

Mobility of charge carriers in the novel green organic semiconductor, Iodine doped Cis 1,4 polyisoprene (Natural Rubber) using SCLC method

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Abstract- Advantages like low temperature processing, cost, and flexibility make organic semiconductors an ideal choice for the new generation electronic devices ranging from LEDs, Solar cells to RFID tags. Many of these devices, especially OLEDs are already conquered the consumer electronics market in a large scale. Ironically the potential for large scale production of these polymeric devices are posing a threat to the emission issues and waste disposal. This warrants the development of green organic semiconductors. It has been shown that natural rubber (cis 1,4 polyisoprene) which is a green and natural polymer abundantly available in tropical areas like Asia can be made into semiconducting by doping process, and can be used in organic electronic devices. However the important parameter of mobility of charge transport in iodine doped natural rubber has yet to be explored or reported. In this paper the mobility of hole transport in iodine doped natural rubber has been reported for the first time using SCLC method. Interesting results are obtained which confirm the potential of iodine doped natural rubber to be an alternative low cost and green organic semiconductor.

Index Terms- Organic electronics, Green organic semiconductors, Mobility by SCLC method.

I. INTRODUCTION

The recent trends in organic electronics focus on the synthesis of new semiconducting materials from green polymers. Use of green organic materials in electronic devices can help to overcome the possibility of organic electronic waste disposal [1] to a great extent. Further the organic semiconducting materials presently used for devices fabrication are of high cost and therefore development of low-cost indigenous materials are essential for organic device commercialization. Natural polymers having large number of double bonds present in its polymer backbone are shown to be [2] transformed to conducting polymers by suitable doping agents. There are many chemical and physical methods reported [2][3][4] for the synthesis of conducting polymers from natural materials. Among these, doping is a facile method for the synthesis of organic semi conducting materials.

cis-1, 4 polyisoprene (Natural rubber), a green polymer, having a typical non-conjugated structure[2] was shown to be a potential natural polymer to form conjugated structure because of the presence of large number of double bonds in its polymer chain.

The conjugation in natural rubber can be made by doping with [3] suitable electron accepting materials, which facilitates charge transfer through the polymer chain. M Thakur reported [2] that natural rubber on doping with iodine, its conductivity gets raised by 10 orders of magnitude. Liming Dai et al. clearly explained [5][3] the mechanism of iodine doping in polyisoprene with the formation of charge carrier complexes. As per this, on doping natural rubber with iodine, as a first step conjugation is induced in the polymer chain followed by the formation of cationic iodine complexes (I³⁻ and I⁵⁻). The charge transfer thus occurs in the polymer chain by double bond shifting. Sreeja et al. optimized [6] the molar ratio for better conductivity Fassena et al.[7] and Shiju et al.[8][9] studied [10][11] the electronic parameters like HOMO LUMO and application of these complexes in organic electronic devices like, OFET, schottky diode etc. Even though a number of characteristics like conductivity, HOMO, LUMO, Bandgap, etc. of conducting cis-1,4 polyisoprene have been reported, there is no report available on the mobility of charge carriers in this green semiconductor. In this context this paper reports for the first time, the evaluation of mobility charge carriers in conducting natural rubber using space charge limited current (SCLC) method.

II. EXPERIMENTAL

1.1 Materials

cis 1,4 polyisoprene, MoO₃ and Iodine are purchased from Sigma Aldrich. Polyisoprene is used without any purification and iodine is re-sublimated before the synthesis. The ITO substrate with surface resistance 10-12 Ω /cm² is also purchased from Sigma Aldrich and is used as substrate for the test device fabrication. The solvent, Toluene (research grade) is procured from Merck and used after proper distillation. Aluminum slugs from Sigma are used for depositing cathode electrode for the test device.

