Memristive behaviour of Carbon Nanoparticle systems

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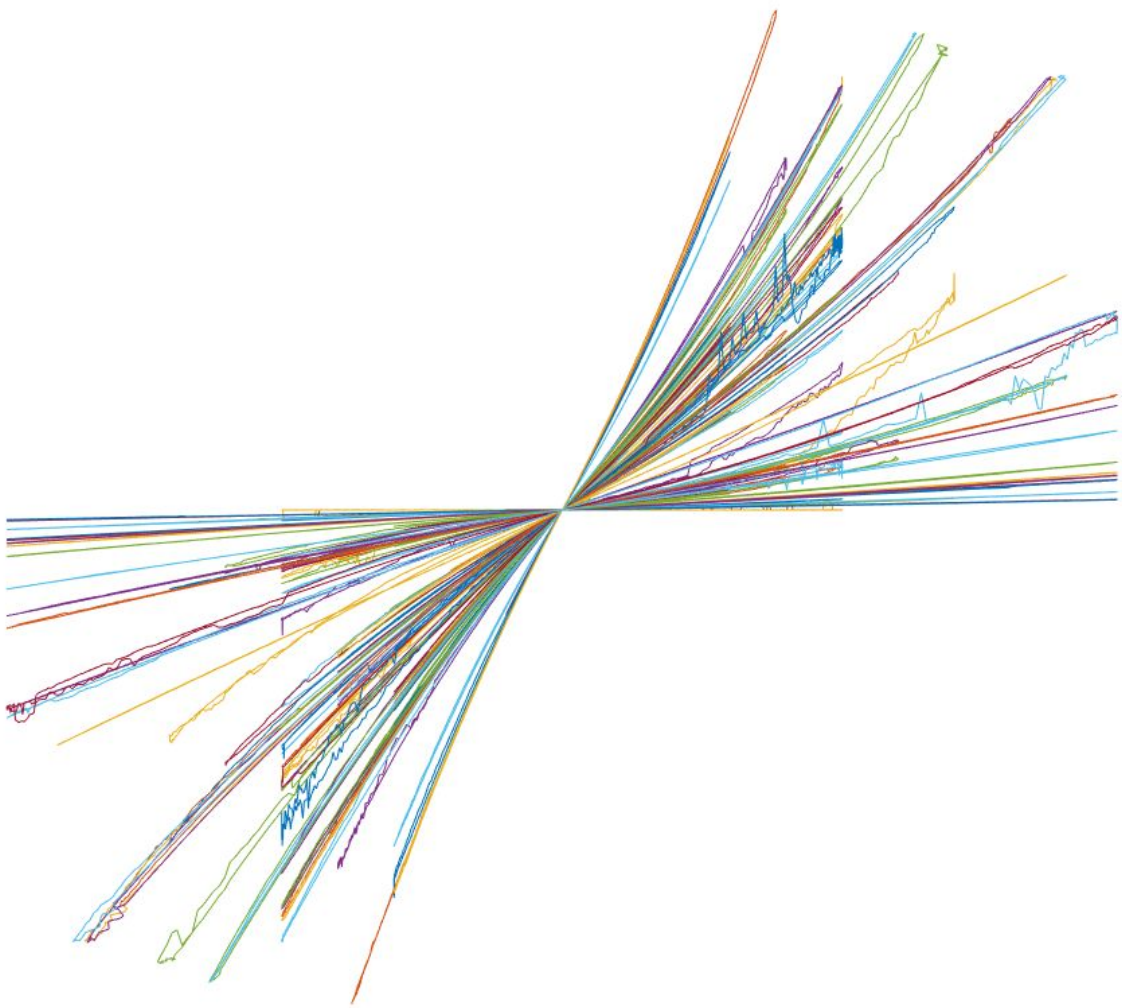

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Abstract

Computer technologies have seen immense growth for over half a century, but now that growth is beginning to slow. Technologies are reaching the physical boundaries of the materials we are using, and in order to continue to continue to advance, we need new materials and technologies. One of the proposed materials is carbon, and one of the proposed technologies is the Memristor.

In this thesis, samples of carbon nanotubes and carbon nanocones were prepared, and tested for memristive behaviour. The samples were tested with sinusoidal voltages to look for memristive characteristics, and experiments revealed clear memristive behaviour. This behaviour was then compared to that seen in Branly coherers. As observed for other coherers, multistable memristive behaviour and bistable resistive behaviour was observed.

Foreword

This thesis represents a part of the Master's degree in Materials, Energy and Nanotechnology at the University of Oslo.

I would like to give thanks to my supervisors Geir Helgesen and Ørjan Martinsen and for allowing me the opportunity to pursue studies in nanocarbon. I would also like to thank my associate supervisor Oliver Pabst, without his continued support, patience and custom built measuring equipment, this thesis would not have been possible.

I would also like to thank Nanyang Technological University for a great exchange during my master studies.

Lastly I would like to thank my friend Kjetil Almaas for sharing frustrations and challenges both scientific and bureaucratic over the course of our studies.

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Introduction

The Ages of human development have always been in large part been differentiated by materials and technologies. From Stone Age to Iron Age to the Nuclear Age, humankind have defined itself by the tools at its disposal. We are currently in the Age of Silicon, the age in which silicon based computer chips have become as omnipresent as the sand they are made from. Silicon chips, however, are reaching their physical limits, and research is being directed towards new materials and new solutions for computing. It is the goal of this master's thesis to shed some small light on the behaviours of carbon nanoparticles when subjected to current, especially looking at possible memristive properties, as carbon nanoparticles are one of many candidate materials that could allow continued growth in computing, just as memristors are one of the many candidates of new components to do the same.

For me, carbon based nanotechnology is one of those studies which echo the promise of the alchemists of old: To take something common, and transform it into something extraordinary. This first chapter will introduce some nanocarbon theory, the field of memristors, their history and application, Branly Coherers as well as the contributions and motivations of this project.

1.1 Materials Theory

1.1.1 Carbon Nanotubes

Carbon nanotubes are, as the name suggests, tubes of carbon, with walls that are only an atom thick. They are an allotrope of carbon, or perhaps more accurately, a class of allotropes of carbon. Carbon nanotubes can be thought of as a graphene sheets rolled up and fused to themselves, and just as sheets can be rolled upon themselves in almost infinite variations, so too is this true for carbon nanotubes.

While carbon nanotubes had been observed before, their discovery is usually attributed to Sumio Iijima in 1991, at which time Iijima determined their crystal structure.(Monthioux, Kuznetsov - Carbon, & 2006, 2006)

The basic tube shape lends itself to a wide variety of aspect ratios and structural layouts depending on the angle the graphene sheet is rolled, and the radius of the tube. Carbon nanotubes can be tuned to an almost infinite number of different physical and electrical states, with many factors affecting properties and the electron structure, such as bending, compression, length, surface adsorption and chirality.

Though there are a myriad of factors, certain patterns lend themselves to certain common properties, of which the most important classifier is whether the tube is *metallic* or *semiconducting,* in fact, the ability to tune their properties from highly conductive to semiconducting is one of the draws of carbon nanoparticles and nanotubes in particular, to be used in nanoelectronics.

In addition to the fascinating electronic properties of carbon nanotubes, they also happen to be the strongest material known to man, both in terms of tensile strength (Observed at 63GPa) and in terms of specific strength (48000 kNm/kg)

The structure of a carbon nanotube can be represented by a pair of indices, (n,m) where n and m are the number of unit vectors along two directions in the crystal lattice of the wrapped graphene sheet.

Due to the aromatic rings present on all carbon nanotubes, they will naturally form into ropes or long bundles from pi stacking, but the sp^2 hybrid bonds responsible for this behaviour also give CNT’s extremely low shear friction when interacting with each other, which is one of the reasons it is hard to make bulk structures out of carbon nanotubes; they simply glide apart.
Being hollow, carbon nanotubes are also able to nest inside each other, creating what is known as multi-walled carbon nanotubes.

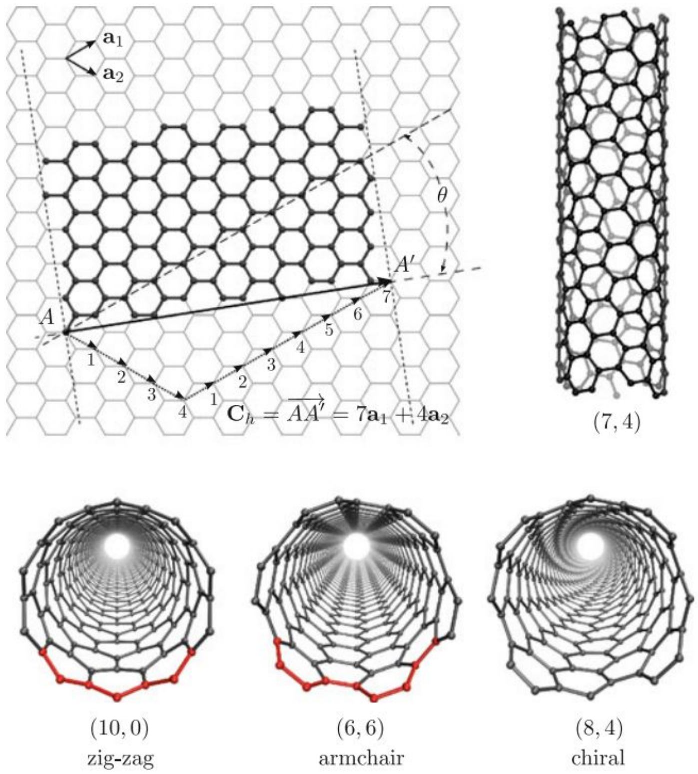

Fig 1. Structure of carbon nanotubes

“Top panel the graphene hexagonal lattice with lattice vectors a1, a2. The chiral vector Ch = 7a1 + 4a2 represents one wrapping of the graphene lattice to form the (7, 4) CNT which is shown on the right; rolling into a tube joins the two dashed lines. The shaded atoms represent the periodic repeating unit of this CNT. The chiral angle θ is defined as the angle between Ch and the a1 vector defining the zig-zag (n, 0) direction. Bottom panel the atomic structures of the zig-zag (10, 0), armchair (6, 6), and chiral (8, 4) CNTs; the zig-zag and armchair edges are indicated in red.” From (Bell, 2015)

1.1.2 Metallic Carbon Nanotubes

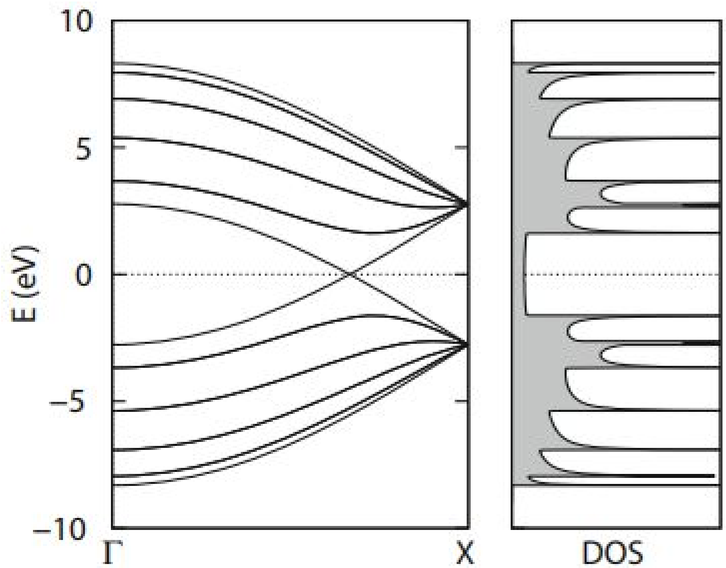

Fig. 2. Band structure and density of states for a (5,5) metallic Carbon nanotube.

