Two centuries of memristors

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Memristors are dynamic electronic devices whose nanoscale realization has led to considerable research interest. However, their experimental history goes back two centuries.

Memristors are nonlinear dynamic electronic devices with widespread applications in computer data storage and neuromorphic implementations. The realization of a nanoscale memristor by Hewlett Packard in 2008[1] came almost 40 years after its theoretical inception[2], and ever since it has precipitated an enormous interest on emerging applications that leverage on the dynamic nature of such devices. Nonetheless, as the research community became acquainted with memristive attributes, it became evident that these unconventional characteristics have been to a great extent observed and documented before. The functional properties of memristors were first documented by Chua[2] and later on by Chua and Kang[3], with their main fingerprint being a pinched-hysteresis loop when subjected to a bipolar periodic signal. This particular signature has been explicitly observed in a number of devices for more than one century, while it can be extrapolated for devices that appeared as early as the dawn of the nineteenth century.

Hysteresis is typically noticed in systems and devices that possess certain inertia, causing the value of a physical property to lag behind changes in the mechanism causing it, manifesting memory[4]. Such causes are typically associated with irreversible rate-dependent electro- or thermodynamic changes that are contingent on both the present as well as the past environment. Particularly in the case of nanoscale memristors, this inertia can be associated with the displacement of mobile ions or oxygen vacancies[5,6], the formation and rupture of conductive filaments[7,8] or even the phase transitions[9] of an active core. And despite the fact that these mechanisms have a more substantial effect in lamella devices, similar attributes can also be supported by considerably larger ionic systems, contingent on the extent of the stimulating cause, the nature of the pertinent ions and the barrier medium that governs their kinetics.

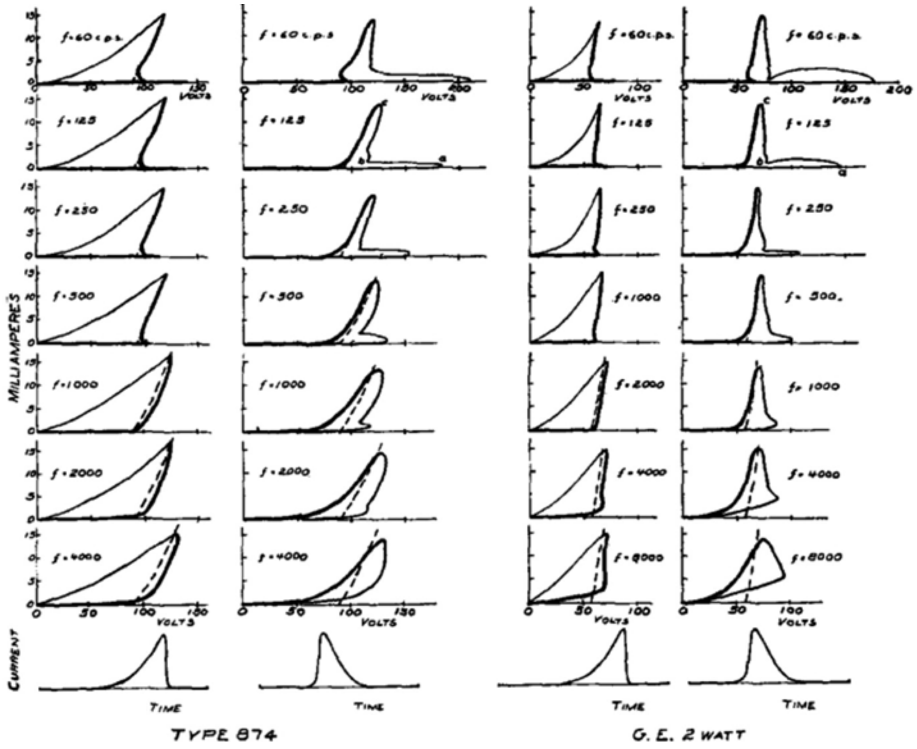

Figure 1 | Dynamic characteristics for two types of tubes and varying current amplitude, constant frequency and current waveform. The rod of type 874 tube was used as a cathode. Image reproduced with permission from ref. 13, © 1938 AIP.