1.2 Synthesis of Iodine doped Natural Rubber

The mixture of polyisoprene and iodine purified by distilling with toluene in the molar ratio, given by, [C=C] : [I₂] = 40:1. 10.73 mg of polyisoprene and 1 mg of iodine are taken in 1 ml of distilled toluene for the doping process. The prepared samples are then sealed in amber vial and stirred for 150 hours continuously for doping reaction to complete. The color of the solution is seen to be gradually changing from purple to dark

brown. UV-Vis spectrum of the sample are taken in equal time intervals during the reaction period to check the extent of doping.

1.3 Test device fabrication (DUT)

The structure of the test devices fabricated are ITO/MoO₃(2nm)/NRI₂/MoO₃(10nm)/Al and ITO/NRI₂/MoO₃(10nm)/Al (schematics are shown in Fig 1 a&b). For fabricating the test devices, first, two ITO substrates are patterned by etching its half portion using zinc powder and 6N

HCl. The etched ITO substrates are cleaned with a cleaning protocol involving a cleaning liquid, Hellmanex purchased from Osilla. The substrates are sonicated in a 1% Hellmanex solution of water for 5 minutes at 70°C. This is followed by the rinsing of the substrates in boiling water twice and then sonication in IPA for five minutes. In the next step, damp rinsing with deionized water (DI) and finally drying under nitrogen flow are employed. Finally the cleaned ITO substrates are treated in a UV Ozone cleaner for 10 minutes.

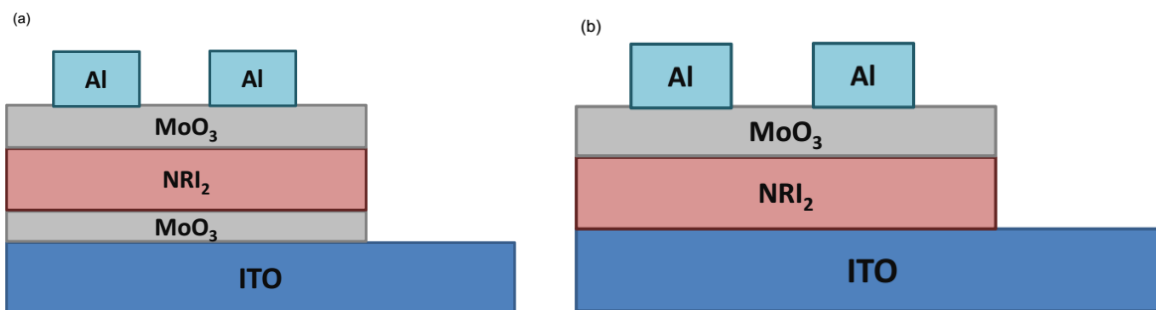


Fig 1. The schematic structure of the test devices (a) Device with hole transporting layer (b) device without hole transporting layer.

A thin layer of MoO₃ (2nm) are first deposited on the cleaned ITO substrates by physical vapor deposition (PVD). The MoO₃ is evaporated by electrical heating in a molybdenum boat under 1X10⁻⁵ mbar pressure through a shadow mask. The polyisoprene iodine complex is then spin coated over MoO₃ deposited ITO substrate at 1500 rpm for 90 seconds to form thin film around 150 nm thickness using SPS make Spin 150 spin coater. Finally another layer of MoO₃ and Al are deposited again by PVD. Here the MoO₃ is applied as Electron blocking (EBL) layer (figure 1. a). One more device (figure 1. b) is prepared without MoO₃ EBL layer in cathode side for understanding the effect of such a layer. Al layers are deposited through a shadow mask by physical vapor deposition at 10-5 mbar pressure. Thus two hole only test devices are fabricated one having EB layer and another without it. As the doped rubber is p-type material the transport is mainly due to holes. The Current –Voltage characteristics of the devices are measured using Keithley 2400 source meter interfaced with a computer using lab-view software.