From (Bell, 2015)

Metallic carbon nanotubes have conduction bands as one would expect from metals, though more ordered, owing to the stricter structure requirements. Metallic carbon nanotubes can theoretically handle current densities up to 4 Giga-amperes per square centimeter, or over one thousand times more than copper.(Hong & Myung, 2007) This makes them attractive for many electronic applications. Carbon nanotubes are, however, not nearly as conductive between tubes as they are the length of a single tube. This is an obstacle to using Carbon Nanotubes for anything other than very small applications.

1.1.3 Semiconducting Nanotubes

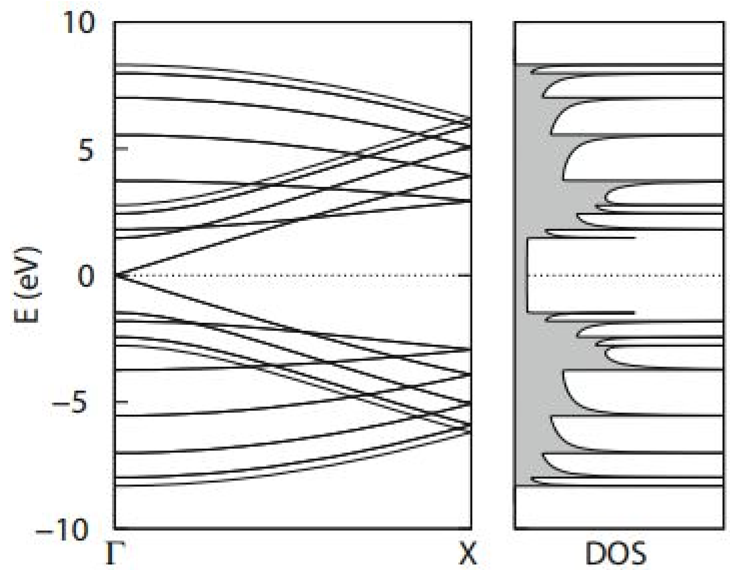

Fig. 3 Band structure and density of states for a (9,0) achiral nanotube.

From (Bell, 2015)

The band gap of semiconducting carbon nanotubes are directly affected by their chirality and diameter, meaning they could potentially be used to create fine tuned nano-circuitry.

Whilst metallic carbon nanotubes are attractive for their high conductivity, semiconducting carbon nanotubes are mainly attractive for their potential as tunable electronic components. There are many examples of using semiconducting CNT's for construction of classic and tunneling field effect transistors.

1.1.4 Carbon Nanocones

Carbon nanocones are, like carbon nanotubes, allotropes of carbon. Like carbon nanotubes they can be thought of as graphene sheets fused to themselves, but in this case rolled at an angle, much like a funnel rolled from paper. Carbon nanocones are distinct from tipped nanowires by the aspect ratio of their height to diameter.

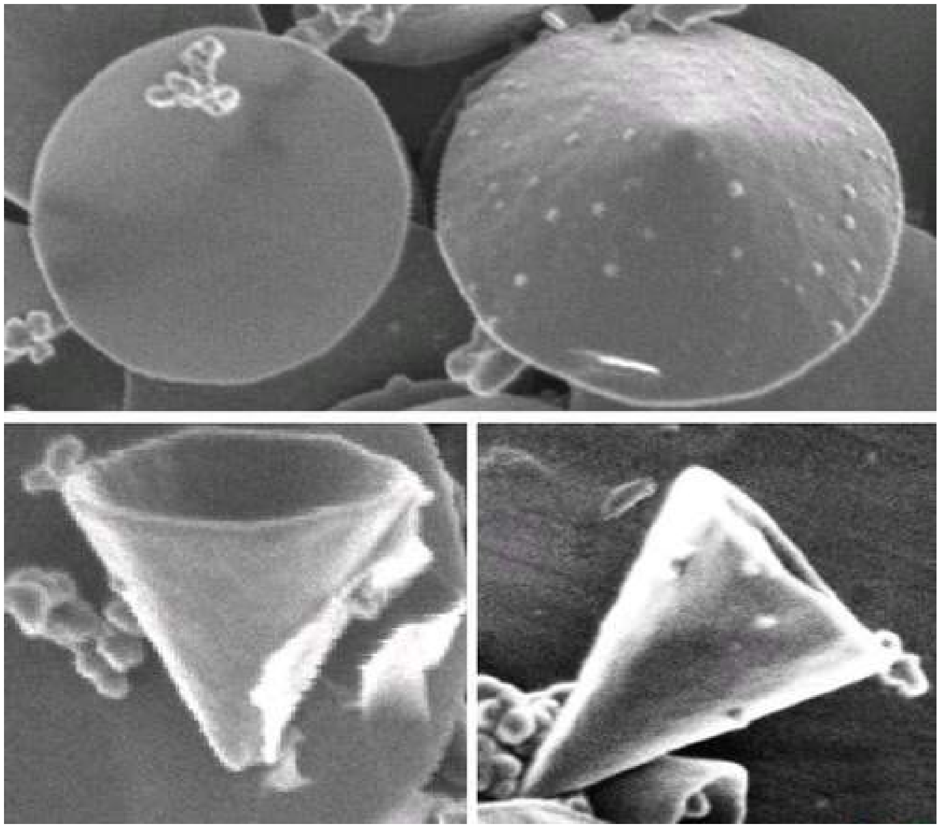

Fig. 4. SEM images of Nanocarbon Disks and Cones

Sem images of a carbon disk (top left image) and free-standing hollow carbon nanocones produced by pyrolysis of heavy oil in the Kvaerner Carbon Black & Hydrogen Process. Maximum diameter is about 1 micrometer. (Naess, Elgsaeter, Helgesen, & Knudsen, 2009)

Nanocones occur naturally on the surface of graphite, or can be produced with the Kværner process, using a plasma torch and finely tuned temperatures and pressures. It has been revealed through electron microscopy, that the cones have preferred apex angles of approximately 20, 40 and 60 degree opening angles.(Naess et al., 2009) This preference is due to the need for one or more rings near the tip to have between three and five carbon atoms instead of graphenes usual six, as the six ring is strictly planar.

In the same study, electron diffraction was performed, suggesting the walls of the cones are a mixture of amorphous carbon and graphene layers, with the graphene layers encapsulated by the amorphous carbon. The amorphous carbon in our samples have been converted into well ordered graphite by annealing the cones at 2700 °C.

Like carbon nanotubes, the cones may stack inside each other, creating multi-walled structures.

1.1.5 Branly Coherer

A Branly Coherer is a centuries old piece of technology, and as will be shown in this thesis, the samples in this project are shown to act as coherers, which in turn act as a specific kind of memristors. The original Branly Coherer is a device made by Edouard Branly, after he observed that conductive powders and other imperfect contacts gained increased conductivity when subjected to strong changes in electromagnetic fields. (Such as a spark.)

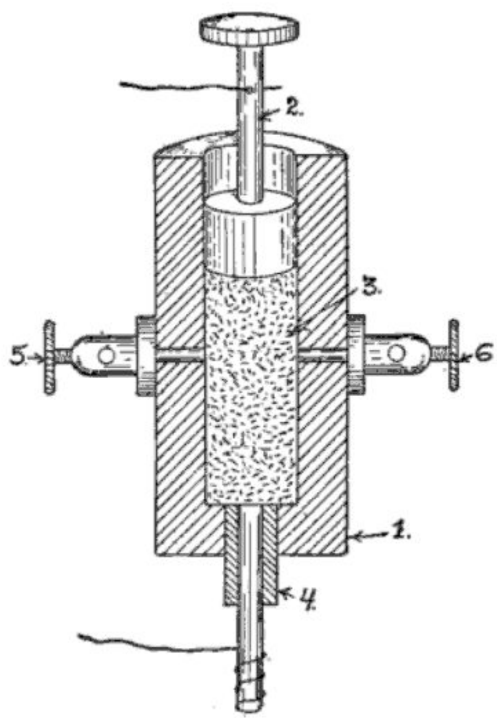

Fig. 5. Original Branly coherer design from (Collins, 1905)

The original coherer came in several forms, including tubes filled with metal balls and spikes touching conducting plates. However, the most recognisable in the context of this thesis is a device consisting of two electrodes interspaced with a granular conductive medium like metal filings. When this device is subjected to a radio signal, the “cohering,” as it has been termed, allows for higher current through the powder. The conductivity could then be reset by physically shaking or tapping on the system. Using this as his baseline, Branly created a series of signal detectors, some of which became the first radio detectors.

1.1.6 Potential Cause of Cohering Behaviour

It has been theorized that the change in conductance in coherers in mainly due to the oxide layer on metal filings. As will be shown in this work, that is unlikely, as the materials being used do not have the oxide layers to support this.

According to (Eric Falcon & Castaing, 2004) the effect is likely a result of joule heating in the contact points between particles, resulting in a micro-welded interface. In many materials, such micro welding would be of little interest, but in a powder of carbon nanotubes, this would mean the creation of current carrying welded interfaces between tubes, opening up the potential for manufacture of composite structures of several smaller tubes. (The potential to use current to fuse tubes has been shown in experiments by (Jin, Suenaga, & Iijima, 2007), where single tubes were moved close to each other in an electron microscope and the tubes fused through a hypothesized combination of joule heating and electromigration effects.)

