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Short Communication

Fabrication and Investigation of Flexible Photo-Thermo Electrochemical Cells based on Cu/orange dye aqueous solution/Cu

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This study presents the fabrication and investigation of flexible photo-thermo electrochemical cells based on Cu/orange dye aqueous solution/Cu. The cell consists of flexible polymer tube casing and Cu electrodes. The polymer casing is filled with 5 wt.% aqueous solution of orange dye, which is an organic semiconductor. Between two copper electrodes the temperature gradient (ΔT) of 7-10 °C is created by low power electric heater or light. It is found that at temperature gradient of 10 °C the open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and the Seebeck coefficient are equal to 18-20 mV, 0.4-0.5 μA and 1.9-2.2 mV/°C, respectively. The output electric power of one cell is up to 0.26 μW on average.

Keywords: Aqueous solution; Orange dye; Photo-thermo electric; Electric power; Electrochemical cell

1. INTRODUCTION

Energy is one of the most important factor for humanity and the standard of life actually is proportional to the energy consumption per capita. For the conversion of various forms of energy to the electrical energy different technologies are well known [1-3]. For example, for the conversion of solar and heat energies the solar cells and the thermoelectric cells based on Seebeck effect are used in practice, respectively [2, 4, 5]. Along with solid state semiconductors a plenty of research work is

devoted to the investigation of liquid cells that can be potentially used for the solar and heat energy conversion into electric power. Cutler and Mallon investigated the Seebeck coefficient of thallium and tellurium liquid compounds of n-type and p-type in the temperature range of 200 °C to 800 °C [6]. It was found that the figure of merit (ZT) was in the range of 0.1 to 0.85, which is considerably high range. Like buoyancy and thermocapillary the thermoelectric mechanism related to convective motion in liquid semiconductors (semimetals) was analyzed by Eidelman [7]. Thermopower in the Ni-Te alloys liquid semiconductors was investigated by Newport et al and it was found that depending on concentration of Ni and Te in the alloys the Seebeck coefficient was in the range of -38 to +22.7 μV/°C [8]. A thermoelectric cell consisted of cylindrical casing with hollow central annulus member was fabricated by Aharon [9]. In this cell the heated fluid is pumped in the central tube from the outer periphery. The gradient of temperature between the inner member and the peripheral surface of the cell results in the generation of the electric power. Male investigated glasses and liquids of chalcogenide semiconductors and observed an unpredictable phenomenon in the temperature range of 20 to 500 °C e.g. in amorphous As-Se-Te and As-Se-Te-Tl systems [10]. The signs of the thermoelectric coefficient and Hall effect voltage were opposite: the Hall coefficients were negative while the thermoelectric coefficients were positive. Usually in semiconductive materials the Hall coefficient and thermoelectric coefficient have same sign because the sign shows type of dominating charge carriers i.e. electrons or holes.

Recently, a liquid selenium based Schottky diode has been fabricated for thermal energy harvesting [11]. This diode shows high open circuit voltage (2.1V). The Seebeck coefficients of non-aqueous electrolytes like tetrabutylammonium nitrate, tetraoctylphosphonium bromide and tetradodecylammonium nitrate in 1-octanol, 1-dodecanol and ethylene-glycol were investigated in the temperature range of 30 to 45 °C. It was found that Seebeck coefficient was equal to 7 mV/K at 0.1M concentration for tetrabutylammonium nitrate in 1-dodecanol [12].

During last few years a number of papers have been published on electric properties of orange dye (OD) and the electrochemical elements based on it. The electrical parameters of orange dye semiconductor diode were estimated by the investigation of I-V characteristics [13]. Electrochemical properties of the cell based on orange dye aqueous (Zn/orange dye aqueous solution/carbon) were discussed in ref. [14]. The photo-electrical behavior of electrochemical sensors based on n-Si/orange dye, vinylethynyl-trimethyl-piperidole/conductive glass was studied in ref.[15]. The investigation of electrical properties of orange dye aqueous solution was also presented in ref. [16], where it was concluded that the conductivity of aqueous solution of OD depends upon its concentration in the water. In continuation of our efforts for the fabrication and investigation of organic semiconductor power devices [17, 18] we present the fabrication and investigation of orange dye based flexible photo-thermo electrochemical cells.