1.4 SCLC method

For extracting the mobility of charge carriers (here holes) Space Charge Limited Current (SCLC) method has been employed. The J-V characteristics of disordered organic semiconductors are seen to follow a power law behavior $J \propto V^n$, (with n=1 for ohmic, n=2 for Trap free SCLC, and n>2 for exponentially distributed trap SCLC regimes). At the lower voltages the conduction is Ohmic with n=1. At higher voltages n increases from 2 to 3 signifying space charge limited conduction (SCLC) with a transition from trap free (TF-SCLC) regime to exponentially distributed trap (EDT-SCLC) regime[12].

In SCLC region current and voltage maintains a quadratic relationship [13] and the current density in this region is expressed by child's law [14].

$$J_{dc} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_e \frac{V_{dc}^2}{L^3} \quad (1)$$

Where $\epsilon_0 \epsilon_r$ is the permittivity of the material where ϵ_r is relative permittivity and ϵ_0 permittivity of free space. The parameters μ_e , V, L and J are electron mobility, applied voltage, thickness of the sample and current density respectively.

The permittivity is calculated from the basic capacitance equation where A is the surface area of the contact and d is the thickness

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (2)$$

This when translated into the log –log plot of J-V gives[15] a liner ohmic region (slope =1) at low voltages which moves to a trap free (TF-SCLC) regime (slope =2) followed by an exponentially distributed trap (EDT-SCLC) regime (slope =3), as the trap states[16][17] start to dominate by localizing charge carriers. However the SCLC region (slop =2) considered here for the mobility calculation as per the equation (1)

III. RESULT AND DISCUSSION

The formation of NRI₂ complex is analyzed by UV-Vis spectroscopy (Avantus AvaSpec-2048 spectrometer). The UV-Vis spectrum of pristine natural rubber and that of iodine doped ones are taken in equal intervals of 5 hours spanning the whole reaction period. Fig 2 shows these UV-Vis spectra of (1) pristine rubber solution in toluene (rose color), (2) that at the start of the reaction -black, after 75 hours – (red color), and after 150 hours (blue color) of reaction respectively.

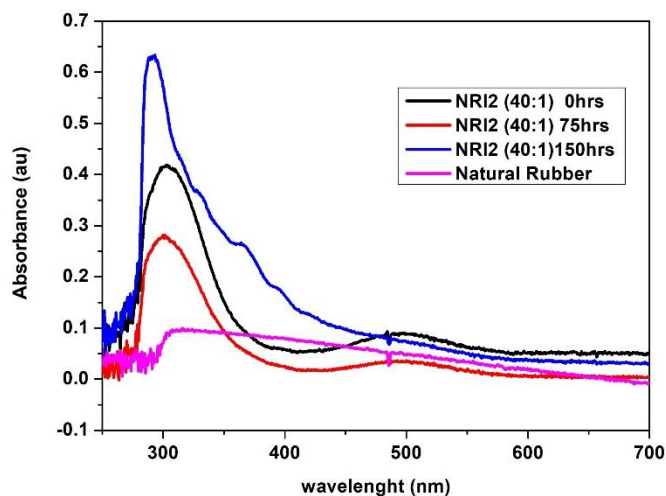


Fig 2: The UV-Vis absorption spectra of NRI₂ sample at 0, 75, and 150 hours of reaction.

It can be seen from the spectra above that at the start of reaction there is a decrease in the absorption for the wavelengths, 300 nm to 400nm and an absorption band at 500nm which is the indication of iodine molecules present in the sample. For 75 hours, the intensity of absorption band at 500nm gets reduced and after 150 hours this absorption band vanishes. The vanishing of absorption band at 500 nm and the presence of new weak absorption peaks in 300 to 450 nm region indicated the doping process. The color of the solution become dark brown at 150 hours of stirring is another indication of the formation of iodine complexes.