In 2013 (Gandhi & Aggarwal, 2013) showed that coherers have memristive behaviours, and in 2014 they published a more detailed study with Leon Chua, the “father” of the memristor. (Gandhi, Aggarwal, & Chua, 2014) Their work has been used extensively in this thesis. They also performed preliminary testing with polished gold balls, and their results lend credence to the coherer effect not being the result of oxide layers.

1.2 Electronics Theory

1.2.1 Impedance

Impedance is a term coined by Oliver Heaviside in 1886, and is the measure of the resistance or *opposition* that a circuit presents to the current when voltage is applied.

The impedance of a standard two terminal circuit is the ratio of the complex representation of the sinusoidal voltage between the terminals to the complex representation of the current.

More simply, impedance extends the concept of resistance to alternating current circuits, but with the added property of *phase.* Put another way: Resistance in a DC circuit is the impedance with the phase angle at zero.

Impedance is a vector made of two properties, the resistance, and the reactance. The resistance, as mentioned above, is a measure of how hard it is for electrons to move through the material, this is expressed in Ohms.

Reactance, is denoted with X and expresses “slowness” or “momentum” in the circuit, based on the extent to which components in the circuit stores and releases energy, as the voltage and current fluctuate through the AC cycle. Reactance is expressed as an imaginary number of Ohms, and is observed when AC passes through a components that has a reactance, meaning it will store or release energy in the form of a magnetic field (inductive, denoted $+jX_L$) or it may be stored and released in the form of an electric field (Capacitive, denoted $-jX_C$)

1.2.2 Memristor

The word memristor is a fusion of the words *memory* and *resistor,* and describes an electrical component that combines the properties of a resistor and memory. The original definition, and coining of the name was first proposed by Professor Leon Chua at the University of California, Berkeley in 1971. In his paper “Memristor - The Missing Circuit Element” Chua defined a memristor as: “a non-linear passive two-terminal electrical component relating electric charge and magnetic flux linkage.”(L. Chua, 1971) In other words, the memristor is a component in which resistance depends on the history of current passed through it.

The existence of memristors was proposed based on the relationships between the four fundamental circuit variables, charge, voltage, current and flux.

The classic basic circuit elements are resistor, capacitor and inductor, defined by their relationship to the four fundamental circuit variables, current, voltage, charge and flux.

$R = dv/di$ for resistors,

$C = dq/dv$ for capacitors

and

$L = d\varphi/di$ for inductors.

Chua made the case that there should be mathematical symmetry, resulting in

$M = d\varphi/dq$ for *memristors.*

A popular illustration of this relationship is shown in figure 6.

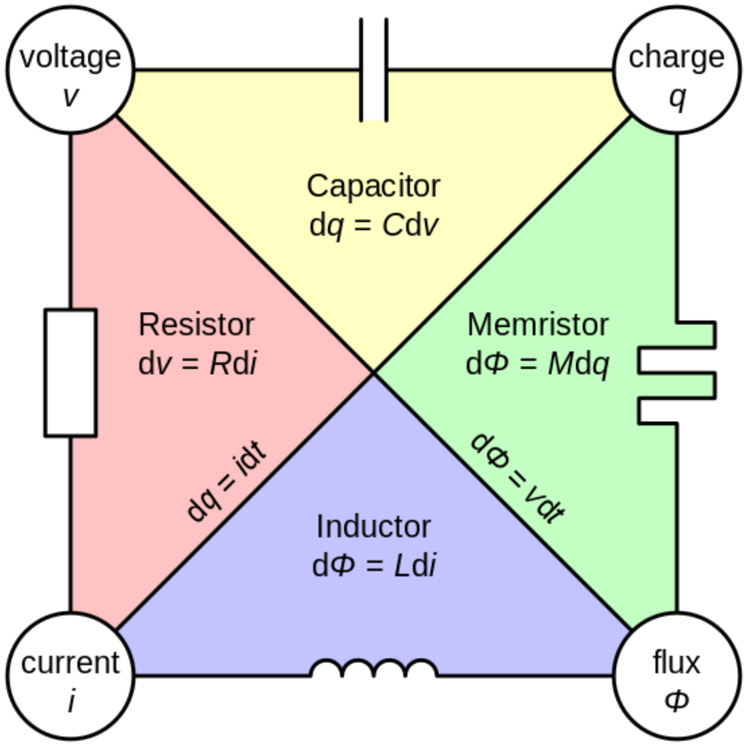

Fig. 6 Popular illustration of memristor symmetry argument.

From (Wikipedia contributors, 2018)

The relationship shown below is very useful:

$$M \equiv \frac{d\varphi}{dq} = \frac{v \cdot dt}{i \cdot dt} = \frac{v(t)}{i(t)} [\Omega]$$

Where M is the memristance.

For an extended period of time, the memristor remained for the most part a theoretical component. Then in 2008 HP labs announced in Nature that they had found the missing circuit element, and presented a basic model of memristors based on Chua's mathematical theory. Since then many common devices have been identified as different kinds of memristor, from the electric arc of 1801 to the Hodgkin-Huxley Axon circuit model of the squid giant axon, to human neurons. Chua has stated, that:

“...memristors are not inventions. They are discoveries and are ubiquitous.”(Adamatzky & Chua, 2014)

1.2.3 The Pinched hysteresis loop

The fingerprint of a memristor is the pinched hysteresis loop. When a memristive device is affected by a periodic current that assumes both positive and negative values, a plot of the IV characteristics will be a pinched hysteresis loop. Leon Chua has stated, that *“If it's pinched it's a memristor.” (Leon Chua, 2014)*

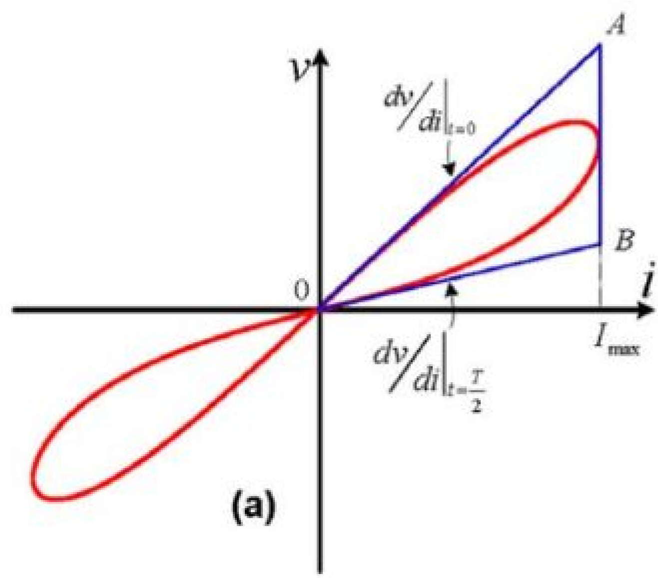

Fig. 7 Example of a pinched memristor I/V loop.

(Adhikari, Sah, Kim, & Chua, 2013)

1.2.4 Non-Linearity & Crossbar arrays

Non-linearity(NL) in electric circuits is simply behaviour where the output does not rely linearly on the input. In this thesis we adopt the measure of nonlinearity used for memristors by (Joshua Yang et al., 2012).

$$NL = \frac{I_{max}}{I_{(0.5V_{max})}}$$

The non-linearity of a memristor system is important for many electronics applications, one of which is crossbar arrays, one of the most promising memristor based memory technologies.

Crossbar arrays are components that consist of a grid of conductors isolated by a memristor or other logical gate. By manipulating which conductors are active, a crossbar array can store information very densely. The maximum number of junctions in a crossbar array is limited, because any junction touching and active conductor is "Half active" with a voltage drop of half that of the active junction. This leads to what is known as sneak currents, and is the main limiter on crossbar size. Therefore computing and storage ability of a crossbar array is determined by how large the nonlinearity is. With a high nonlinearity, the sneak currents flowing through half selected memristor-junctions are much lower.

1.2.5 Multistable Memristive Behaviour

Multistable memristive behaviour is the phenomenon where a memristive device can hold a memory at several different resistances, depending on the strongest pulse to have affected the system. This behaviour was observed in (Gandhi & Aggarwal, 2013). As a device is exposed to larger and larger peak currents, it programs itself with different resistance values and a different nonlinearity profile. When the input current is smaller than the strongest current that the system has experienced, there will be hysteresis loops following the nonlinearity profile brought on by the stronger current. This multistability is one example of a memristor like effect, but there is a second effect that is more in line with the classical thinking for memristors, which we will get to in a moment.

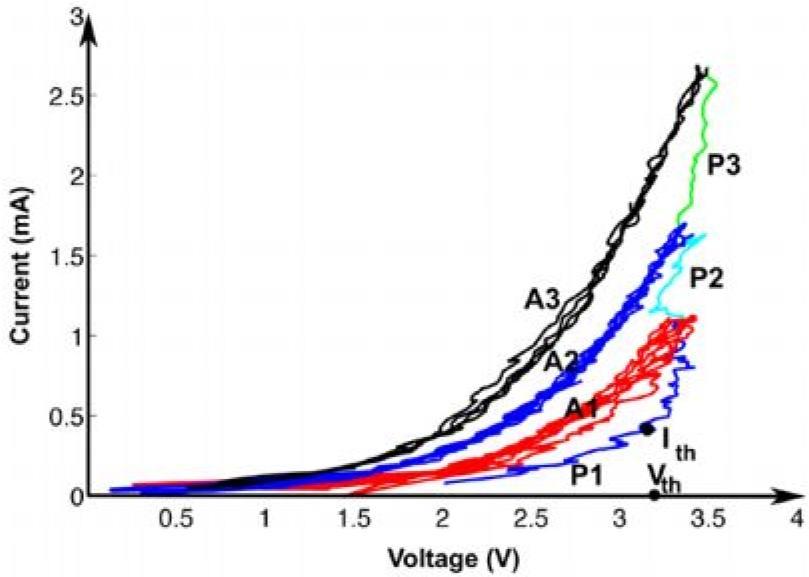

Fig. 8 Example of multistable memristive behaviour.

The different current is programming different resistance values. From (Gandhi et al., 2014)

1.2.6 Bistable Resistive RAM

Bistable memristive RAM behaviour is a kind of programmable behaviour that may be read without changing the state and can be put into two different states, and freely switched between these states. In the case of a memristor like ours, the programming happens due to positive or negative bias, and can be read with lower voltages.