Essentially, this signature memristor property is quite characteristic for all devices in support of a discharge phenomenon, no matter what the conveying medium is. For example, naturally occurring ionic systems, such as biological ion channels, allow the passive displacement of ions due to an electrochemical gradient along the cell's membrane, which sets the probability of an ion channel being in an open or closed state. The intra- and extracellular current conduction per channel is governed by distinct rate-limiting dynamics[10], attributed to the conformational changes of the channel's pore during gating charge movement[11], and therefore a pinched-hysteresis loop should inherently appear when an appropriate periodic signal is applied. Chemical diffusion and ion migration are considered as the facilitating mechanisms for most functional properties of organic and inorganic systems; both of them being in essence distinct forms of ionic discharge. Hence, almost all naturally occurring and artificially made systems can be classified as being memristive. It is not a surprise that memristance has also been observed in human blood[12].

In particular, discharge lamps are recognized as being rather dynamic because the time required for ionization and deionization to take place depends not only on the instantaneous current flow, but also on the current that has previously flowed through it as well as the rate of change of current. When a potential difference (PD) is applied across a gas-discharge tube that is sufficiently larger than the static ignition

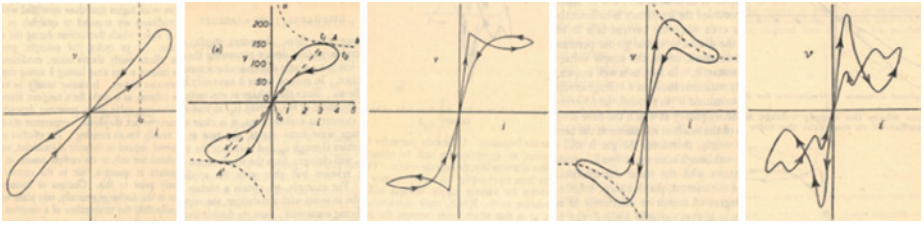

Figure 2 | Dynamic characteristics of memristors. From left to right: tungsten filament, high-pressure mercury-vapour lamp, low-pressure mercury tube, discharge tube and sodium tube. Image reproduced from ref. 14.

potential of the tube, the current flow increases rapidly. However, the deionization time is observed to be substantially larger than the time that it takes to decrease this current flow abruptly, rendering an increase in the tube's resistance as deionization occurs. This dynamic response was especially observed for two types of glow discharge tubes, as depicted in Fig. 1 by Reich and Depp in 1938[13], manifesting one of the earliest known demonstrations on the vacuum tube's capacity to act as a variable resistor. The resemblance of these results with the current–voltage characteristics observed for example in the case of nanoscale TiO_2 memristors[1] is apparent.

An excellent analysis of the dynamic characteristics of devices exhibiting discharge phenomena was presented by V. J. Francis[14], where alike dynamic characteristics were observed for tungsten filaments, high-pressure mercury-vapour lamps, low-pressure mercury tubes, discharge tubes and sodium tubes, as illustrated in Fig. 2. These loops are typically observed when a device is excited by a periodic PD, causing the maxima and minima of this PD to be out of phase with the corresponding maxima and minima of the current flowing through the device. Representative phase plots in Fig. 3 demonstrate this phenomenon for a low-pressure mercury lamp serially connected with a capacitor, a resistor and an inductor.

The stratified discharge in a vacuum tube is essentially a magnified version of the thermionic emission[15] as exhibited by the electric arc[16], which is considered as the predecessor of discharge tubes. The larger the distance between the electrodes, the larger the PD must be to establish discharge. On the other hand, when the separation gap is miniscule, a few volts are sufficient for mobilizing ions across this barrier, which is also the case in nanoscale implementations of memristors. The functional property of the electric arc depends on a discharge phenomenon that has been mainly observed for carbon electrodes placed a few millimetres apart with a relatively large PD being applied across them.

