Novel Conducting Polymer Current Limiting Devices for Low Cost Surge Protection Applications

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Abstract

We report on the development of novel intrinsic conducting polymer two terminal surge protection devices. These resettable current limiting devices consist of polyaniline nanofibres doped with methane sulphonic acid electrochemically deposited between two 55 μm spaced gold electrodes. At normal applied voltages the low resistance devices act as passive circuit elements, not affecting the current flow. However during a current surge the devices switch from ohmic to non-ohmic behaviour, limiting current through the device. After the current surge has passed the devices reset back to their original state. Our studies show that a partial de-doping/re-doping process caused by the rapid diffusion of moisture out of or into the polymer film during joule heating/cooling is the underlying mechanism responsible.

Keywords : conducting polymer, nanowire, nanofibre, surge protection, current limiter, polyaniline, moisture sensor

1. Introduction

Low and medium power, resettable, two-terminal surge protection devices are commonly made using a composite matrix material, consisting of either conducting metal or semiconducting particles (carbon, borides, silicides) embedded within an electrically insulating polymer material of high thermal expansion coefficient (polyethylene, epoxy).[1,2] Often called polymeric positive temperature coefficient (PPTC) devices they function by having many conducting pathways[3,4] that break during overcurrent conditions because of thermal expansion of the insulating polymer caused by joule heating in the conducting material.[5,6] The resulting high resistance state reduces the current to safe levels, thereby providing in-line protection for circuits and devices. After the current surge has passed the polymeric material cools and contracts, which re-establishes the current paths and returns the device back to its original operating condition. The current-voltage properties of such devices are shown in Figure 1. For some applications I-V characteristics showing saturation (B) and a slight foldback (C) are suitable, whilst the idealized behaviour for circuit protection consists of full foldback (D) with the characteristics of negative differential resistance and complete suppression of the current.

In this paper we present an alternative strategy for making devices, consisting of only a single component material based on an intrinsic conducting polymer. This approach has the advantages of low cost, ease of fabrication and fast response times. The current limiter is synthesized using inexpensive starting materials and device fabrication involves a simple one-step electrochemical deposition procedure using relatively low cost equipment. The lightweight, flexible and air stable conducting polymer circuit protection device would be well suited for integration into new organic flexible devices and integrated circuits[7].

2. Materials Synthesis and Device Fabrication

The current limiter device consists of a thermally insulating ceramic substrate with two top-deposited gold electrodes (4-6 μm thick) that are laterally separated by a 55 μm gap containing the conducting polymer. An additional insulating layer (Dupont 5415A, 8-12 μm thick) covers the gold electrodes so as to define a circular electrode region (6.67 mm diameter) of fixed area for the electrochemical deposition of the polymer. A schematic of the device is shown in Figure 2 (inset) with the patterned region surrounding the hemispheres (green) being the insulating layer that restricts the electrochemical deposition to just the two gold hemispheres. Polyaniline doped with methane sulfonic acid is electrochemically deposited onto the gold electrodes using a bath consisting of 0.5 M polyaniline (Aldrich, 99.5%) and 2.0 M methane sulfonic acid (MSA) (Aldrich, 99.5%) in de-ionized water. A standard 3-electrode configuration was used consisting of an Ag/AgCl electrode (reference), platinum wire (counter) and gold electrodes (working). The Pt wire diameter was 0.5 mm and the counter-working electrode distance was approximately 15 mm. The electrochemical deposition was carried out at a fixed potential of 0.85 V for 55 seconds using a BiStat 3200 potentiostat. Initially, deposition occurs on the gold electrodes but then bridges across the 55 μm gap. After deposition the devices were washed multiple times in de-ionised water and kept in an air tight container for storage. Scanning electron microscopy shows the films to have a nanofibre sphaghetti-like morphology with a high surface area to volume ratio, as shown in Figure 2. This spaghetti-like morphology is similar to that often seen in electrochemically deposited polyaniline under certain growth conditions or with specific dopants[8].