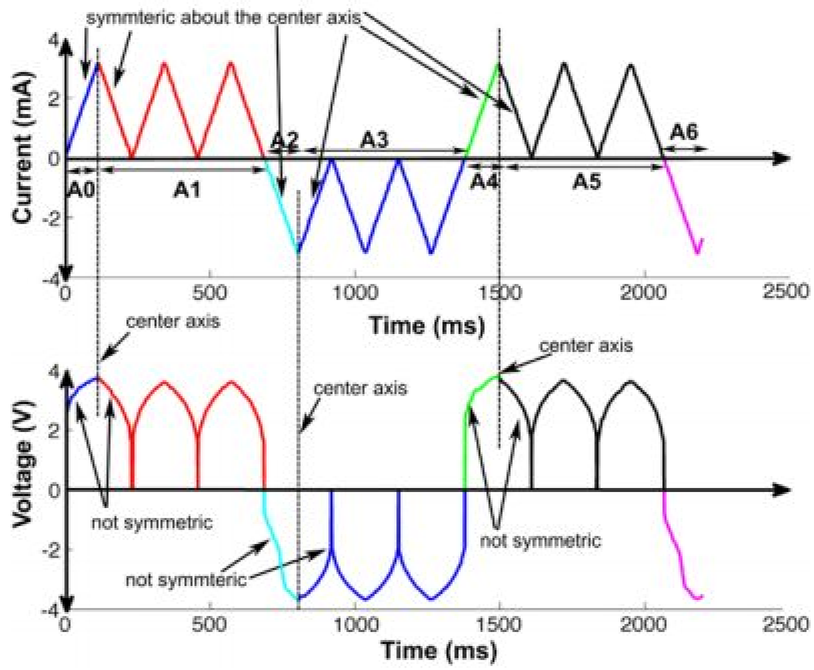

Fig. 9 Bistable memristive behavior

(a) Input current vs. time, (b) Voltage across device versus time.
The switching behaviour when going from a positive to a negative bias and back can be clearly observed.From (Gandhi et al., 2014)

2. Materials & Methods

2.1 Experimental Setup

The first experiments were exploratory in nature, testing the limits of our equipment, and adding resistances where needed as the equipment was originally meant for bioimpedance measurements. (Which deal with much higher resistance.) For these initial experiments the experimental vessel was a simple plastic tube with a cross-section of 0.5mm and electrodes in each end. The measuring equipment was the same as that described below.

After the first exploratory experiments were finished, glass vessels were designed to be able to look for changes, as well as accommodate different aspect ratios, the addition of fluids, and potential addition of inert gas.

The main experimental vessels consist of a glass vessel made up of four microscopy slides glued together with UV-cured locktite or thermal glue, arranged so there is a middle channel. The size of the channel was varied between samples to allow for different configurations.

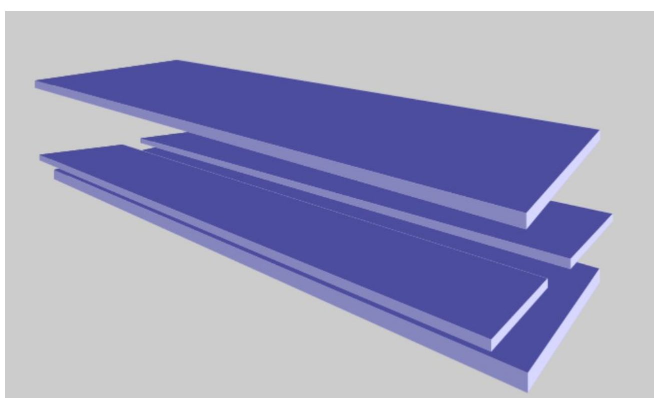

Fig. 10 Exploded view of vessel

These are standard 5cm glass microscopy slides.

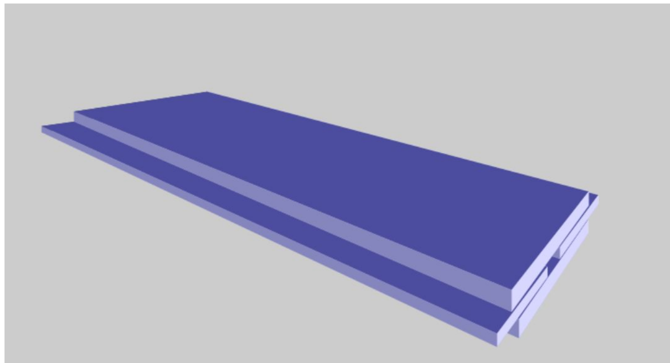

Fig. 11 Assembled View of vessel

Same slides, assembled, showing the central void.

An electrode is glued into each end of the channel, and a powder of carbon nanotubes or nanocones added to the channel before the vessel is glued shut.

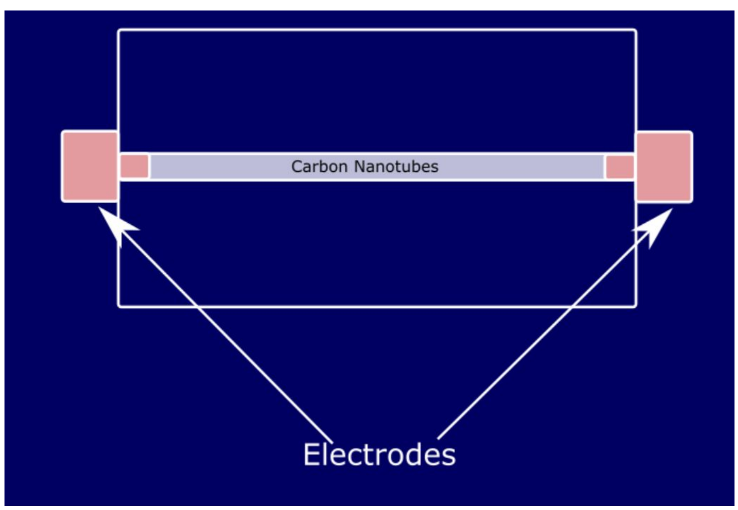

Fig. 12 Overview of sample

The final samples look like this:

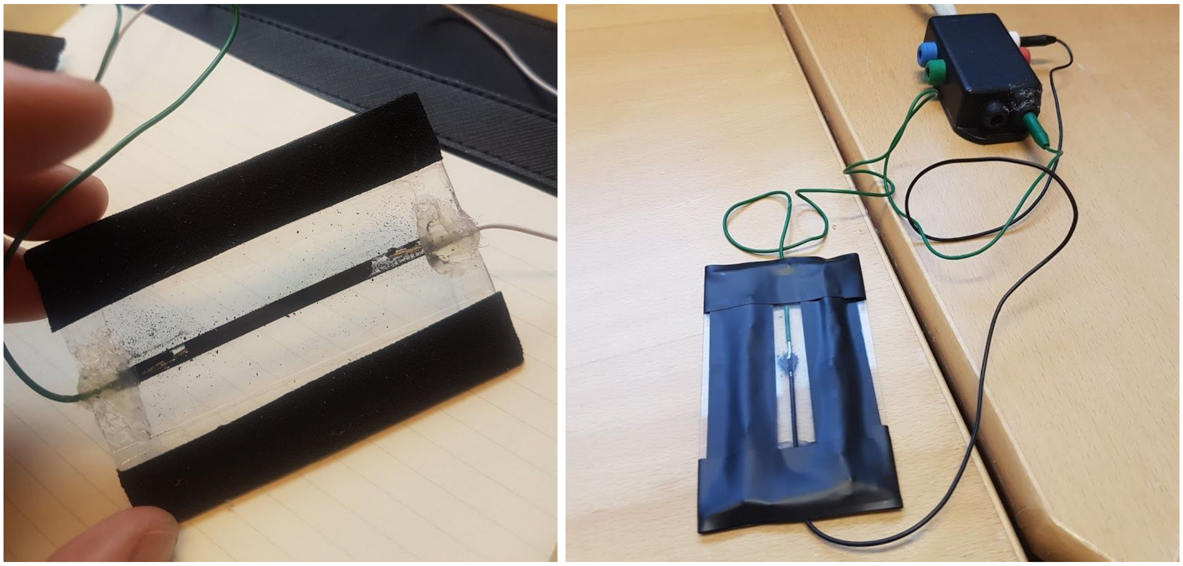

Fig. 13 Final design of Sample holders

On the left: The 4cm loose packed sample that was used for exploratory experiments. The astute reader might notice the almost complete absence of powder near one of the electrodes. Even so, the residue stuck on the vessel walls were enough to carry measurable current.
On the right: The most used carbon nanocone sample, with an electrode gap of 1mm, attached to the ports of our measuring apparatus.

In the figure above, can be seen the 40mm gap sample. The large gap and loose packing allowed us to test several different configurations of the nanoparticles, from continuous powder to nearly breaking the circuit in one end. There were several samples created to look at effects from packing density, with gaps of 1mm to 40 mm. As will be shown in the data, even just a single slide can adopt a large range of states, and the focus was therefore ultimately placed on the two 1mm gap slides, one for nanocones and one for nanotubes.

2.2 Measuring Technique

The instrumentation used for these experiments is a modified version of the instrumentation used in (Pabst, Tronstad, & Martinsen, 2017) and consists of a two electrode system. A data acquisition box generates a sinusoidal output, taking the role of oscilloscope and function generator.

Multiple runs were conducted with samples of different widths, from 1 mm to 40 mm, at different voltage amplitudes and frequencies. This data was then processed in Matlab to characterize the ranges of outcomes in lobe area, non linearity and max current.