While fabricating the test device for current voltage characterization, MoO₃ was used as an electron blocking layer (EBL) in between the doped rubber layer and Al in the first device. MoO₃ was used as Hole transport layer (HTL) in between the ITO and doped rubber to facilitate smooth flow of holes to the ITO electrode. The role of the MoO₃ both as HTL at anode side and EBL at the cathode can be seen from the band matching diagram shown in the figure below: 6.25eV is the work function of MoO₃ while 2.9eV and 5.2eV are the LUMO and HOMO of the iodine doped natural rubber. This band diagram clearly shows the role of MoO₃ as HTL and EBL respectively. Thus while both the test devices works with holes as the major charge carrier and the additional HTL layer in device (a) helps a better smooth collection of charges compared to device (b).

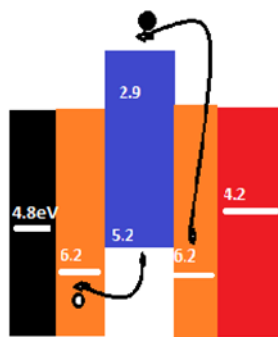


Figure 3: Band diagrams of the various layers in the test device A indicating the role of MoO₃ layer in helping the hole

movement at the ITO interface and hole blocking at the Al interface

The InJ-V characteristics of the test devices with and without EBL are plotted in Fig 4. The plot shows linear characteristics for the low voltages where as it changes to exponential as the voltage rises. In the case of device without hole transport layer, at the low voltages the current remains linear, while at high voltages the exponential behavior of current is found to be lesser than that of device with hole transporting layer

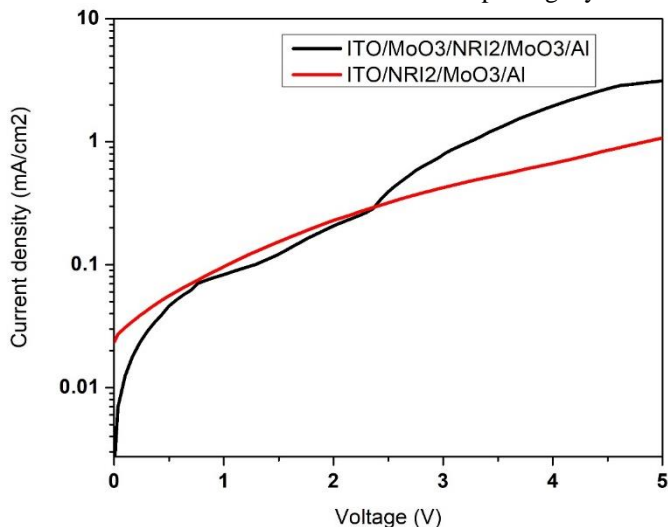


Fig 4. The semi logarithmic J-V plot of ITO/MoO₃/NRI₂/MoO₃/Al and ITO /NRI₂/MoO₃/Al devices.

The double logarithmic graph of devices with hole transporting layer and without hole transporting layer are plotted in fig 5 and fig 6 respectively. The SCLC voltage region is determined [13] for each devices from the double logarithmic plot of J-V characteristics. As the current varies exponentially the slope of the plot changes. The region where slope is 2 is considered as SCLC region, where the relation between current and voltage is expressed as $J \propto V^2$. The device with hole transporting layer have SCLC region at low voltages when compared with device without hole transporting layer. The lnJ versus lnV plot is fitted for equation (1) at the SCLC region and the value of mobility is extracted. The fitting is depicted in the plots with red color. The capacitance of the devices are measured using a capacitance meter and the value of permittivity is calculated using equation (2). The mobility values are calculated using equation (1). The mobility values of the devices are tabulated in Table 1. It is interesting to note that the mobility values remain the same order of magnitude in both cases indicating that the work function - LUMO difference between iodine doped rubber and Al is sufficiently high to prevent electron injection to the effect of affecting mobility values. However here MoO₃ will help to block the electrons from passing to the anode and also to avoid Al diffusion to the semiconductor surface at the interface. Passivation effect of the ITO surface reduce the chances of shorting the device.

