Estimation of Richardson Constant for Natural Organic dye Based Cells using Orange-lemon and Apple-green

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Abstract

The Richardson constant is one of the most important parameters to analyze the current conduction process in the metal organic Schottky contact. But there are very few reports available on the estimation of effective Richardson constant for the natural dyes. In this work, we have estimated the values of effective Richardson constant for two different natural dyes namely Orange-Lemon and Apple-Green. A thin organic film of these herbal dyes was sandwiched in between Indium Tin Oxide-coated glass and a Copper plate by spin coating technique. The current-voltage-temperature response of the cells was investigated at a temperature interval of 303K to 333K using Keithley 2400 source meter. The effective Richardson constants for these dyes have been estimated which are 110 x 10^{-3} A/cm^{2}K^2, and 118 x 10^{-3} A/cm^{2}K^2 for OL and AG dye respectively, which is different from the conventional value of 120 A/cm^{2}K^2. These values will help us to study different electrical parameters for these natural dyes.

Keywords: *Natural dye, Schottky contact, Richardson constant.*

1. Introduction

The thermionic emission process in Schottky contacts is the widely used to describe the current conduction process through the metal-natural organic dye junction [1-3]. But the low current flow through these junctions is the most important limitation for the natural organic dye based devices. The thermal stability of most organic or natural organic dye based electronic and photo-electronic devices strongly depends on the relationship between the Schottky Barrier Height (SBH) and temperature. Because the current flow to an electronic and photo-electronic devices based junctions is fully controlled by the SBH of the junction [4]. So the SBH for different metal-organic junctions must be estimated. The Schottky thermionic emission theory is the common suggestion to calculate the barrier height of the junction with the saturation current and the temperature for the thermionic emission process [5]. The Richardson constant (A^*) is a fundamental parameter that characterizes the thermionic emission process in Schottky junctions [6]. Mostly the value of the effective Richardson constant is assumed to be the theoretical value. In order to measure the current-voltage (I-V) response to accurately obtain the SBH it is necessary to know the actual value of A^* for these junctions. Different material based junctions show different value of A^*. Ag/p-SnSe shows the A^* value of 7.72 Acm^{-2}K^{-2} [7]. The value of the Richardson constant for Al/PVA:n-PbSe polymer nanocomposites Schottky diode is 5.72x10^{-8}Acm^{-2}K^{-2} [8]. But there are no such reports available on the estimation of A^* value for different natural dye based junctions.

In this work, we are trying to estimate the value of A^* for two different natural dyes namely Orange-Lemon (OL) and Green-Apple (GA). These dyes are completely environment-friendly. Also, the dyes have no harmful effect on the human body and are cost-effective. These dyes are generally used to colour food, drinks, etc. Finding the values of A^* for these dyes will help us to estimate the SBH value and hence helps us to measure the different electrical parameters accurately. We use the Schottky diode structure where Indium-Tin-oxide coated glass (ITO) has been used as the front electrode and a copper plate (Cu) as a back electrode and the dye was sandwiched between them. In an ideal Schottky diode, the carrier conduction process in forward bias is dominated by the emission of carriers from the semiconductor over a spatially homogeneous barrier into the metal [9]. The measurement current (I) vs voltage (V) relation is done by using a Keithley-2400 source meter with the temperature variation from 303K to 333K (30^0 to 60^0).

2. Materials

The OL dye is also known as Sunset-Yellow Dye (SY) or Cosmetic Ingredient (C.I.)-15985. The chemical structure is given in figure 1. The SY dye is a petroleum-derived orange azo dye. This dye has pH-dependent maximum absorption at about 480 nm at pH-1 and 443 nm at pH 13 with a shoulder at 500 nm [10, 11]. According to both EU and WHO/FAO guidelines, 0–4 mg/kg SY dye has no carcinogenicity, genotoxicity, or developmental toxicity [10]. The IUPAC name of the SY dye is 'Disodium 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate ($C_{16}H_{10}N_2Na_2O_7S_2$)'. Generally, the SY dye is used in foods, cosmetics, and drugs such as candy, desserts, snacks, sauces, and preserved fruits [12-15].

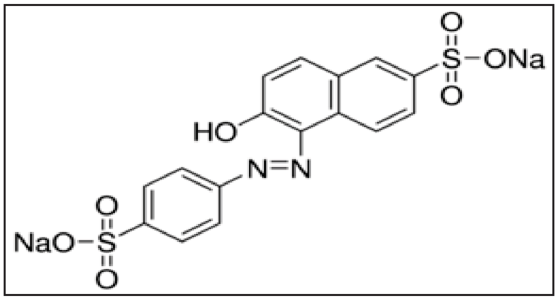


Fig.1. Chemical Structure of OL dye.