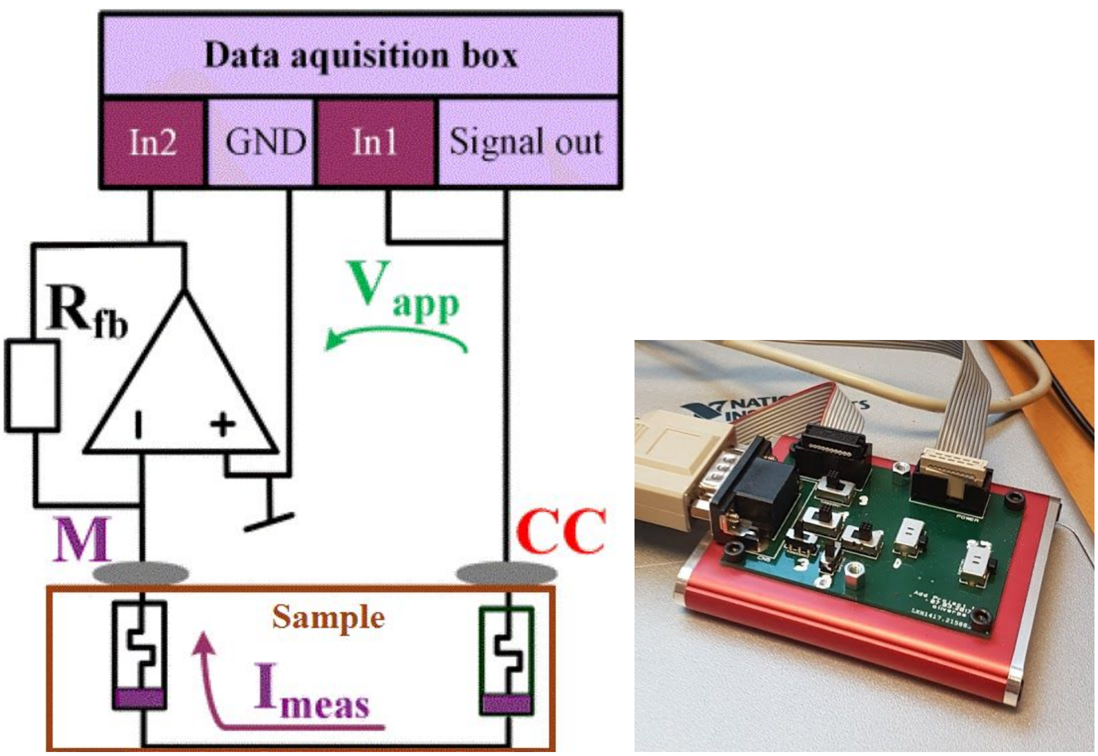

Fig. 14. Measuring equipment

On the left: Circuit diagram of instrumentation.
On the right: Picture of the instrumentation.

2.3 Data Processing

All data processing was done by importing the Excel files from our measuring equipment into Matlab using the *xlsread* command, and handling them as sets of data there. There are three main plots used.

2.3.1 Hysteresis plots

The hysteresis plots are a simple case of plotting the current and voltage data sets to each other.

2.3.2 Lobe area

The lobe area calculation uses the *trapz* function to integrate over half of each lobe, and subtracting one from the other. In spite of the inaccuracies of the trapz function, the accuracy is sufficient for our purposes given that each lobe consists of 250 tightly spaced points.

2.3.3 Resistance

Since the behaviour of this device is non-linear, the term resistance is not a constant, but varies with the current, voltage and state of the system. We treat this as a Non-linear DC resistance, as is also used in (Gandhi et al., 2014) for ease of computation and comparison. Resistance over time was calculated very simply as a series of momentary resistances for every point in the data.

3. Results

3.1 Initial results

It was clear from early on despite our very varying measurements, that we were seeing hysteresis loops in our exploratory experiments, albeit with small memristive values. With the phrase “if it’s pinched, it’s a memristor” in mind, consider the following IV graph for two full periods:

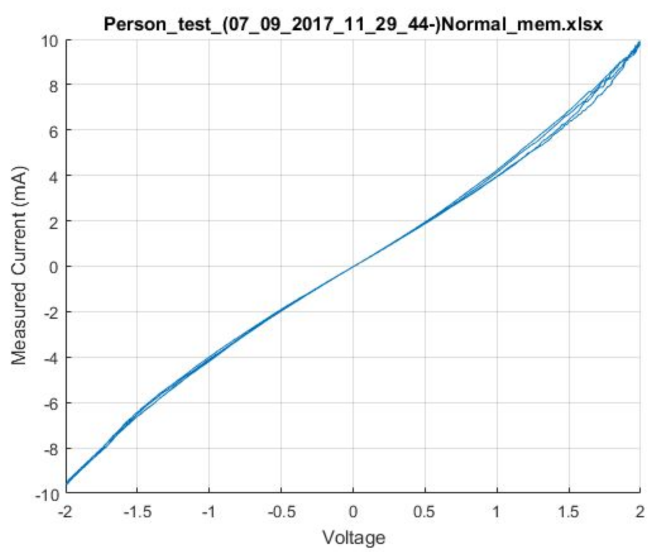

Fig. 15. The “Fingerprint” I/V loop for a memristor, from an early carbon nanotube sample.

This run on a carbon nanotube sample clearly showed the fingerprint of a memristive system and further samples were prepared and analyzed. As more test were run on our powder samples, a challenge was discovered.

3.1.1 Variance in single samples

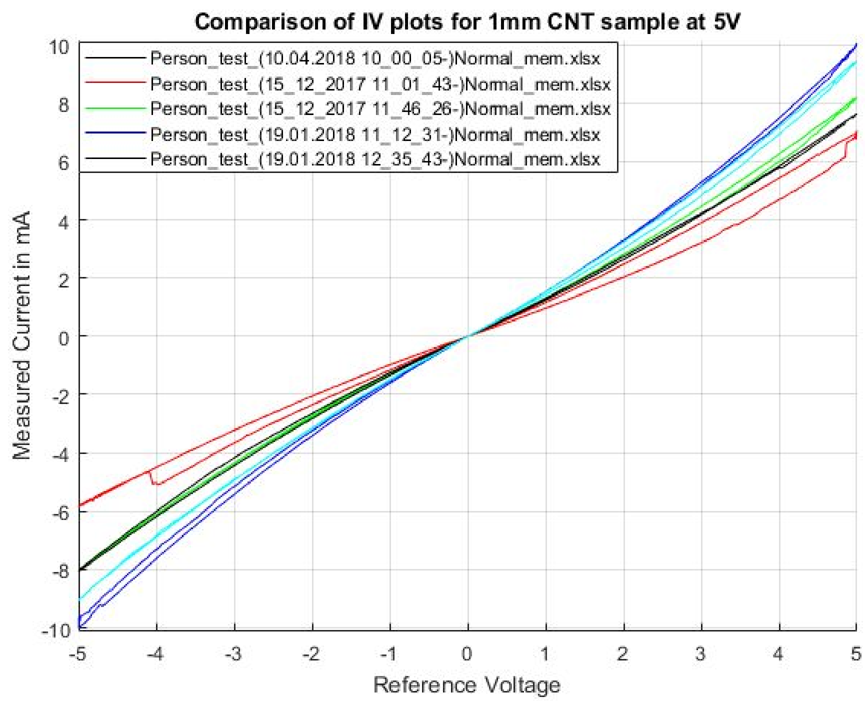

Fig. 16 Multiple distinct IV loops for the same 1mm sample, using the same parameters (5V AC, 0.05Hz.)

The above IV curves in Fig. 6. all represent different runs on the same sample, using the same parameters. It soon became apparent that due to the various configurations available in such a large network (in this case 1mm x 1mm x 1mm), even the individual samples can adopt vastly different characteristics.

After running several experiments and collecting data, it became clear that the more compacted the carbon nanopowder, the less memristive behaviour was observed, and that the larger samples had more unpredictable results.

As this was the case, although there is extensive data available for all samples, focus has been placed on 2 samples, both loose packed samples with 1 mm electrode gaps, one with carbon nanocones, and one with carbon nanotubes. The memristive behaviour was still present in the other samples, but for the sake of characterization they will not be included here.

3.1.2 Confounding factors tested for

When first encountering the discrepancies between runs, several attempts were made to identify what could be causing these differences. Further research may rest assured that we tested the slides from 0C to 50C with little to no conclusive results. Sound and vibration (using a smartphone) was also tested for, and found to have little to no effect. For some time we thought magnetic fields may be the cause, as carbon nanotubes have been shown to be magnetostrictive. Placing a magnet on the samples also seemed to clearly change the conductivity of the samples, however, after further experiments were showing inconsistencies, it was discovered that the slight weight of the magnet on the glass slides or in the converse situation the weight distribution of the glass slides when placed on top of the magnet, bent them imperceptibly, which seemed to be the cause of the changes. In short, the different properties of the same sample on different runs seems to be a result of the near infinite configurations the powders can assume in a 1mm x 1mm x1mm enclosure, especially when affected by even small mechanical disturbances. It also disproved one of our earliest hypotheses, namely that in such a large network, such changes would average out.

3.1.3 Physical switching between configurations

When testing a sample, an attempt was made to tap the sample to change the characteristics of the network. Plotting the area of each lobe as a function of time we can see a switch from one state to another:

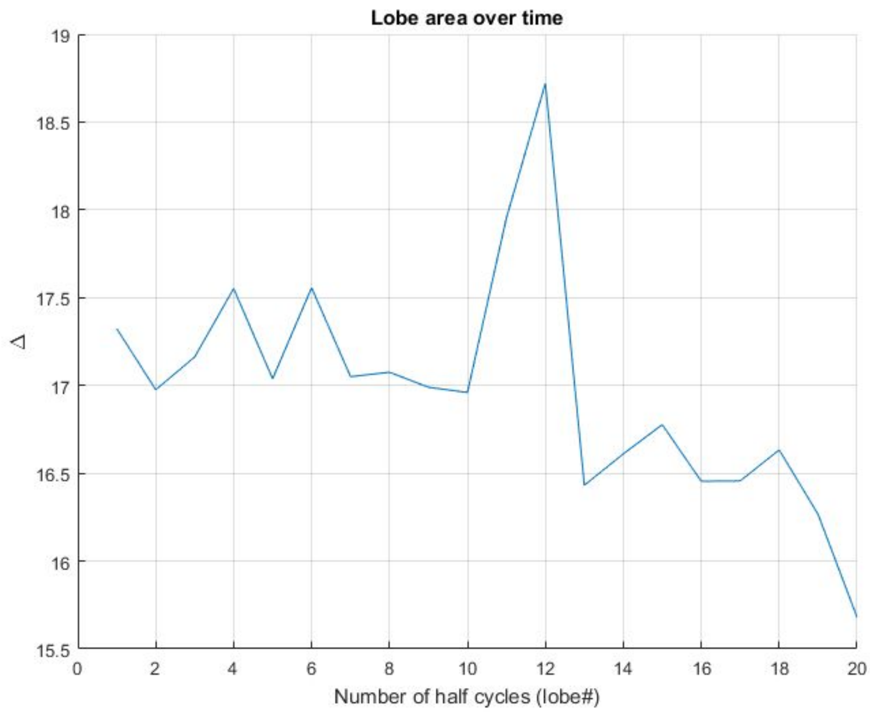

Fig. 17. Lobe area of two different memristive states.