Electrical testing of the devices was carried out using two home-built systems. For high speed I-V sweeps a computer controlled power supply (0-12 V, 0-10 A) with 16 bit analogue to digital converters (200 kHz) was used for sourcing and reading of the voltage/current. For the high speed pulse measurements an Elektro-Automatik PS8200-70 3U (0-200V, 0-70 A) power supply was used in conjunction with an IGBT Transistor (600 V, 200 A), a Farnell PG101 Pulse Generator and an Agilent DSO-X 2002A digital storage oscilloscope. This system allowed high speed pulses with measured rise times better than 2 μs at the maximum voltage used (100 V).

3. Results

Fast I-V sweeps (10 V/s) were used to simulate the conditions of a current surge. Multiple sweeps were performed from zero and ranging up to a maximum voltage of 5 - 10 V. Between each sweep the device was allowed to recover for 1 minute to allow the device to reset back to its original starting resistance. Figure 3(a) shows the typical I-V characteristics for a single device in ambient air (approx 70% relative humidity) with sweeps to increasingly higher maximum voltages. Each sweep shows non-linear current limiting behaviour at high voltages leading to increased device resistance. A measure of the current limiting behaviour of the device can be made by comparing the current at 10 V

with the ohmic response current on the graph (straight line). At 10 V the current has been reduced by 40%.

Devices were also measured under vacuum conditions to ascertain the effects of adsorbed gases/moisture on the devices. The devices were placed in a turbo molecular pumped vacuum chamber and pumped for 12 hrs at a base pressure of 3.5×10^{-6} mbar. During pump-down the resistance of the devices typically increased by about 60%. This can be attributed to the removal of loosely bound water in the film which increases the resistivity of the polymer (see discussion). I-V sweeps were then performed on the polymer devices in vacuum using the same conditions as those used previously, as shown in Figure 3(b). In this case no current limiting behaviour was observed. This unambiguously shows that water in the polymer films is linked with the current limiting properties of the material.

The effect of moisture content on the current limiting properties of the devices was done by measuring the I-V properties of devices in a controlled environment of different relative humidity. Figure 4a) shows the I-V characteristics of devices with relative humidity ranging from 10% to 90%. The graph indicates that the current limiting behaviour of the device is dependent upon the relative humidity. For the highest levels of relative humidity, 80% and 90%, the I-V curves clearly show very good current limiting properties with behaviour similar to that of the current saturation in curve B of Figure 1. Figure 4b) shows the I-V properties of the same device at a fixed humidity level of 90% with sweeps to increasingly higher maximum values, 5 V to 10 V. At this humidity level the device shows very good current limiting properties over the range of applied voltages.

The speed of switching of the devices was investigated by applying a series of high voltage square wave pulses (2 - 100 V) to the devices whilst monitoring the current. The data was used to plot a graph of the normalized resistance vs. time as shown in Figure 5. The graph shows the response of the devices increases rapidly for pulses of higher voltage i.e. 75 and 100 V. In the case of pulses of low voltage (2 V), the resistance of the device does not significantly change, indicating the passive nature of the devices under normal operating conditions.

To investigate joule heating in the devices during a current surge the temperature of the devices was monitored using an infra-red thermal imaging camera. Figure 6a shows a typical infra-red image of the polymer region between the two gold electrodes during a voltage sweep up to an applied bias of 5 V. The image indicates that a large amount of joule heating occurs during a current surge. Most of the heating occurs in the polymer filled gap between the two electrodes with temperatures typically reaching as high as 200°C.

Thermogravimetric analysis (TGA) was used to determine water loss from the polymer at elevated temperatures. Figure 6b shows TGA measurements performed on Pani-MSA that has been scraped from the devices. The TGA plot indicates weight loss in the polymer occurs at several temperature ranges. The first region of weight loss, approximately 13%, occurs at 50-100°C and can be attributed to the loss of water from the polymer.[9,10] The second region of weight loss, 210-350°C, also similar to that seen in other polyaniline films, is typically attributed to loss of the dopant molecules. The final region of weight loss, occurring for temperature above 450°C, is ascribed to decomposition of the polymer.