2. EXPERIMENTAL

The photo thermoelectric cells were fabricated by using the commercially available organic semiconductor material orange dye $C_{17}H_{17}N_5O_2$) with molecular weight of 323.35 g/mol and density

0.9 g/cm^3. The IUPAC name of OD is 3-[N-Ethyl-4-(4-nitrophenylazo)phenylamino]propionitrile. The type of conduction of OD used for experiments was confirmed as p-type by the "hot-probe" method. The molecular structure of OD is shown in Fig.1.

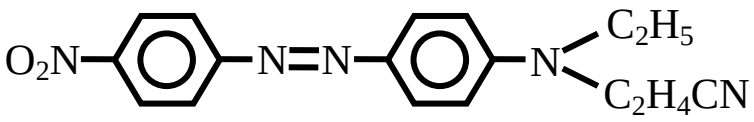

Figure 1. Molecular structure of orange dye ($C_{17}H_{17}N_5O_2$)

The cells were fabricated by using flexible polymer tubes of internal diameter 4 mm and length 4-5 cm. The 5wt.% aqueous solution of the OD was used as an electrolyte. The copper plates having 4 mm diameter and 2 mm thickness were used as internal electrodes. Schematic diagrams of the fabricated flexible Cu/orange dye aqueous solution/Cu photo and thermo electrochemical cells are shown in Fig.2.

The voltage and currents were measured by HIOKI 3256 Digital HiTESTER. Gradient of temperature was created by low power electric heater or light and measured by FLUKE 87 by using thermocouples. The filament lamp was used as a light source, while the intensity of light was measured by KYOCERA JIM-100. Industrially made resistor (5W 6.8Ω) was used as small power heater. As a source of electric power the power supply PS-03A was used.

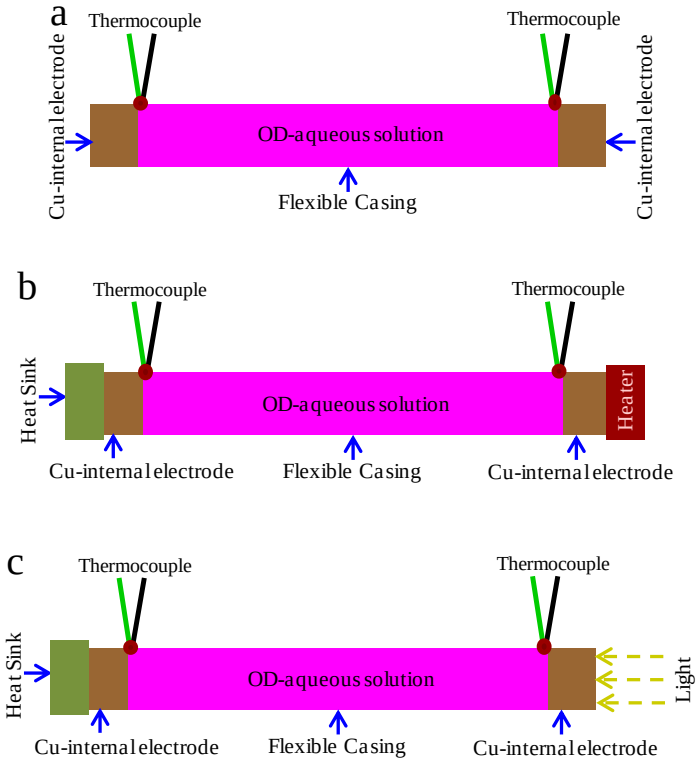

Figure 2. Flexible Cu/orange dye aqueous solution/Cu photo-thermo electrochemical cell (a), the cell at experiments with low power electric heater (b) and the cell at experiments with heating by light source