Here we see the lobe area spike high as the tapping happens (Cycle 10 through 12), and then the system enters a state with less memristive behaviour after the spike.

This change in states is also very clearly visible in the IV plot.

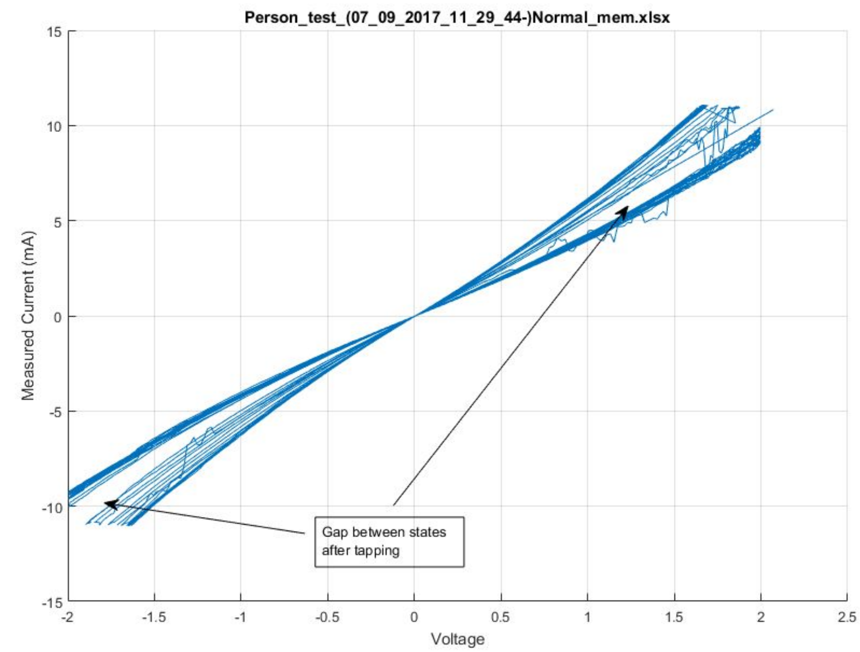

Fig. 18. Two different IV characteristics before and after tapping.

This multi-configuration behaviour was observed for both carbon nanotubes and carbon nanocones, and shows a definite need to treat carbon nanoparticles as a complex network of conductors rather than simple granular media.

3.2 Branly Coherer behavior

When comparing our data with the work of (Gandhi & Aggarwal, 2013) it becomes very clear that our samples are conforming to their models for Branly coherers and memristors. This is interesting for several reasons, perhaps most of all because it disproves one of the main theories for how these coherers work. The only point where our samples differ significantly in behaviour is the strict cohering behaviour reported.

3.2.1 Cohering Behaviour

Potentially because of the many different conductive paths of the samples, the classical sudden cohering behaviour was not observed. Rather, there was a gradual shift from linear to non-linear behaviour as the current increased. It is possible there was cohering action too minute to be detected by the equipment. In this plot of the resistance over time for carbon nanocones at a max voltage of 1 to 5 volts, it is clear that the resistance becomes less linear as the max voltage increases, but there is no clear distinction between the multistable memristive behaviour and the more linear behaviour of the 1V sample.

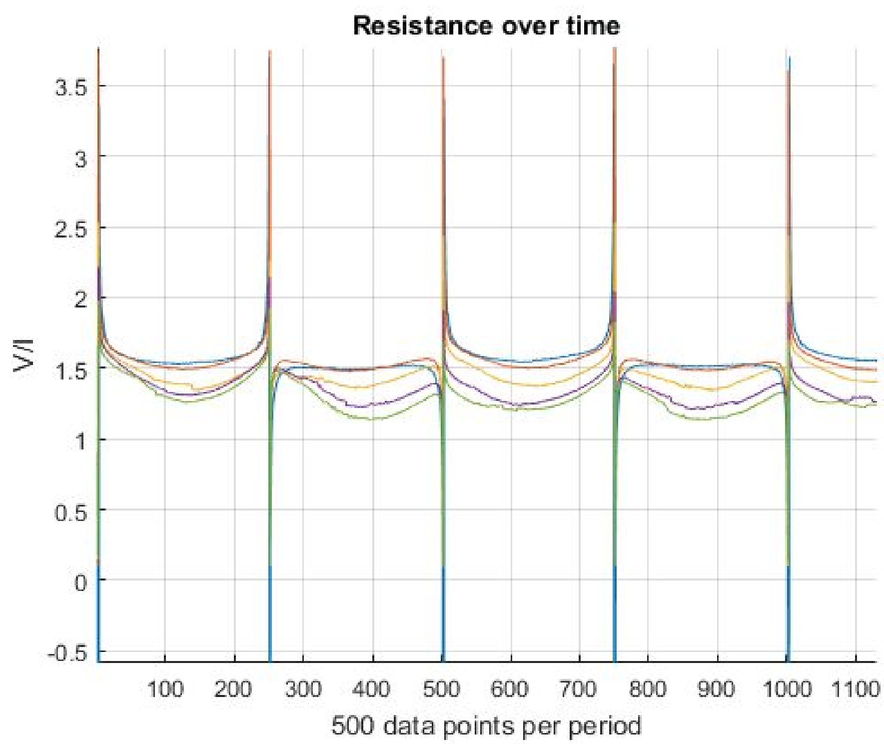

Fig. 19. Resistance over time for 5 different voltages.

showing gradual transition from linear to more apparent non-linear behaviour. Sample is Carbon Nanocones, 1mm gap.

3.2.2 MSMB in Carbon Nanocones

The carbon nanocones were tested at incremental voltages without disturbance from 1V to 9.9 V, and then again at 5V which resulted in the following IV plot:

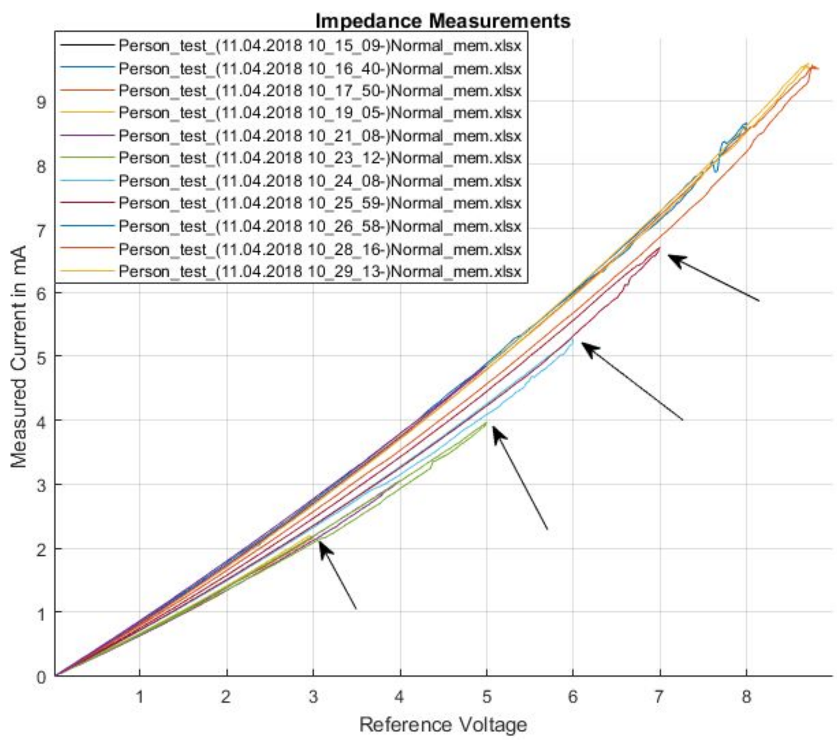

Fig. 20. Multistable memristance states from different max voltages.

Starting at 1V going up to 9.9V. Arrows indicate the apex of 3V, 5V, 6V and 7V for comparison and clarity.

Here it is apparent that the system has retained a memory of the previous max current, presenting a different curve for each ascending voltage.

Isolating the first 5V run, the 9.9V run and the second 5V run there is a clear difference, between the initial run, showing easy readability.

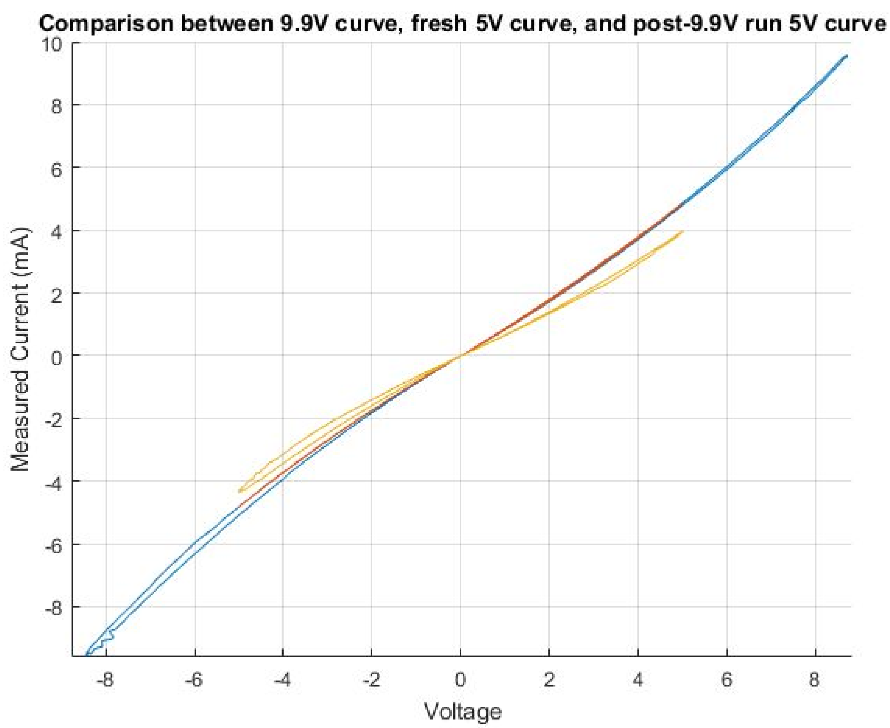

Fig. 21. Programming and reading Carbon Nanocones.

Graph of an initial 5V curve (yellow), the following 9.9V curve (blue) and a curve at 5V after the 9.9V curve (Red). The programming of resistance can clearly be seen.