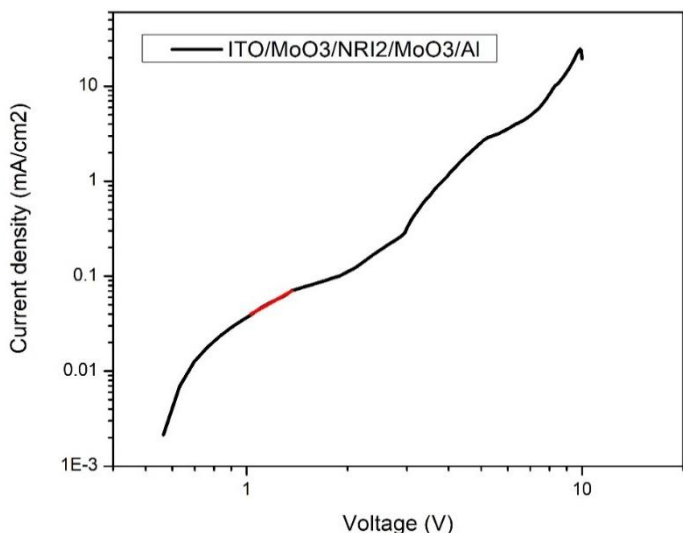


Figure 5: Fitted double logarithmic J-V curve of ITO/MoO₃/NRI2/MoO₃/Al device

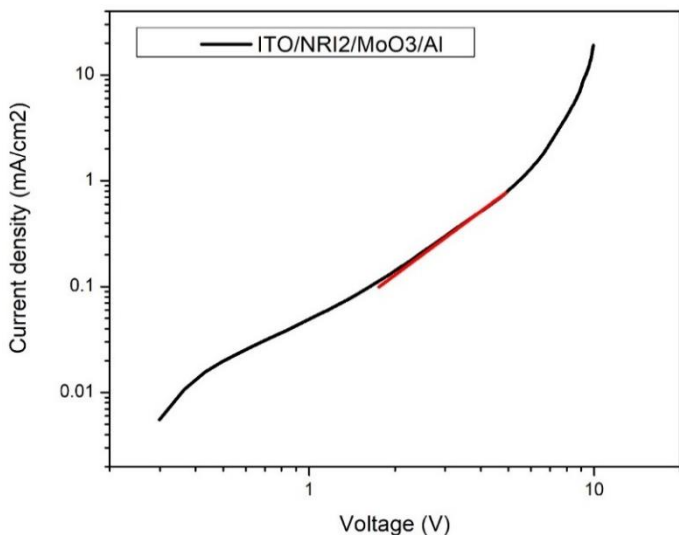


Figure 6 Fitted double logarithmic J-V curve of ITO/NRI2/MoO₃/Al device

Table 1: The mobility value of NRI₂test devices

Sl No	Device strucure	Mobility Cm ² /Vs
1	ITO/MoO ₃ /NRI2/MoO ₃ /Al	3.906 X 10 ⁻⁴
2	ITO/ NRI2/MoO ₃ /Al	3.345 X 10 ⁻⁴

IV. CONCLUSION

The green organic semi conducting material from natural rubber is synthesized by doping with iodine. The extent of doping is analyzed using UV-Vis spectroscopy and the time required for the effective doping is optimized. The mobility of the material is calculated by fabricating test devices and their results are obtained. The effectiveness of MoO₃ of as cathode buffer layer is also discussed and found that its effect is discerning in terms of the

order of mobility values and it acts more as a passivation layer. The mobility values of the like, OSC, OFET etc.