4. Discussion

Polyaniline in its conducting form[11] has been around since the early 1980's however few investigations have been made of their electrical properties during high overcurrent conditions or under the influence of high electric fields. Under very high electric fields, theoretical studies on polyacetylene[12] have indicated that for electron injection into the polymer from metal electrodes, polarons may not form when the electric field exceeds > 6× V/cm. For fields in excess of V/cm the same study showed that polaron dissociation may occur. In the case of bipolarons, models[13] indicate that in electric fields of ~2.6× V/cm to 2× V/cm bipolarons propagate along the polymer backbone with some shape change but remain strongly coupled to the lattice. Only in strong fields, exceeding 5× V/cm, do bipolarons dissolve and free charge carriers instead determine the charge transport. Our relatively thick devices, consisting of 55 μm of Pani-MSA between two metal electrodes have electric fields of ~1.8× V/cm for applied voltages of 10 V. This is 3 orders of magnitude lower than that expected to cause polaron or bipolaron dissociation, thus the observed electronic switching in the devices is unlikely to be due to these effects.

Our experimental data instead points to a mechanism of de-doping/re-doping due to the release/uptake of water within the polymer. The main evidence for this is that no current limiting behaviour is observed for devices under vacuum conditions, whereas for devices in air, increasing moisture content leads to improved current limiting behaviour (Fig. 4a). The best level of performance, as shown by the observation of current saturation in devices for voltages above 2-3 V occurred when the relative humidity was 90%. In this case there was a reduction of more than 70% of the absolute current when compared with that expected for ohmic behaviour at the same maximum voltage.

For devices under vacuum no current limiting behaviour was observed. The lack of switching for devices under vacuum can be explained by the absence of water in the polymer film, which is typically removed from the polymer during the pumping process, as has been observed by others.[17] Its well-known that the conductivity of polyaniline depends not only on the degree of oxidation but also the degree of protonation.[14] Thus water partially proton dopes the polymer, making it more conducting, and conversely, it's removal leads to partial de-doping and loss of conductivity. Since a large amount of the water in the polymer is already removed during the pumping process, joule heating during a current surge does not cause significant further loss of water, so there is not much change in the polymer's resistivity due to loss of water. Interestingly however, the I-V characteristics of devices in vacuum show the opposite behaviour to devices measured in air i.e. increasing current (or higher conductivity) at higher voltages (Figure 3b). This can be attributed to the underlying, intrinsic conduction mechanism in polyaniline. In this case joule heating increases the temperature of the polymer which in turn increases the hopping probability for conduction, as expected for a thermally activated hopping mechanism. The conduction mechanism in Pani-MSA has previously been shown[15] to be consistent with three-dimensional variable-range hopping (VRH).

For devices in air the current limiting properties of the devices are due to water being rapidly driven out of the polymer because of the increased temperature of the device caused by joule heating. Evidence for this is shown by the high temperature of the devices attained during a typical current surge, being ~200°C, which is above the temperature in which water is desorbed from polyaniline but below that which typically causes polymer degradation and irreversible changes in the conductivity. Loss of water from the Pani-MSA material at higher temperature was verified in the samples by thermogravimetric analysis, which shows a high degree of water loss at 50-100°C with decomposition not occurring until (>450°C). This is in agreement with stability studies performed on a variety of

differently doped polyaniline   which indicate loss of water or solvent (50-100°C), de-doping (250-300°C) and finally decomposition (>500°C). Enhanced current limiting properties were observed when the relative humidity was increased (Fig.4a). This can be attributed to a greater initial moisture content within the polymer film, which leads to a greater loss of conductivity when it is removed during a current surge.

It is well known that the presence of moisture enhances the conductivity of doped polyaniline.[16,17,18,19,20,21] (unlike the case of polypyrrole in which additional water leads to lower conductivity[22]) From NMR spectroscopy studies[23] it has been established that water molecules facilitate charge transfer in the polyaniline backbone leading to an increase in the polymer conductivity. A 'variable-size metallic island' model[24,25] has been proposed in which the boundary between protonated highly ordered regions (metallic island) and unprotonated amorphous regions, shifts due to changes in the amount of water in the film. The presence of water acts to increase the amount of order in the conducting polymer, transforming partly localized polarons into either delocalized polarons or bipolarons. The water molecules themselves are expected to be adsorbed at two sites: the N-sites and the site of the dopant molecule, although we note that in the case of MSA, no studies have been made to ascertain whether water is bonding in the vicinity of the MSA dopant.