3.2.3 MSMB in Carbon Nanotubes

The carbon nanotubes showed similar behaviour to the carbon nanocones, using a run at 4V followed by a run at 9.9V, followed again by a run at 4V the change in conductance brought about by the high voltage becomes apparent. It is not as pronounced in the carbon nanotubes as it was in the carbon nanocones.

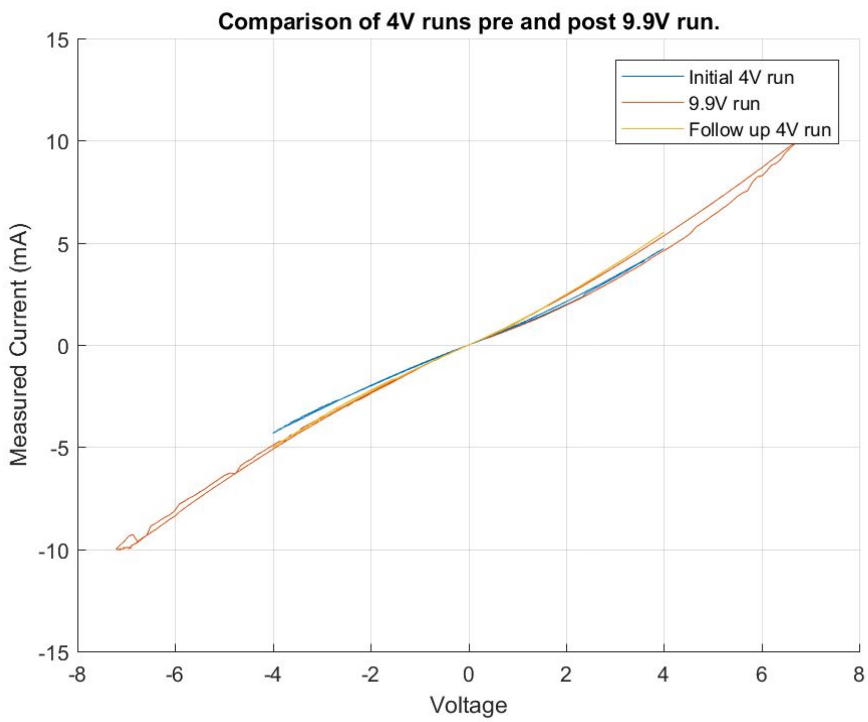

Fig. 22. Programming and Reading Carbon Nanotubes

Graph of an initial 4V curve (Blue), the following 9.9V curve (Orange) and a curve at 4V after the 9.9V curve (Yellow). The programming of resistance can clearly be seen.

3.3 Bistable Resistive RAM

As reported by (Gandhi et al., 2014) for other coherer type memristors, even after settling into one of the multistable states, there are still memristive effects. This persists not only after high voltages, but also over many cycles.

3.3.1 Bistable Resistive RAM behaviour in Carbon Nanocones

When a bipolar input is applied, the system switches between two different resistance states, and the current response is asymmetric when switching.

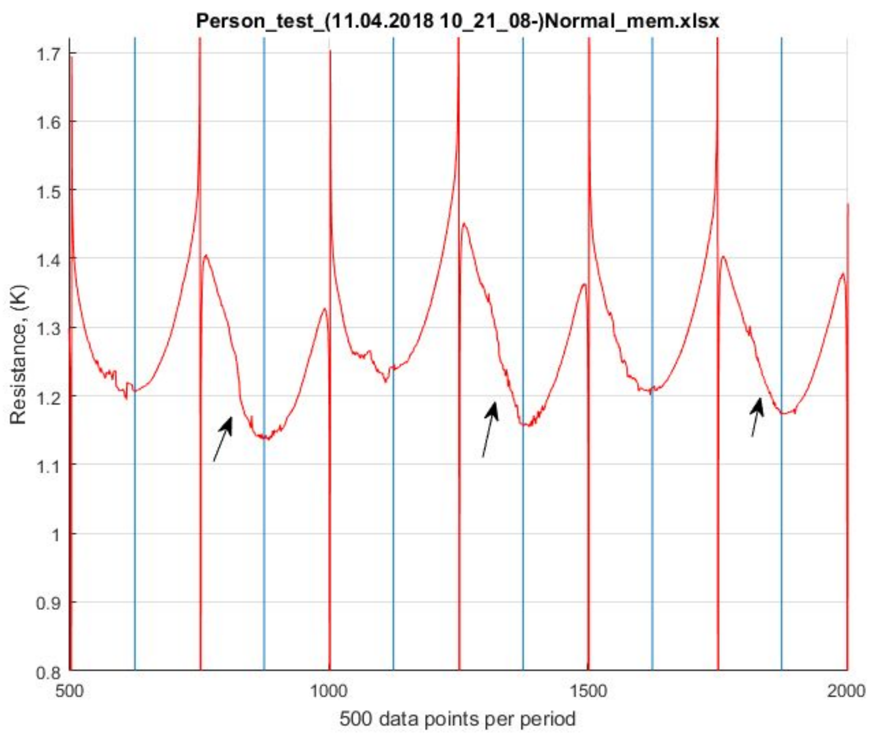

Fig. 23 Asymmetrical response showing switching for carbon nanocones.

5V AC, 0.05Hz. Arrows indicate clear asymmetry. Blue lines indicate peak voltage.

3.3.2 Bistable Resistive RAM behaviour in Carbon Nanotubes

As with the carbon nanocones, the application of a bipolar input switches the system between two different resistance states, and the current response is asymmetric. The switching between memristive states is stable for many cycles, as can be seen in fig. 25.

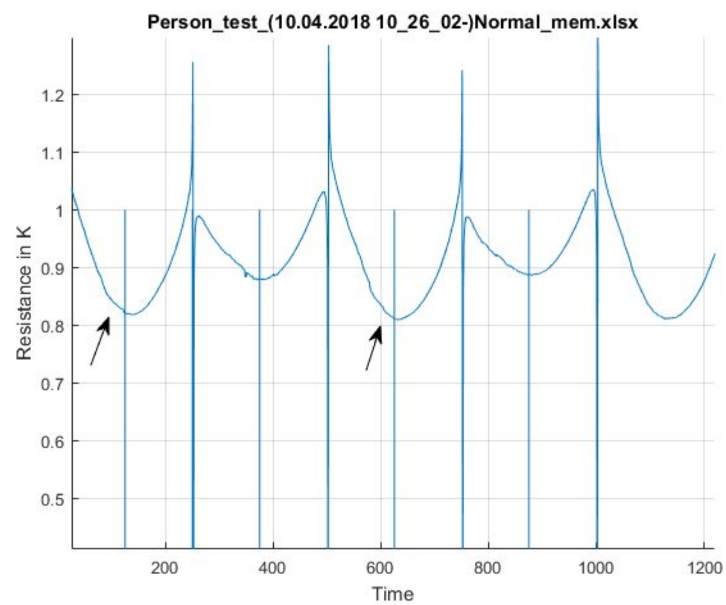

Fig. 24 Asymmetrical response showing switching for carbon nanotubes.

5V AC, 0.05Hz. Arrows indicate clear asymmetry.

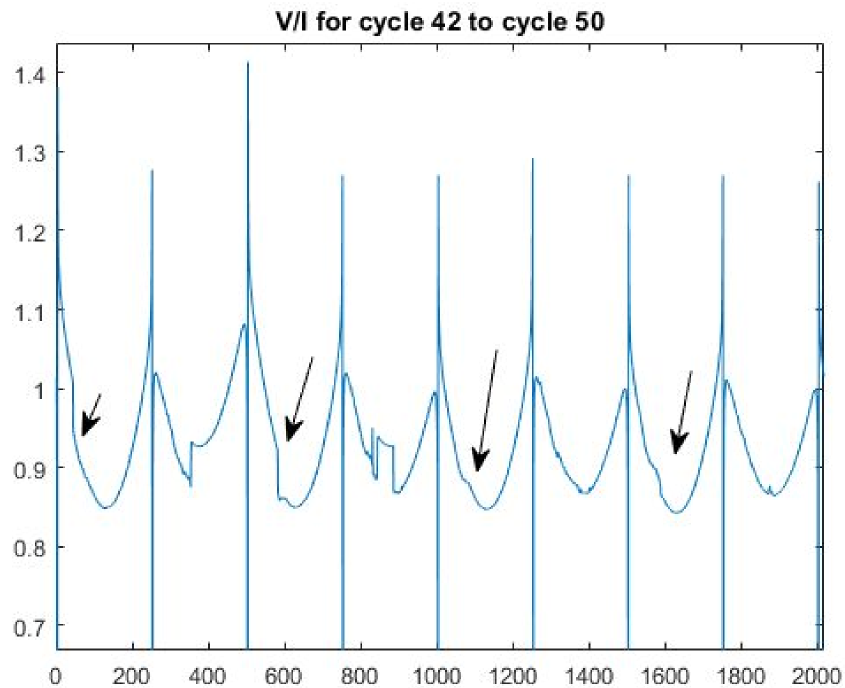

Fig. 25 Asymmetrical response showing switching for carbon nanotubes after 42-50 cycles.

5V AC, 50Hz Arrows indicate asymmetry.

3.4. Conductance change in carbon nanotubes

Looking at the data for several runs of carbon nanotubes, some runs has a trend where the resistance was slowly increasing. More runs were done, and the trend was shown to be present in only a few samples. The result has been included for anyone who encounters this effect, as though it did not happen in the majority of runs, it happened in several.

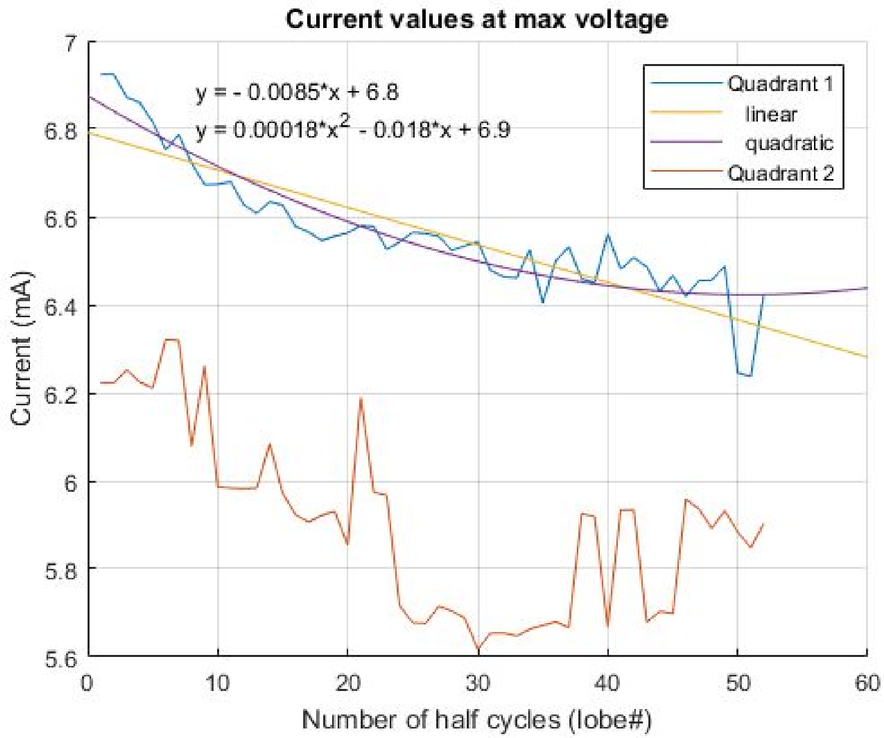

Fig. 26. Apparent rise in resistance, not observed for all runs.