Hertha Ayrton was one of the first eminent engineers to have extensively studied the 'hissing' electric arc[17]. She proved that if air was excluded from the arc, or when nitrogen was introduced in isolation, the hissing did not occur (Fig. 4). Her discovery eventually led to the development of gas-discharge tubes. Most importantly, she noticed that the characteristic curve of an alternating current arc shows lower voltages when the current is decreasing than when it is increasing, which is dependent on the supply current, the length of the arc, and the thermal conductivity of the electrodes as well as the pressure of the surrounding gas. This rate-limiting response was later exploited by Duddell[18], who interpreted it as an oscillating arc; essentially demonstrating hysteresis. Duddell[19] pointed out that "if it were possible to obtain perfectly pure carbon electrodes, then the resistance of the arc between them would be very high, so high that it might be impossible to maintain a true arc between them at all". He also expressed the opinion that "traces of impurities, such as the vapours of the alkaline earths, are essential to provide the carriers of the electric charges in the vapour column, so as to render it conducting". And although this was mentioned more than a century ago, this statement was rather prophetic when considering that nowadays nanoscale memristors leverage on intrinsic defects for establishing distinct conductive states.

Other studies exemplifying the rate-limiting response of the electric arc were carried out towards the end of the nineteenth century, with Frith *et al.*[20] observing that the current flowing through a hissing arc was oscillatory. At the same time it was demonstrated that when an electric arc was driven with relatively high-frequency alternating currents, there was no effect on the overall resistance of the arc. Likewise, this was also noted eight years before Frith in a paper by Luggin[21], where he observed that when the current was alternated with sufficient rapidity, the PD would rise and fall in phase with the current, demonstrating a linear resistance. If however the current was alternated at lower frequencies, the electric arc could in fact exhibit a negative resistance. Analogously, it is nowadays shown that nanoscale memristor implementations based on metal oxides can demonstrate a negative differential resistance[22]. Quite a few scientists have demonstrated that air was unable to insulate when a PD was adequate enough to heat the bounding carbon electrodes, with Blondlot indicating that the 'leaking currents' obey a nonlinear trend and thus do not comply with Ohm's law[23].

Similar effects have however been observed in the case of thermally sensitive

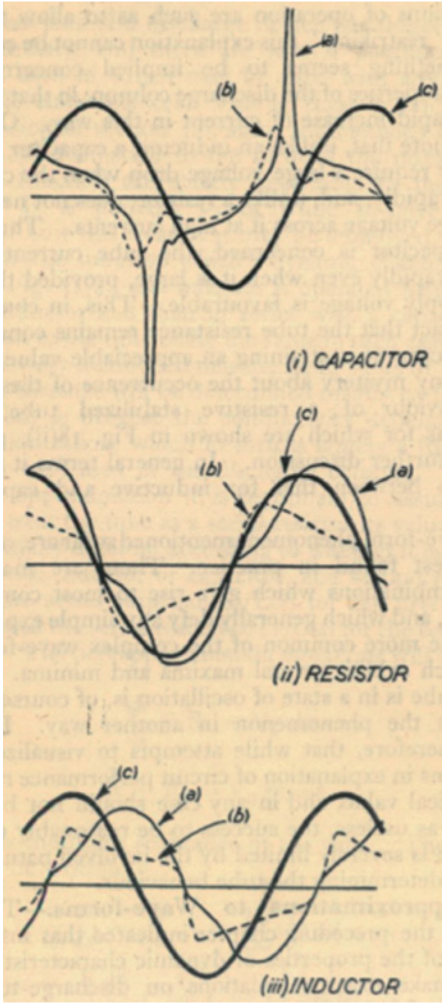

Figure 3 | Memristor phase relations. Curves a, b and c show the tube current, tube voltage and mains voltage, respectively, for a low-pressure mercury lamp, with various series stabilizers. Image reproduced from ref. 14.

