Novel Intrinsic Conducting Polymer Current Limiting Device (CLD) for Surge Protection

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Abstract—In the past many uneconomic solutions for limitation and interruption of short-circuit currents in low power applications have been introduced, especially polymer switch based on the positive temperature coefficient of resistance (PCTR) concept. However there are many limitations in the active material, which consists of conductive fillers. This paper presents a significantly improved and simplified approach that replaces the existing current limiters with faster switching elements. Its elegance lies in the remarkable simplicity and low-cost processes of producing the device using polyaniline (PANI) doped with methane-sulfonic acid (MSA). Samples characterized as lying in the metallic and critical regimes of metal insulator transition have been studied by means of electrical performance in the voltage range from 1V to 5 V under different environmental conditions. Moisture presence is shown to increase the resistivity and also improved its current limiting performance. Additionally, the device has also been studied for electrical resistivity in the temperature range 77 K-300 K. The temperature dependence of the electrical conductivity gives evidence for a transport mechanism based on variable range hopping in three dimensions.

Keywords—Conducting polymer, current limiter, intrinsic, moisture dependence, polyaniline, resettable, surge protection.

I. INTRODUCTION

N previous studies many solutions for current limiter device have been introduced which are commonly used for low to medium voltage systems. Among them, a promising hybrid system with conducting filler where a combination of carbon black and conductive polymer composites that forms a very effective current limiter [1]-[4]. Ceramic composites, V₂O₃ compounds, BaTiO₃-based compounds are among the other materials that has been used as the metal particles in these system. In the presence of sufficiently low currents, the resistive Joule heating of the polymer over-current protectors will cause the protector to self-heat at faster rate than its thermal dissipation rate. Thermal equilibrium is re-established when the device resistance reaches a value very much higher than its initial value, reducing the device power generation to a level equal to its dissipation rate. Thus enables the device to reduce circuit current to a safe level, protecting the circuit components from over-current damages. The high resistance achieved during switching is explained by reducing of moisture in the polymer film as the current heats the device at the same time [5], [6].

In these devices, under overload conditions, current dependent Joule heating is utilized to raise the material

temperature above the PTCR switching temperature thereby increasing the resistance and limiting the current [7], [8]. The recovery of a low device resistance upon elimination of the high power input is assumed to result from a reconnection of the separated de-localized area due to the absence of moisture caused by joule heating on the material l[9]. Due to the resettable advantage, polymer current limiters can been used to limit current in a variety of applications, such as audio and video equipment, telecommunications, battery protection, transformers and more [10], [11].

Keeping in mind the importance of low cost surge protection we have developed a current limiting device based on intrinsic conducting polymer. However, our present understanding of the physics of device operation is not sufficiently developed to allow an efficient search for useful current limiter and device designs. A better understanding should speed the development of this technology for the ultrafast switching applications that could revolutionize the circuit protection industry.

A. Material and Device Configuration

Polyaniline was deposited on the ceramic with gold electrodes (Tyco Electronics) employing MSA (Aldrich, 99.5%) as electrolyte medium. Polymer current-limiter device were made using the specification of the substrate shown in Fig. 1. A standard three-electrode setup with platinum (Pt)wire and Ag/AgCl as counter electrode (CE) and reference electrodes (RE), respectively, were used together with the gold as the working electrode (WE). The Pt wire thickness was 0.5 mm and the distance between the electrodes were approximately 15 mm. The electrolyte solution of 200 mL (2.0 MSA, 0.5 M aniline in D.I water) was introduced into a beaker with a plastic screw lid for electropolymerization. an electrochemical analyser (BiStat Using 3200) electropolymerization was performed potentiostatically at 0.85V/Ag/AgCl. Green colour PANI-MSA film was deposited by performing electrolysis for approximately 55 seconds. The film was washed in de-ionised water and kept in an air tight container for future use. The resistance of the device was measured after the device was rinsed in deionised water. Samples are then characterised by means of current-voltage sweeps. Results will be discussed in the following section.

II. RESULTS AND DISCUSSION

The device characteristic can be determined by measuring the current-voltage relationship at several different maximum applied bias from 1 V to 5 V. The device current-voltage (I-V) characteristics also been recorded during the decrease of

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voltage down to zero for each cylcle (IV 1 - IV 5) as shown plotted in Fig. 1.