The Apple-Green (AG) dye is also known as Fast Green FCF also called Food green 3, FD&C Green No. 3, Green 1724, Solid Green FCF, and C.I. 42053, is a turquoise triarylmethane food dye. At a low-density solution, the FG dye gives the Apple-green shade. It can be used for canned green peas and other vegetables, jellies, sauces, fish, desserts, and dry bakery mixes at a level of up to 100 mg/kg [16]. The chemical formula of the AG dye is $C_{37}H_{34}N_2O_{10}S_3$. Figure 2 represents the chemical structure of the AG dye

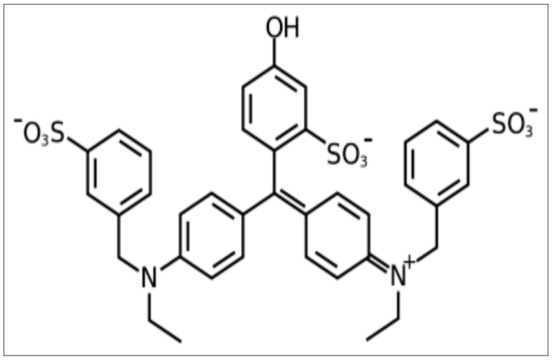


Fig.2. Chemical Structure of AG dye.

3. Experiment

3.1 Cell preparation

ITO glass plate and Cu plate of dimensions 2cm×6cm are cleaned using distilled water. Then they are immersed in extran solution and sonicated for 15 minutes. The substrates are then immersed in isopropanol and sonicated for 10 min after that The substrates are heated in an oven for 2 hours at a temperature of 80°C. Then the electrodes are washed with ethanol and dried and kept in a vacuum with a desiccator.

The 30% PVA solution is prepared by 1 gm of PVA, measured using Dhona-100DS measurement unit, mixed with 30 ml of de-ionized water and stirred with a magnetic stirrer for 1 hour with 313K. Here PVA plays the role of an inert binder [17]. Using the Dhona-100DS measurement unit we measure 1 mg of OL and AG dye and dissolved them separately with 0.5 ml of previously prepared 30% PVA solution using the Ultrasonic Sonicator for 30 min in room temperature.

Using a spin coater we spin coat the prepared samples separately on the previously cleaned ITO glass slides with 1500 r.p.m and semi-dried in a vacuum with a desiccator. After this step, we place the Cu plate as a back electrode on the sample to make a Metal-Dye-Metal (MDM) structure. These devices are then kept in a vacuum with dark condition for 12 hours before characterization to dry. The schematic diagram of the cell is given in figure 3.

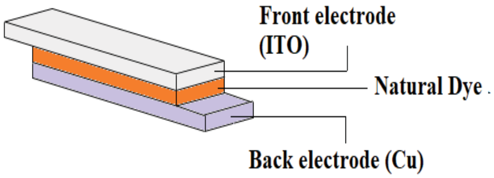


Fig.3. Schematic diagram of ITO/Dye/Cu cell.

3.2 Measurement

The dark current-voltage-temperature (I-V-T) characteristics of the cells have been measured using a Keithley 2400 source unit and the temperature varies and measured from 303K to 333K simultaneously with a Regulated Heat Source unit. During measurement, the bias voltage is varied from 0V to 5V in steps of 0.5V with 1500 ms delay. The simple circuit diagram of our experiment is given in figure 4. The experiments have been done in a dust-free space using a glove box with a dark atmosphere.

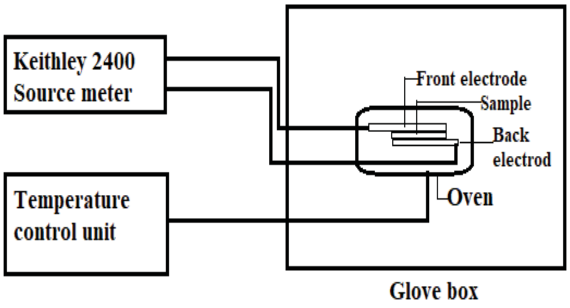
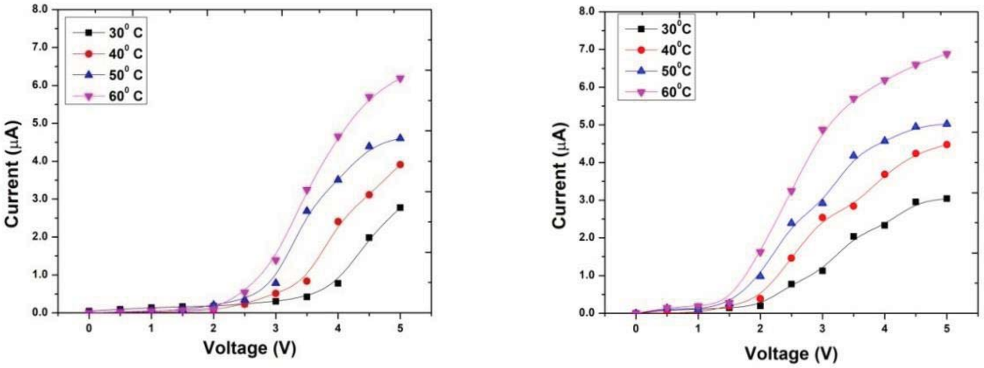


Fig.4. Schematic circuit diagram of temperature-dependent I-V-T characteristics.