The differences between the I-V curves in air (Figure 3a) and vacuum (Figure 3b) are interesting. In the case of the measurements in air, the increasing voltage and subsequent joule heating leads to loss of water and de-doping of the polymer, which causes the resistance of the device to increase. Whereas, in the case of the measurements in vacuum, a large part of the water in the film has already been removed so higher applied voltages leads instead to lower material resistivity, as a consequence of the increased probability of thermally activated hopping at higher temperature. This may seem at odds with one another since at some point the device in air will lose all of its moisture in the heating process and then should behave similarly to the device in vacuum. However, a direct comparison between the two graphs is complicated by the fact that the device in vacuum heats substantially more quickly than that in air.

The fast response time of the devices is also interesting. At high applied voltages, 100V, the response time is within a few microseconds. The nano-sized structure of the polymer nanofibres, having only small diameters and high surface to area volumes, likely play a role, allowing water to be more easily removed from within the fibre. If water is removed from deep within the fibre as well as close to the surface then conduction along the fibre is more strongly affected since all current paths in the fibre are affected. The porous morphology of the material itself is also an advantage since water can more easily diffuse into and out of the material through the many voids in the spaghetti-like structure. In contrast to the current surges at 10 V, the performance of the devices at small voltages (2 V) is negligible. This behaviour is ideal for in-line current surge protection as the device does not interfere with the normal operation of the circuit or external device.

Preliminary measurements indicate very good stability over a 24 hour period with repeated current surges. This is in agreement with thermal stability studies performed on a variety of polyaniline films with different dopants, which show Pani-MSA to have one of the highest stabilities.[26] Stability studies of the devices are currently underway and will be presented in a follow-up paper along with new results that show enhanced switching performance for devices with modified electrodes.[27]

5. Conclusions

We have demonstrated a new type of current limiter device that has potential for use in low and medium power surge protection applications. A particular advantage of the approach is the low cost starting materials and inexpensive method of fabrication. The current limiter is based upon a single component material, an intrinsic conducting polymer (Pani-MSA) with a nanofibre spaghetti-like morphology. At normal applied voltages the low resistance device act as a passive circuit element, not affecting the current flow. However during a current surge the devices switch from ohmic to non-ohmic behaviour, limiting current through the device. After the current surge has passed the devices reset back to their original state. Our studies show that a partial de-doping/re-doping process caused by moisture rapidly diffusing out/into the polymer film during joule heating/cooling is the underlying mechanism responsible. The current limiting properties of the devices are enhanced at higher relative humidity thus encapsulated devices containing mixed conducting polymer hydrogel components could be used to make devices with optimized properties.
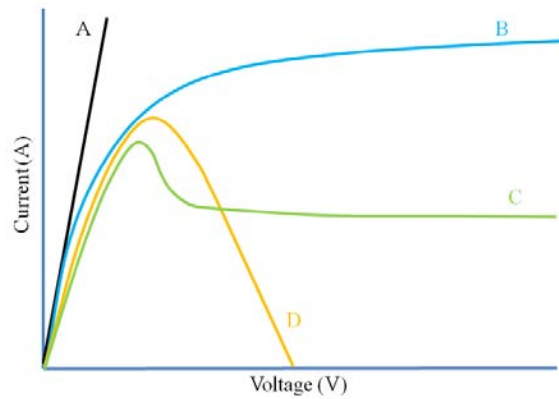
Figure 1. I-V curves showing ohmic behaviour (A), saturation (B), slight foldback (C) and full foldback (D). The idealized I-V properties for circuit and device protection are represented by curves similar to D, however even devices exhibiting the properties of B can be useful for handling high power dissipation.
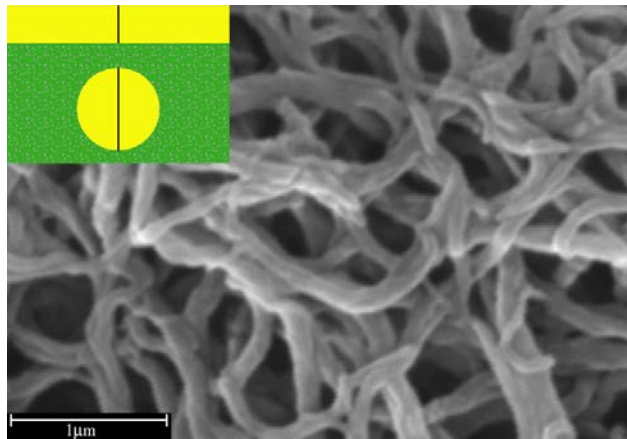