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REFERENCES

- [1] T. B. Singh, "PROGRESS IN PLASTIC ELECTRONICS DEVICES," *Annu. Rev. Mater. Res.*, vol. 36, no. 5, pp. 199–230, 2006.
- [2] M. Thakur, "A Class of Conducting Polymers Having Nonconjugated Backbone," *Macromolecules*, vol. 21, no. 3, pp. 661–664, 1988.
- [3] L. Dai and J. White, "Soluble conducting polymers from Polyisoprene," *Polymer (Guildf.)*, vol. 32, no. 12, pp. 2120–2127, 1991.
- [4] F. Cataldo, O. Ursini, and G. Angelini, "Radiation-cured polyisoprene/C60fullerene nanocomposite. Part I: Synthesis in hexane and in toluene," *Radiat. Phys. Chem.*, vol. 77, no. 6, pp. 734–741, 2008.
- [5] L. Dai and J. W. White, "Iodine-induced uncoiling of polyisoprene random coils in solution," *Eur. Polym. J.*, vol. 30, no. 12, pp. 1443–1447, 1994.
- [6] R. Sreeja, S. Najidha, S. R. Jayan, P. Predeep, M. Mazur, and P. D. Sharma, "Electro-optic materials from co-polymeric elastomer – acrylonitrile butadiene rubber (NBR)," vol. 47, pp. 617–623, 2006.
- [7] P. Predeep, D. Devasia, J. Aneesh, and N. M. Faseena, "Organic bistable memory device from natural rubber (cis 1,4 polyisoprene)/fullerene nanocomposite thin films," *Microelectron. Eng.*, vol. 107, pp. 54–57, Jul. 2013.
- [8] K. Shiju, T. Praveen, J. Manuvel, and R. Davis, "Toward Sustainability in Organic Electronics: A Performance Check for DNA Complexes as Dielectric Layer in P3HT based OFET," *Asian J. Appl. Sci.*, vol. Volume 05, no. Issue 04, 2017, pp. 669–676.
- [9] V. Liyana, N. Amina, K. Shiju, and P. Predeep, "Organic Field Effect Transistor with Silica Nanoparticles on Gate Dielectric," *Asian J. Appl. Sci.*, vol. 7, no. 8, pp. 696–704, 2014.
- [10] J. Aneesh, T. A. Hameed Shahul, N. M. Faseena, G. D. Sharma, and P. Predeep, "Organic bistable memory device based on a novel pyrrolo-pyrrole derivative, PPbAN," *Optoelectron. Adv. Mater. Rapid Commun.*, vol. 6, no. 11–12, pp. 1104–1106, 2012.
- [11] K. Shiju, T. Praveen, J. Aneesh, and J. Manuvel, "Organic field effect transistor with conductivity enhanced PEDOT: PSS composite electrodes," *AIP Conf. Proc.*, vol. 1536, no. 2013, pp. 1139–1140, 2013.
- [12] D. Joung, A. Chunder, L. Zhai, and S. I. Khondaker, "Space charge limited conduction with exponential trap distribution in reduced graphene oxide sheets," *Appl. Phys. Lett.*, vol. 97, no. 9, p. 093105, Aug. 2010.
- [13] S. M. Tuladhar, D. Poplavskyy, S. A. Choulis, J. R. Durrant, D. D. C. Bradley, and J. Nelson, "Ambipolar charge transport in films of methanofullerene and poly(phenylenevinylene)/methanofullerene blends," *Adv. Funct. Mater.*, vol. 15, no. 7, pp. 1171–1182, 2005.
- [14] S. W. Tsang, S. K. So, and J. B. Xu, "Application of admittance spectroscopy to evaluate carrier mobility in organic charge transport materials," *J. Appl. Phys.*, vol. 99, no. 1, p. 13706, 2006.
- [15] J. O. Oelerich, D. Huemmer, and S. D. Baranovskii, "How to find out the density of states in disordered organic semiconductors," *Phys. Rev. Lett.*, vol. 108, no. 22, p. 226403, May 2012.
- [16] J. Sworakowski and G. F. L. Ferreira, "Space-charge-limited currents and trap-filled limit in one-dimensional insulators," *J. Phys. D. Appl. Phys.*, vol. 17, no. 1, pp. 135–139, Jan. 1984.
- [17] J. M. Montero and J. Bisquert, "Interpretation of trap-limited mobility in space-charge limited current in organic layers with exponential density of traps," *J. Appl. Phys.*, vol. 110, no. 4, 2011.

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