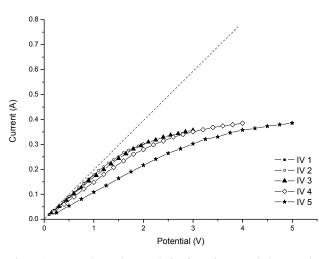


Fig. 1 Current-voltage characteristics for polymer switch. Dotted lines indicated how the comic response should be. Inset shows the device schematic

This device shows increase in current as voltage applied is increased with hysteresis on the decreasing voltage line. The maximum current applied is fixed to 1 A and the initial resistance of the device is less than 1 Ω . This particular sample did not show complete limitation of current as the voltage is increased up to 5 V, but the concept of resistance increasing when the current reach certain value can be observed as the current only reaches the maximum of 0.18 A, at maximum applied bias. The device was then removed from any electrical connections and left in room temperature to allow recovery of the low resistance. It is a known fact that the presence of moisture increases the conductivity of the polyaniline and significantly affects the electronic properties [12], [13]. Some water molecules in the polymer are tightly bound but others are found to be relatively free and mobile[14, 15]. The increment of resistivity due to the applied voltage can be reflected by the moisture loss in the polymer.

To confirm the moisture effect, another sample which is freshly produced has been tested in vacuum condition. The chamber where the sample is placed was pumped out for 12 hours until a pressure of 3.5 x 10-6 mBar was reached. The result plotted in Fig. 2 shows almost linear relationship increasing in the current-voltage sweep. It is believed that pumping the samples under vacuum easily removes water molecules adsorbed by the N-sites in the metallic islands as water contributes to enhanced conductivity by increasing the size of metallic islands. Moisture presence leads to additional spin and charge delocalization, most probably by solvating the dopant anions and thereby reducing electrostatic interaction between the positive charge and the anions. According to previous studies the presence of water plays an essential role in the conduction process on polyaniline in term of electron hopping between localized states with the assistance of proton transfer [16], [17].

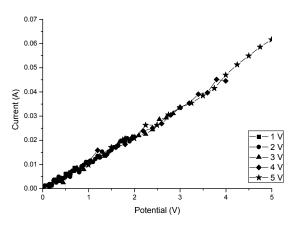


Fig. 2 Current-voltage characteristics in vacuum

This has shown in the results in Fig. 2 for electrical measurements performed in vacuum that resistivity of sample increases therefore decreasing all the currents corresponding to the voltage sweeps in vacuum. Upon placing the samples in vacuum chamber, it can be seen the increase of resistivity where pumping reflects an increase in the width of barrier between metal islands and decrease in conductivity [6], [14].

It has been proposed that the presence of moisture plays an important role in the new term of conduction mechanism based on electron hopping between localized states, with the help of proton transfer. This new conduction term is known as proton exchange-assisted conduction of electrons (PEACE).It is also apparent that the current decreases as the voltage is increased [12]. Thus as the voltage increases, the rate on energy deposition by joule heating increases and hence the resistance of the device must increase and at the same time acting as a current limiter. During high voltage load (overcurrent), the temperature of the polymer spot becomes close to transition temperature and the voltage loss is strongly increased due to drastic resistivity increase, which causes the formation of hot spots. This phenomenon can be explained by the infra-red image in Fig. 3.

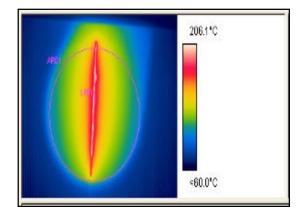


Fig. 3 The infra-red camera images up to maximum applied bias of 5 V illustrate the hot spot during IV sweep which relates to the increase in temperature on the device

The conduction mechanisms of electronically conducting polymers have attracted attention during the last 15 years. Rather soon, most of the experimental observations showed that the temperature dependence of the DC conductivity, σ , could be described by the following type of law. $\sigma =$ $\sigma_0 \exp{-(T/T_0)^{\alpha}}$ with $\frac{1}{4} \leq \alpha \leq \frac{1}{2}$. Such a type of law is characteristic of highly disordered system. To understand the mechanism for the current limiting device, temperature dependence measurement has been performed in cryostat. The temperature was controlled by an oxford Instrument ITC4 temperature controller. During the measurements the sample temperature was monitored carefully to avoid any self-heating in the sample. Conductivity measurements were made over the range of 77K to 300K. A current of 500µA was passed through the device and the potential different between the electrodes were measured. The temperature was raised to 300K in steps of 5K with conductivity measurement made every 2 minutes. Results obtained are plotted in Fig. 4.

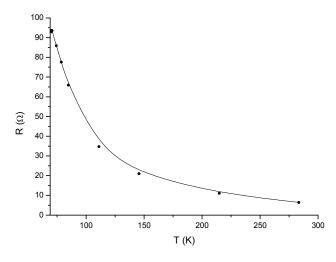


Fig. 4 Temperature dependence from77K to 300K

A basic for understanding low temperature electrical carrier transport in disordered material has been given by Mott's seminal paper, predicting a $T^{-1/(d+1)}$ dependence of variable range hopping where d, is the hopping space dimensionality [18]. Conducting polymers are predominantly polycrystalline or amorphous in character and have a substantial amount of disorder. As a result of hopping or tunnelling conduction is generally observed and the dependence of Fig. 5 can be represented by the 3D variable range hopping model in equation below.

$$\sigma_{(t)} = \sigma_0 exp\left[\left(\frac{T_0}{T}\right)^{1/4}\right] \tag{1}$$

where T_0 is the Mott's characteristic temperature and σ_0 is the conductivity at room temperature.