3. RESULTS AND DISCUSSION

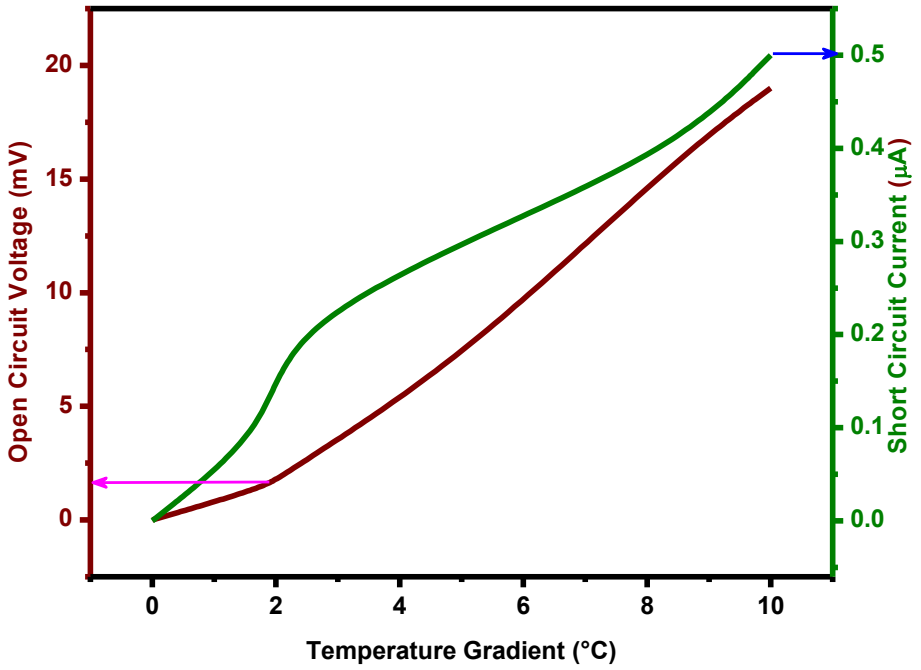

Figure 3. Open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) versus temperature gradient (ΔT) relationships of the Cu/orange dye aqueous solution/Cu cell

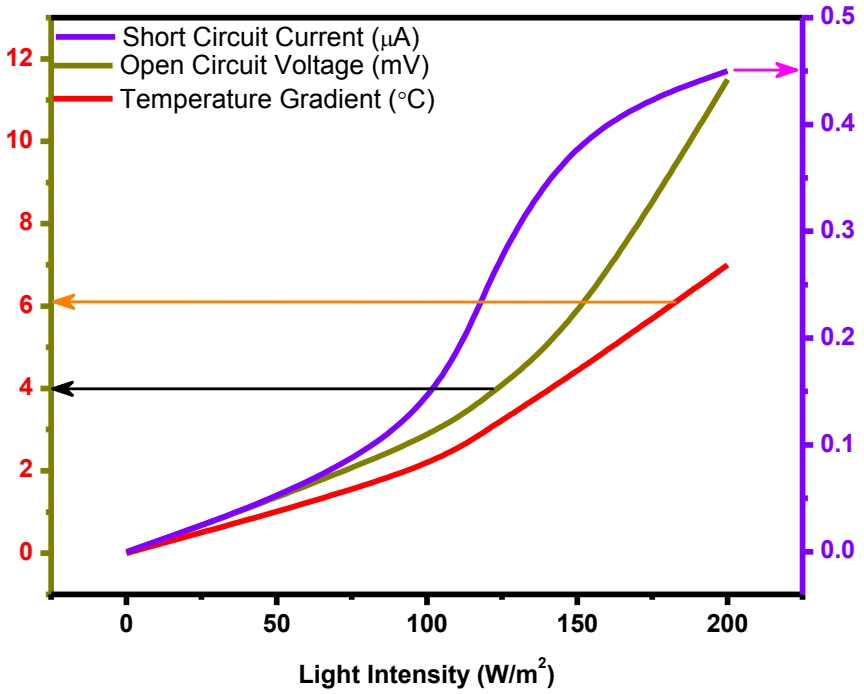

Figure 4. Open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and temperature gradient (ΔT) versus light intensity relationships of the cell

Fig.3 shows relationships of open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) versus gradient of temperature (ΔT) for the Cu/orange dye aqueous solution/Cu photo-thermo electrochemical

cell. It can be seen that V_{oc} and I_{sc} increase with increase in ΔT up to 10 °C approximately quasi-linearly. Figure 4 shows relationships of open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), versus intensity of light (G) for the Cu/orange dye aqueous solution/Cu cell. The Fig.4 also reveals the dependence of ΔT on G. It can be seen that relationships presented in Fig.3 and Fig.4 have much similarities, except the values of largest temperature gradient that was achieved at particular experimental conditions. The temperature gradient created by small power electric heater and light was 10 °C and 7 °C, respectively. The comparison of Seebeck coefficient-temperature gradient and Seebeck coefficient-light intensity relationships of the cell are also given in Fig.5.