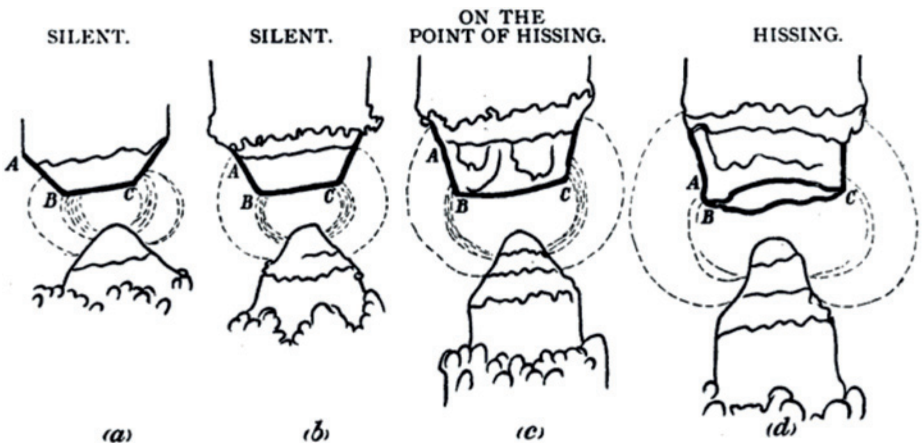

Figure 4 | The 'hissing of the electric arc' as presented to the Institution of Electrical Engineers in 1899 by Hertha Ayrton. Air causes hissing and inconstant light when it comes into contact with the carbon crater of the arc lamp. To the best of our knowledge, the noise-like waveforms associated with this hissing phenomenon presented two years later by Duddell[18] is the first chaotic phenomenon reported in electrical engineering, and possibly in all man-made devices. Therefore the hissing arc qualifies as the first chaotic electrical circuit, instead of the Van der Pol oscillator[35]. Image reproduced from ref. 17.

resistors, also known as thermistors[24]. The first reported thermistor was attributed to the British physicist Michael Faraday in 1833, based on his study on the semiconducting behaviour of Ag_2S. In his book[25], Faraday writes: "On applying a lamp under the sulphuret between the poles, the conducting power rose rapidly with the heat, and at last the galvanometer needle jumped into a fixed position, and the sulphuret was found conducting in the manner of a metal. On removing the lamp and allowing the heat to fall, the effects were reversed, the needle at first began to vibrate a little, then gradually left its transverse direction, and at last returned to a position very nearly that which it would take when no current was passing through the galvanometer". What was clearly happening is that the PD applied across the poles was insufficient to allow current conduction across the barrier. Thermionic emission was eventually being facilitated by the thermal energy, provided by the lamp, which supplemented the missing energy necessary for exceeding the barrier's potential. Not surprisingly, Ag_2S has recently been employed to facilitate resistive switching in nanoscale elements[26], which demonstrate rate-limiting functionality[27] similar to what was observed almost two centuries ago by Faraday. But who was the first one to observe this peculiar response, which without argument is the signature property of memristors? No one else but the inventor of the electric arc and also Faraday's mentor, Sir Humphry Davy.

One of the greatest scientific breakthroughs of mankind occurred in 1800, with Alessandro Volta establishing the voltaic pile[28] that facilitated unprecedented PDs. Humphry Davy leveraged the voltaic pile for observing the effect of large currents on, living things, chemical decomposition and heating and producing sparks. In his letter printed in *Nicholson's Journal*[29], Davy writes "The earlier experimenters on animal electricity noticed the power of well burned charcoal to conduct the common galvanic influence. I have found that this substance possesses the same properties as metallic bodies in producing the shock and spark when made a medium of communication between the ends of the galvanic pile of Signor Volta". Later on, in a lecture before the Royal Institution given in 1801[30], Davy describes some experiments on the spark yielded by the pile, stating: "When, instead of the metals, pieces of well-burned charcoal were employed, the spark was still larger and of a vivid whiteness", and again "The spark is most vivid when the charcoal is hot". Clearly, this is not the definition of the electric arc, but of a spark, as the electric arc requires the establishment of a continuous luminous filament without intermittent gaps.

Davy's failure of acknowledging his discovery of the electric arc from early on was due to the lack of a sufficiently large PD that would have enabled him to initiate and sustain a continuous luminous filament from a deionized state. In 1808 Davy requested the purchase of a large galvanic battery, comprising 2,000 pairs of serially connected copper and zinc plates, that was installed in the Royal Institution. In his experiment in 1808, as recounted in the *Philosophical Transactions* for 1810[31], Davy demonstrates a functional electric arc: "…charcoal, even when ignited to whiteness in oxymuriatic or muriatic acid gases, by the Voltaic battery, effects no change in them; if it has been previously free from hydrogen and moisture by intense ignition in vacuo." This was better comprehended though in his 1812 book *Elements of Chemical Philosophy*[32], where he writes "When pieces of charcoal about an inch long and one sixth of an inch in diameter, were brought near each other … a bright spark was produced, and more than half the volume of the charcoal became ignited to whiteness, and by withdrawing the points from each other a constant discharge took place through the heated air, in a space equal at least to four inches, producing a most brilliant ascending arch of light, broad, and conical in form in the middle." Although, Davy originally exploited this incandescent device for electrolysis, his contributions are far more reaching. As we now know he set the foundations not only for lighting but also analogue computing, with implications both in the early days when vacuum tubes were used and hopefully for the future as memristor-based computing emerges.

