitor component. Energy storage has become increasingly important, and double-layer capacitor technology has seen an ever-expanding role in applications involving energy conservation, electric power load leveling, and high-power millisecond-to-second-long pulse delivery, engine starting being but one important example.

The need for improved capacitor technology is imperative as our world becomes increasingly electrified. For example, transportation, which has long been the domain of petroleum-based internal combustion, is rapidly moving to hybrid electric and toward all electric. Advanced low-voltage capacitors are needed to facilitate more power-efficient and compact portable electronic devices for communications, medical applications, and high-power electronics. Applications include implantable defibrillators and power electronics for power conversion and distribution in hybrid electric propulsion systems. Advanced high-voltage capacitors are needed for reactive compensation of electric power systems, energy storage and distribution related to the interfacing of renewable energy sources to the power grid, and for energy storage for pulsed power applications such as electromagnetic-based pulse power systems. To meet the present and future demand, substantial advances beyond the present state-of-the-art in dielectric materials and capacitor technology are required. Higher energy density dielectric materials that enable the fabrication of capacitors that can operate at temperatures above 150°C and can handle high-voltage and high-ripple current at frequencies over 20 kHz for power electronics are not presently available. Technology for fabricating compact, high-voltage, high-current, high-repetition-rate capacitors that deliver energy in sub-microseconds is also needed.

In the remainder of this series we will have detailed introductions to the various capacitor technologies followed by papers that get into various aspects of the technical details of those technologies. Looking forward, we hope this series will serve as a baseline and foundation for future development.

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