The experimentally obtained maximum values of Seebeck coefficient were sufficiently large (1.9-2.2 mV/°C) as compared to the Seebeck coefficient (α) of traditional and even new thermoelectric materials; for example, for the C60 thin film n-type and p-type thermoelectric cells, plasma treated carbon nanotubes (CNTs) and few layers graphene (FLG) the α is equal to 190-390 μV/°C, 350 μV/°C at 670K and 700 μV/°C, respectively [19-21]. The last achievements were obtained in the new materials mostly due to enhancement of phonon scattering and band gap opening.

The thermoelectric effects that were observed in a number of liquid (melted) semiconductors, for example presented in the introduction, are actually Seebeck effect because all these inorganic semiconductors are the electronic semiconductors where electrons and holes are charge carriers [10]. Unlike to these materials in electrolytes ions play the role of charges usually at electrode-electrolyte interface chemical reactions take place [22]. These reactions result in generation of electrode potentials that are temperature dependent as well [22]. Therefore we can guess that measured value of Seebeck coefficient is also affected by the temperature dependency of electrode potentials and the values of electrode potentials as well. In the case of identical electrodes probably the contribution of electrochemical processes is minimized i.e. the values of electrode potential "theoretically" should be equal to zero," practically" can be low and/or constant.

The electrochemical reactions related to OD aqueous solution were presented in ref. [14, 23]. The reactions concerned to Cu electrode in electrochemical cell (Daniel cell) are described in ref.[22]. Electrode potential and the temperature coefficient at 298 K in aqueous solution for Cu electrode are equal to +0.337 V and +0.01mV/°C [22]. Therefore it can be considered that the Seebeck coefficient of the cell will depend on the nature of metallic electrode as well. The influence of the electrodes to the value of Seebeck coefficient can be increased if two properly selected different kinds of metallic electrodes will be used in the electrochemical cell. The investigated cells potentially can be used for low power application in medicine and in instrumentation for the measurement of gradient of temperature as well.

The simulation of the experimental results shown in Fig.5 is carried out by using the following exponential function [24];

$$f(x) = e^{x} \quad (1)$$

The modified form of the above function for the simulation of Seebeck coefficient-temperature gradient relationships of the cell is the following;

$$S/S_o = e^{10k_1\Delta(\Delta T)/\Delta T} \quad (2)$$

While for the Seebeck coefficient-light intensity relationship the modified form of the function is the following;

$$S/S_o = e^{k_2 \Delta G} \quad (3)$$

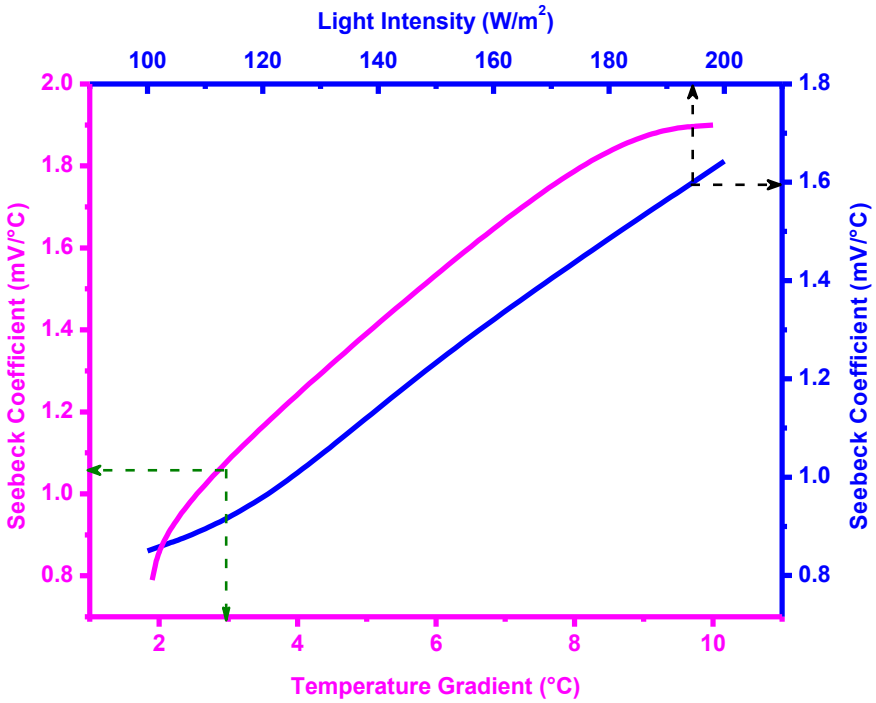

Figure 5. Thermoelectric voltage-temperature gradient and thermoelectric voltage-light intensity relationships of the cell