In the variable range hopping's model charge transfer involves of change from one metallic island to another through amorphous region. In the metallic region, the localization of carriers arises even for weak disorder because of quantum interference of static scattering. At higher temperatures, phonon scattering dominates impurity scattering [9], [18]-[20]. This crucially destroys the elastic scattering interference responsible for electron localization and explains the high conductivity with increase in temperature.

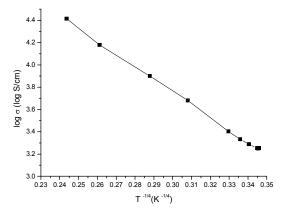


Fig. 5 The 3D variable range hopping model applied to conduction in PANI-MSA

III. CONCLUSIONS

The results described above demonstrate a novel type of switching behaviour of intrinsic conducting polymer current limiting device subject to certain voltage level. The understanding of this switching mechanism is mainly due to moisture factor which is a good sign of preliminary understanding of the device. The polymer conducting mechanism in the device produced was presented to be 3D variable range hopping, but clearly more work will be required to clarify the relevant physical parameters that can be identified to improve the performance of the current limiting device and their influence in terms of water presence.

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REFERENCES

- Steurer, M., et al., A novel hybrid current-limiting circuit breaker for medium voltage: principle and test results. Power Delivery, IEEE Transactions on, 2003. 18(2): p. 460-467.
- [2] Friend, R., Materials science: Polymers show they're metal. Nature, 2006. 441(7089): p. 37-37.
- [3] Geniès, E.M., et al., *Polyaniline: A historical survey*. Synthetic Metals, 1990. 36(2): p. 139-182.
- [4] Heeger, A.J., Nobel Lecture: Semiconducting and metallic polymers: The fourth generation of polymeric materials. Reviews of Modern Physics, 2001. 73(3): p. 681.
- [5] Duggal, A.R. and L.M. Levinson, *High power switching behavior in electrically conductive polymer composite materials*. Vol. 71. 1997: AIP. 1939-1941.

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- [6] Lee, K., et al., *Metallic transport in polyaniline*. Nature, 2006. 441(7089): p. 65-68.
- [7] Huang, W.-S., B.D. Humphrey, and A.G. MacDiarmid, *Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes.* Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 1986. 82(8): p. 2385-2400.
- [8] Kulkarni, V.G., L.D. Campbell, and W.R. Mathew, *Thermal stability of polyaniline*. Synthetic Metals, 1989. 30(3): p. 321-325.G. R. Faulhaber, "Design of service systems with priority reservation," in *Conf. Rec. 1995 IEEE Int. Conf. Communications*, pp. 3–8.
- [9] Javadi, H.H.S., et al., Conduction mechanism of polyaniline: Effect of moisture. Synthetic Metals, 1988. 26(1): p. 1-8.
- [10] Inzelt, G., Applications of Conducting Polymers, in Conducting Polymers. 2008, Springer Berlin Heidelberg. p. 225-263-263.
- [11] Janata, J. and M. Josowicz, Conducting polymers in electronic chemical sensors. Nat Mater, 2003. 2(1): p. 19-24.
- [12] Kahol, P.K., A.J. Dyakonov, and B.J. McCormick, An electron-spinresonance study of polymer interactions with moisture in polyaniline and its derivatives. Synthetic Metals, 1997. 89(1): p. 17-28.
- [13] Nechtschein, M., et al., Water effects in polyaniline: NMR and transport properties. Synthetic Metals, 1987. 18(1-3): p. 311-316.
- [14] Nechtschein, M., et al., Water effects in polyaniline: NMR and transport properties. Synthetic Metals, 1987. 18(1-3): p. 311-316.
- [15] Strumpler, R., G. Maidorn, and J. Rhyner, *Fast current limitation by conducting polymer composites*. Journal of Applied Physics, 1997. 81(10): p. 6786-6794.
- [16] Skotheim, T.A., R.L. Elsenbaumer, and J.R. Reynolds, Handbook of Conducting Polymers. 1998: M. Dekker.
- [17] Sheng, P., B. Abeles, and Y. Arie, *Hopping Conductivity in Granular Metals*. Physical Review Letters, 1973. 31(1): p. 44-47.
- [18] Mott, N.F. and G.B. Physicist, *Metal-insulator transitions*. 1990: Taylor & Francis London.
- [19] Sheng, P., Fluctuation-induced tunneling conduction in disordered materials. Physical Review B, 1980. 21(6): p. 2180-2195.
 [20] Lux, F., Properties of electronically conductive polyaniline: a
- [20] Lux, F., Properties of electronically conductive polyaniline: a comparison between well-known literature data and some recent experimental findings. Polymer, 1994. 35(14): p. 2915-2936.