Figure 2. Scanning electron microscope image of the conducting polymer nanofibres and showing a spaghetti-like morphology. The inset (top left) is a schematic of the device consisting of two gold electrodes (gold hemispheres) separated by a narrow gap (black line). The patterned region surrounding the hemispheres (green) is an insulating layer that restricts the electrochemical deposition to just the two hemispheres. The two rectangles at the top are gold contact pads for electrical connections.
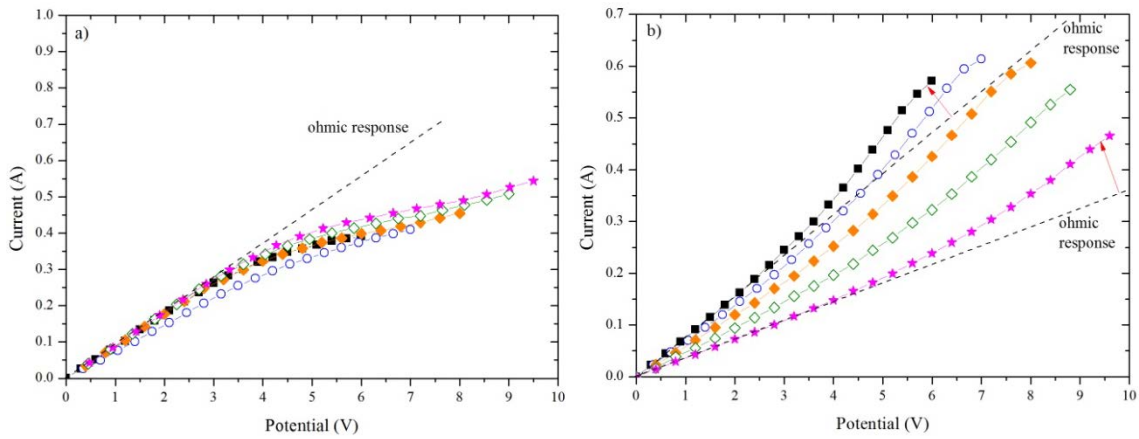
Figure 3. Current-voltage characteristics up to applied voltages of 10 V for a conducting polymer current limiter device in a) ambient air (approx 70% relative humidity) and in b) vacuum. Current limiting behaviour is observed in air while under vacuum the opposite behaviour is observed. The symbols refer to sweeps to 6 V (■), 7 V (O), 8 V (◆), 9 V (◇), 10V (★). Dashed lines act as guides to the eye for an ohmic response.
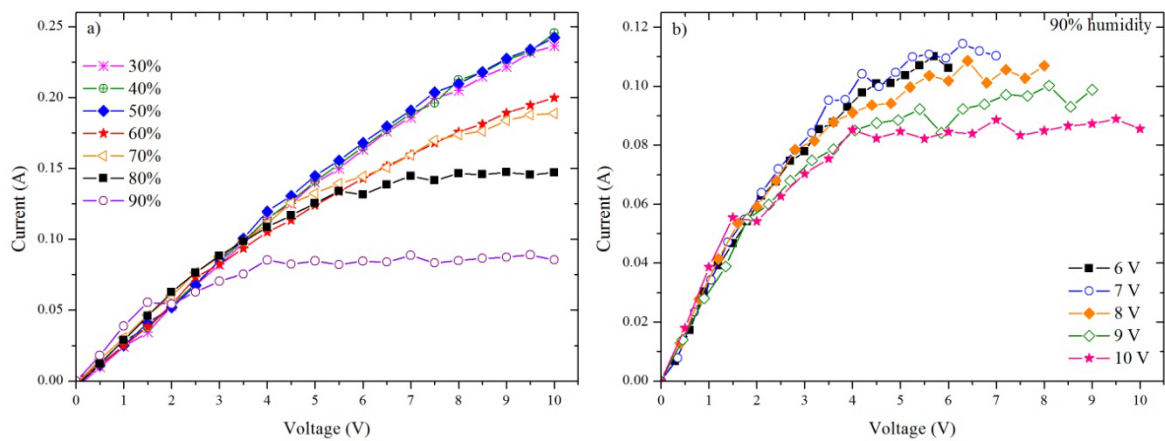