The memristor is not an invention. Rather it is a description of a basic phenomenon of nature that manifests itself in various dissipative devices, made from different materials, internal structures and architectures[33]. We end this historical narrative by noting that even though the memristor has seen its light of joy only recently in 2008, and has been recognized as the fourth circuit element along with the resistor, capacitor and inductor, it actually predates the resistor, which was formally published by Ohm in 1827[34], and the inductor, which was formally published by Faraday in 1831[25]. ❒

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When Brownian diffusion is not Gaussian

Bo Wang, James Kuo, Sung Chul Bae and Steve Granick

It is commonly presumed that the random displacements that particles undergo as a result of the thermal jiggling of the environment follow a normal, or Gaussian, distribution. Here we reason, and support with experimental examples, that non-Gaussian diffusion in soft materials is more prevalent than expected.

Fickian diffusion is the dominant form of molecular and supramolecular transport. It is also the simplest time-dependent random process: a random walk for which the mean square displacement (MSD) is proportional to elapsed time. In fact, Einstein's celebrated analysis of Brownian motion assumes that big particles in a fast-moving small-molecule solvent follow random walks[1]. The assumption was based on an extreme separation of timescales — associated with the slow-moving particle and the fast-wiggling solvent molecules — which leads to the classic statistical-mechanics treatment embodying a coarse-grained fluctuating force as a Gaussian-distributed stochastic temporal series[2]. Indeed, when random walks are viewed as a succession of steps, it follows from the central limit theorem that for sufficiently long times the dynamics have to be Gaussian and the diffusion Fickian[3]. Yet recent direct observations in systems without a large separation of timescales — for example, the diffusion of colloids on phospholipid fluid tubules and in biofilament networks[4,5] (Fig. 1a) — repeatedly find the distribution of displacements in Fickian diffusion to deviate from Gaussian (Fig. 1b). System-specific interpretations have been proposed[6,7] but the finding of non-Gaussian Brownian diffusion calls for a general perspective.

Intriguingly, non-Gaussian probability distributions of mobility are increasingly recognized in a variety of physicochemical and socio-economical systems: Brownian motion in supercooled liquids[8–12] and close to jamming transitions[13–19], far-from-equilibrium systems such as granular gas and plasma[20–23], flow and drainage[24–28], friction[6,29,30], turbulence[31,32] and also financial and political fluctuations[33,34]. With this Commentary we wish to draw attention to the common thread: slowly varying, heterogeneous fluctuations of the environment (Fig. 1c) that lead to the observation of non-Gaussian behaviour at comparable or slower timescales than that for the onset of Fickian diffusion (Fig. 1d).

Patterns of non-Gaussian diffusion

As long as diffusion remains Fickian, non-Gaussian distributions of particle displacements (here denoted by the function $G_s(r,t)$, where $r(t)$ is the displacement at time t) spread proportionally to the square root of elapsed time and with the diffusion coefficient D. Generally, the central portion of a non-Gaussian distribution function can be approximated by a Gaussian function, $G_s(x,t) \propto \exp[-x^2/2\sigma^2(t)]$, with width σ and, where x is one-dimensional displacement whereas the remaining tail can roughly be described by an exponential curve, $G_s(x,t) \propto \exp[-|x|/\lambda(t)]$, with exponent $1/\lambda$, where λ is the characteristic decay length. Hence, the Gaussian centre and the exponential tail can be identified with hypothetical diffusion coefficients D_{Gauss} and D_{tail}, respectively, differing from the average diffusivity D. Decoupled diffusivities can be found for instance in random walks in dense colloidal suspensions, for which microscopic motion splits into trapped and hopping dynamics[10–13]. Yet the general phenomenology has been observed in a broader range of experimental and simulation work[4–34]. As illustrated in Fig. 2, $G_s(r,t)$ falls into four families according to whether the exponential tails are larger, comparable to, or smaller than the average diffusivity.

As to the temporal evolution of these distributions, there are notable general trends. Typically (but not exclusively) the central portion of the distribution