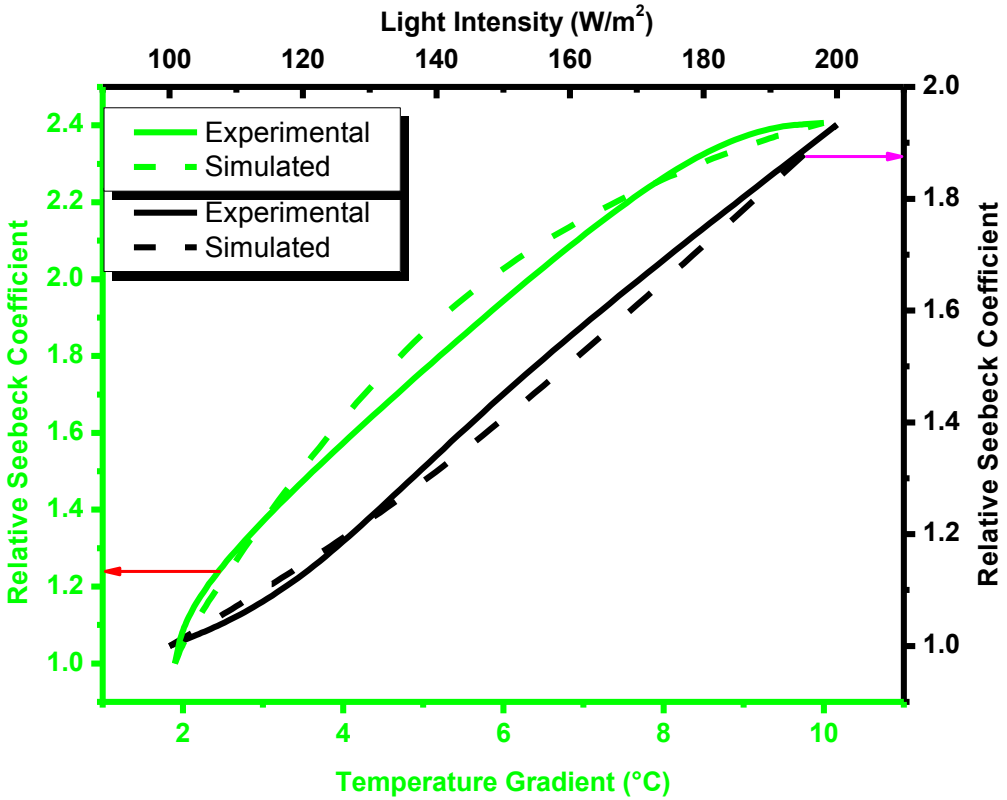

Figure 6. Comparison of simulated and experimental results of the cell

Where *So* and *S* are the initial and instantaneous values of Seebeck coefficients, ΔT is the temperature gradient, $\Delta(\Delta T)$ is the change in temperature gradient ($\Delta T=\Delta T-\Delta T_o$) and ΔG is the change in light intensity. The k_1 is the Seebeck coefficient-temperature gradient factor and k_2 is the thermoelectric voltage-light intensity factor. The values of k_1 and k_2 are 1.08×10^{-1} and 6.6×10^{-3}, respectively. The normalized experimental and simulated results of the cells are shown in Fig.6. It is apparent from the Fig.6 that the simulated results are in good comparison with the experimental results.

4. CONCLUSIONS

The investigation of the fabricated flexible Cu/aqueous solution of orange dye/Cu photo-thermo electrochemical cell showed that the cell have sufficiently large Seebeck coefficient (up to 1.9-2.2 mV/°C) for practical applications. Further improvement can be obtained by selection of metallic electrodes, including different electrodes with positive and negative electrode potentials and with large temperature coefficients.

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