Figure 4. a) Typical current-voltage characteristics of a device at different relative humidity. b) Current voltage sweeps up to 6-10 V in a 90% humidity environment.
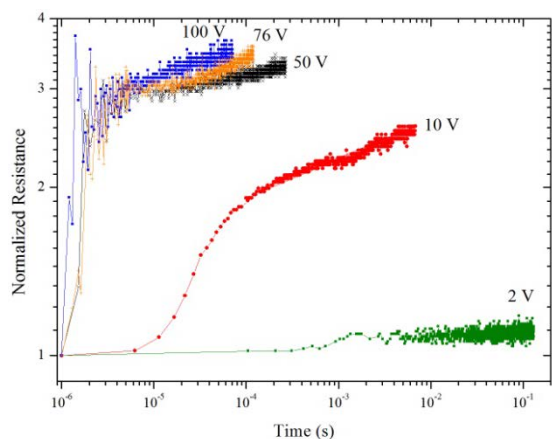
Figure 5. Normalized resistance vs time graph of a conducting polymer current limiting device with the application of a series of applied voltage levels. For high applied voltages the device shows a very fast response times (~μs). Note: In each case a square wave voltage pulse was applied having a rise time better than 1 μs.
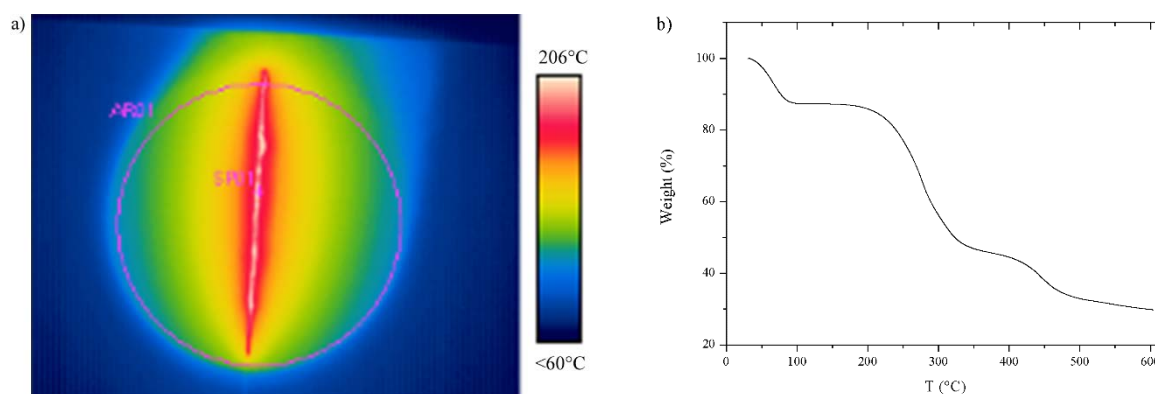

Figure 6. a) Infra-red camera image of a Pani-MSA current limiting device during an I-V sweep to 5 V. The image shows the central part of the device reaching a temperature of 206°C. b) Thermogravimetric analysis from room temperature to 600°C for Pani-MSA and showing sizeable loss of moisture at 50 - 100°C.

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