3.5.1 Nonlinearity in carbon nanocones

Using the definition of nonlinearity as defined in the introduction:

$$NL = \frac{I_{max}}{I_{(0.5V_{max})}}$$

The nonlinearity is plotted as a function of time (cycles), and shown to be within 1.45 and 1.7 even after cohering at 9.9V.

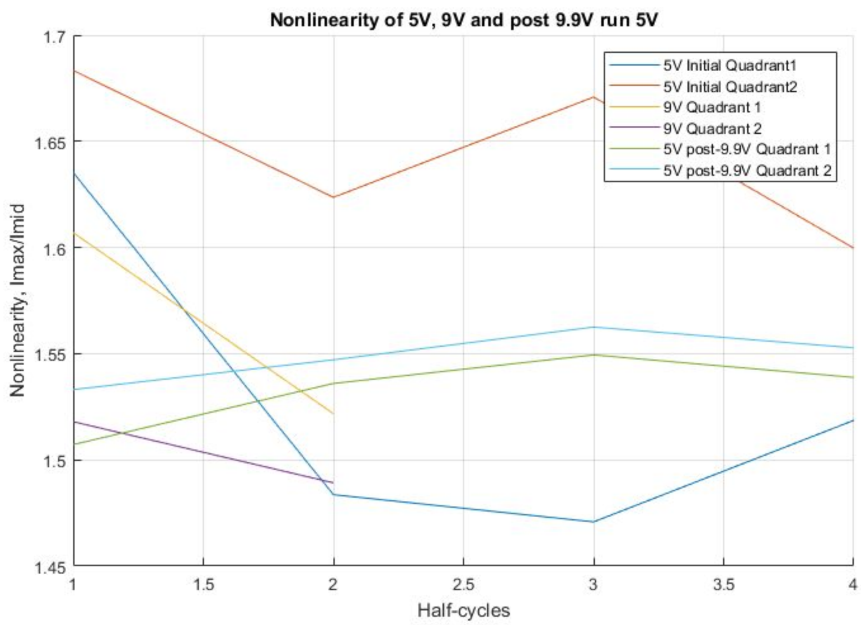

Fig. 27. Nonlinearity in Carbon nanocones.

Nonlinearity for carbon nanocones at different voltages.

3.5.2 Nonlinearity in carbon nanotubes

Similarly as for carbon nanocones, the nonlinearity of selected datasets for carbon nanotubes was calculated over time, showing nonlinearity between 1.5 and 1.65. There was a brief moment of linear behaviour at 9V, as evidenced by the light blue and green lines at a value of ~1.

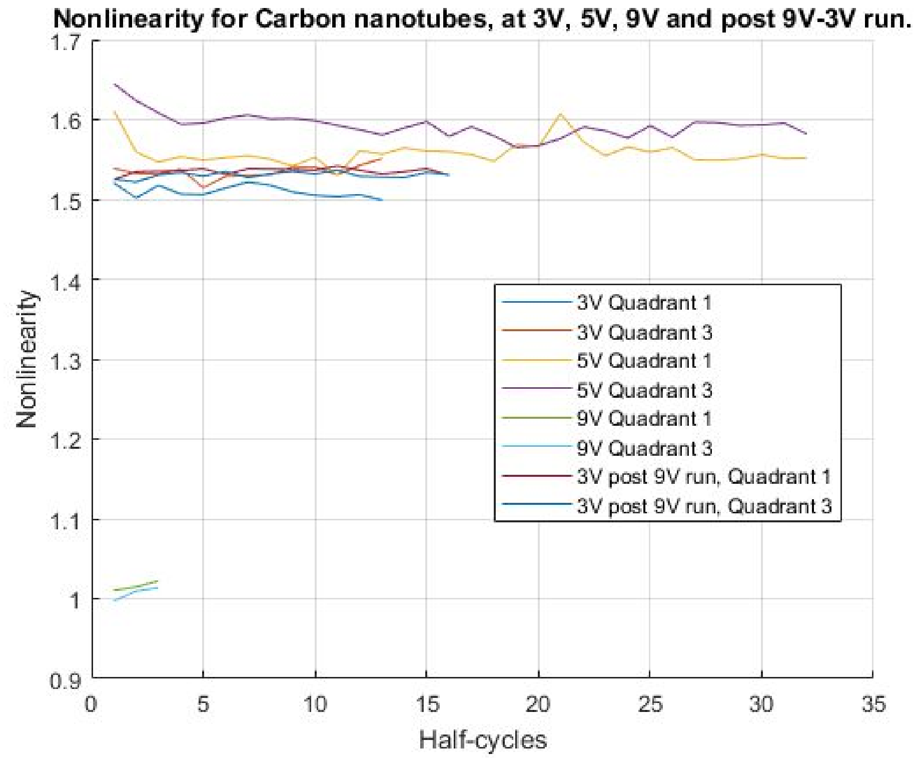

Fig. 28. Nonlinearity of carbon nanotubes

4. Discussion

4.1 Coherer behaviour and mechanisms

We have by now clearly established that carbon nanotubes and carbon nanocones exhibit memristive behaviour in bulk. This memristance can be divided into two categories, a max current based memristance, and a smaller cyclical memristance.

This behaviour fits well with the behaviour of coherer devices in general by (Gandhi & Aggarwal, 2013)

As discussed in the introduction, there are several theories about the mechanism behind the Branly coherer effect, including micro-welding, joule heating, and rearrangement of oxide layers. Based on the results obtained here we find we can exclude some mechanisms. While there is literature to support oxide based memristors (E. Falcon, Castaing - American journal of physics, & 2005, 2005) this is unlikely to be the case here, as carbon nanotubes and cones do not have a proper oxide layer. There is still the possibility of this happening in the interface between our copper electrodes and our carbon nanoparticles, but our experiments are more in line with the cat whiskers described in (Gandhi & Aggarwal, 2013), who also did preliminary experiments with polished gold balls, and concluded oxide layers an unlikely mechanism. Based on the results obtained, we also conclude that the programmed multistable memristive behaviour and the bistable switching seem to act very differently, and as such are likely due to different mechanisms.

4.2 Possible Mechanisms of Multistable behaviour

Excluding oxide layers, the other two leading theories for the mechanism behind the multistable behaviour are Joule heating (without melting) and micro-welding.

General joule heating without welding is a possibility, but carbon nanotubes have very high thermal conductivity, and so we would expect to see this behaviour affected in samples with active cooling or heating, but this was not observed. Further, the high thermal conductivity of our samples would suggest that any heat would be quickly dissipated. Even when tested several minutes after a previous run, the system would keep its memory of the earlier max current. Thus, we may conclude the mechanism is not simply Joule heating, but must involve some sort of permanent change, either in arrangement of particles, or atoms.

This leaves the process of micro-welding as the most likely mechanism for the multistable memristive behaviour.

4.3 Possible Mechanisms of Bipolar switching

As for the mechanism of the bipolar switching, there is less certainty.

The theory of Joule heating is unlikely, as thermal mechanisms are independent of the direction of the current, and this is not what has been observed.
Micro-welding would result in permanent changes, or, a bridging/short circuit cycle, which does not fit the data, and thus cannot be the cause of this behaviour.

In fact, none of the proposed theories for Branly coherers seem to apply to this behaviour.

Based on the similarity in the behaviour of our samples and those of (Gandhi and Aggarwal 2013), it is likely they share the same mechanism. We can make an educated guess that the effect is based upon polarisation at the interface between particles, but further research is required to be certain.

5. Conclusion

The goal of this project was to look for memristive behaviour in carbon nanotubes and nanocones, as well as to try to establish what potential mechanisms may be behind these memristive behaviours. Two types of memristive behaviour were found in both, the multistable memristive behaviour, and the bistable memristive behaviour. These behaviours were discovered to fit observations of other memristor devices made from very different materials, suggesting there is some fundamental mechanisms at play. These two behaviours further seem to have two different causes, and I believe two very different directions for future applications and research.

6. Potential future Research and Applications

6.1 Crossbar application

The nonlinearity found for carbon nanotubes and carbon nanocone systems was in the order of between 1.5 and 1.7. This in itself is not particularly high, but if memristance in carbon nanotube systems increases at smaller dimensions like with many other memristive systems, future research may want to look at memristance in carbon nanopowder systems at scales approaching the nanometre scale. If there exists memristive behaviour between individual carbon nanotubes, building carbon crossbar memory may be possible. There already exists extensive research on the possibilities of neuromorphic computing and artificial intelligence, as well as the benefits resistive ram and memristor crossbar applications. (Zhang et al. 2018) (Liu et al. 2018)

6.2 Carbon Nanotube macro-structures

If micro-welding is indeed the mechanism behind the current controlled multiple memristance states, as this research implies, there exists an avenue towards micro-welding of carbon nanoparticles under less controlled conditions than those used by (Jin et al., 2007). If this can be achieved, industrial production of longer composite carbon nanostructures may be possible. As was discussed in the introduction of this thesis, carbon nanotubes have the highest specific strength of any known material, as well as very high current carrying capacity. If we were to be able to harness this incredible material on a larger scale, things like space elevators and truly global energy grids, previously in the realm of science fiction, would be possible.

Appendix

All data sets used for this project are available at this link:
https://drive.google.com/drive/folders/0B3sLr2yyH75GTFZTZ1dsMHpmVzg?usp=sharing
Help understanding them, as well as access to all the programs are available upon request to at: Reynolds@scienceandsolutions.com

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