4. Result

The I-V-T characteristics for both the dyes namely OL and AG dye at room temperature are shown in figure 5(a) and 5(b) respectively. From the plots, we have observed that the current flow has been increased exponentially with the increasing forward bias voltage. From both figures 5(a) and 5(b), we can observe that both the dyes show good rectifying behaviour at all temperatures.

In inhomogeneous Schottky-barrier diodes (SBD), the total area contributing to the current transport is both bias and temperature-dependent, and the carrier conduction process in forward bias is dominated by the emission of carriers from the semiconductor over a spatially homogeneous barrier into the metal.



(a) *(b)*

Fig.5. I-V-T characteristics of (a) OL dye (b) AG dye.

We have analyzed the flow of current according to Richardson-Schottky thermionic emission theory [18]. The forward-bias I–V relation of a Schottky diode can be expressed as:

$$I = [AA^{*}T^{2}\exp(\frac{-q\phi_{b}}{kT})]\exp[\frac{qV}{nkT}] \qquad (1)$$

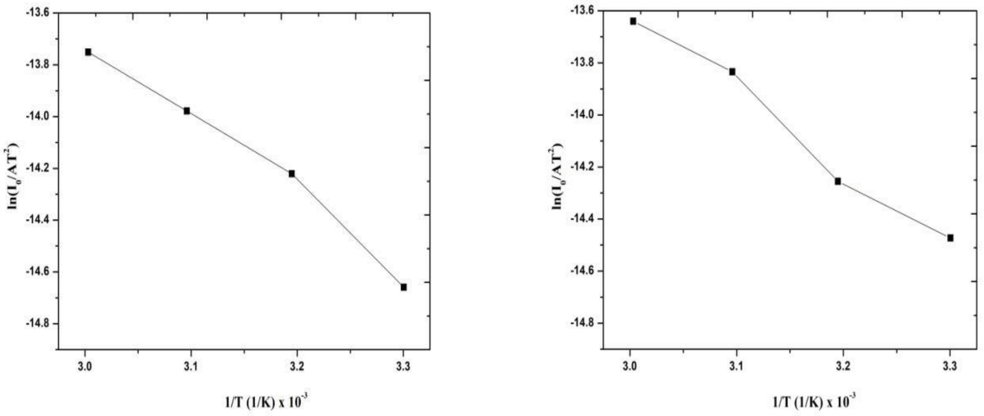
where ‘q’ is the charge carrier, ‘k’ is the Boltzmann constant, ‘T’ is the temperature in Kelvin, ‘n’ is the ideality factor which shows how closely a diode follows the ideal diode equation, ‘A’ is the area of the device, ‘ϕ_b’ is the barrier height of the junction, and ‘A^*’ is the effective Richardson constant. The reverse saturation current ‘I_0’ is given as:

$$I_0 = AA^{*}T^{2}\exp(\frac{-q\phi_{b}}{kT}) \qquad (2)$$

Taking ‘log’ in the equation (2), we have:

$$\ln(\frac{I_0}{AT^2}) = \ln(A^{*}) - q\frac{\phi_b}{kT} \qquad (3)$$

A typical Richardson plot of $\ln(\frac{I_0}{AT^2})$ versus $\frac{1}{T}$ extracted from the I-V-T characteristics for OL and AG dyes are shown in figure 6(a) and 6(b) respectively.



(a) *(b)*

Fig.6. Typical Richardson plot extracted from I-V-T data of (a)OL and (b) AG dye

Table 1 shows the Richardson constant (A^*) of both the dyes. The most significant observation from the Table 1 is that the extracted values of the A^* for both the dyes are different from the conventional value of n-type and p-type semiconductors.

Table 1. Extracted effective Richardson constant value for different dyes.

Name of the Dye	Value of A^* ($Acm^{-2}K^{-2}$)
OL	110×10^{-3}
AG	118×10^{-3}

5. Conclusion

In this study, ITO/Dye/Cu structure was prepared using OL and AG dye with a spin-coating technique with in a vacuum. The current-voltage-temperature (I-V-T) characteristics of the OL and AG dye were studied with the temperature range 303K-333K under dark condition. We can see that the Richardson plots are nearly straight line. The Richardson constant values for OL and Ag dyes are 110×10^{-3} $Acm^{-2}K^{-2}$ and 118×10^{-3} $Acm^{-2}K^{-2}$ respectively. We can extract the accurate SBH value by the linear correlation between Richardson constant and effective barrier height. For the study on the ideality factor and other electrical and opto-electrical parameters, charge transport mechanism for those dyes, this A^* values will be very much helpful. Further studies using these natural organic dyes are going on in our lab.

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