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Fabrication of an electrochemical cell based on Rhodamine B Dye for low power applications

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Abstract
In this study an electrochemical cell based on Rhodamine B as an organic dye was fabricated for the first time. Several electrochemical measurements was used to investigate the electrochemical properties of Zinc/Rhodamine B aqueous solution/carbon. These electrochemical measurements include: polarization charge/discharge characteristics of the voltage/current versus time, life cycles electrochemical and impedance measurements. It is found that the Rhodamine B as organic dye-electrochemical cell is rechargeable and stable throughout these measurements. The measured values of open-circuit voltage and short-circuit current of the studied cell were 0.969 V and 0.416 mA, respectively. The calculated power shows a maximum peak that approaches 0.1068 mW at 0.511 V. The electrical energy and the capacity of the Rhodamine B cell were -186.991 kJ/mole and 25.535 kC (7.093 Wh), respectively. The impedance measurements showed the interaction between the electrochemical cell components. The Rhodamine B cell showed stability and constant charge/discharge behavior appeared in the voltage/current-time curves and throughout the life cycle measurements. The Rhodamine B electrochemical cell can be used as a candidate for low power applications, electrochemical sensor and electronic applications.

Keywords: Organic semiconductor dyes, Rhodamine B, Life cycle, Impedance

1. Introduction
Organic semiconductors have been investigated very intensively during the past decade. The study of the electric and electrochemical properties of organic materials and their use as the active component in optoelectronic and electro-optical devices have been made by many authors [1]. This is mainly due to low cost, simplicity of device fabrication, interesting electrical, electrochemical and optical properties, and environmentally harmless or friendly technology.

Dyes are widely used in various products such as textiles, paints, papers, printing inks, plastics, fibers, rubbers, ceramics and food industries. Dyestuffs are the major constituents of industrial waste water, which is produced from these industries. In recent years, dyestuff pollution of the ecological environment has caused widely public concern. Approximately, 10,000 different dyestuffs are used to textile industry [2, 3].

A considerable amount of works have been devoted to organic materials, allowing a better understanding of their properties as well as the physical processes, which take place in materials and devices. Meanwhile, commercial products making the use of organic materials have started to appear in the market, especially in the field of display flat screen (car radios, digital cameras, cell phones, computers, televisions) [4].

Searching for new electrolyte for electrochemical cell is a hot subject in recent years for many scientists all over world, the first dye electrochemical cell was fabricated and measured in 2006 [5] as Zn/orange dye aqueous solution/carbon cell. This cell was stable and rechargeable.

Batteries using different electrolytes are playing an important role in the science and technology and device applications, from portable electronics on one side to electric vehicles on the other side [5]. Organic dyes can be used as an electrolyte nowadays, due to its high solubility in aqueous solutions, inexpensive, and it is possible to change their properties by other materials. Organic dyes have excellent solubility in water, good absorption in

visible spectrum, stable in normal conditions and harmless [5]. Therefore, it would be useful to use this material in electrochemical devices for storage , conversion of energy and as sensors in instrumentation [5].
Rhodamine dyes family was among the oldest and most commonly used of all synthetic dyes and used in different industrial areas. Initially, they were used for cloth coloration. Owing to their unique optical properties, they served as water tracing agents, fluorescent markers for microscopic structure studies, photosensitizers, and as laser dyes [6, 7]. It is often used as a tracer dye within water to determine the rate and direction of flow and transport. Rhodamine dyes fluoresce and can be detected easily and inexpensively with instruments called fluorometers. They are used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy [8]. The previous work on Rhodamine B (Rh.B) organic dye was studied by I.S. Yahia et al [9-11] including the optical properties, ac and dc electrical conductivity and Schottky diode applications. They found that Rh.B is an organic semiconductor with optical band gap equals 1.97 eV and its activation energy under dc field equal 0.16 and 0.42 eV, respectively[9-11].
The aim of this study is to fabricate an electrochemical cell based on Rhodamine B (Rh.B) and investigate its electrochemical properties using different electrochemical techniques. The Rhodamine B (Rh.B) will be used as an electrolyte in zinc-carbon cell. The electrochemical properties of a zinc/Rh.B in aqueous solution/carbon cell was measured and discussed. These measurements includes: current–voltage characteristics, charge/discharge characteristics of the voltage/current–time, and life cycles were measured. The extracted electrochemical cell parameters such as open circuit voltage, short circuit current, electrical energy and the capacity of the Rh.B electrochemical cell will be thought.

2. Experimental technique

Rhodamine B [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]diethylammonium chloride (Rh.B), was obtained from Sigma-Aldrich with high purity. The molecular structure of RhB was shown in Fig.1.

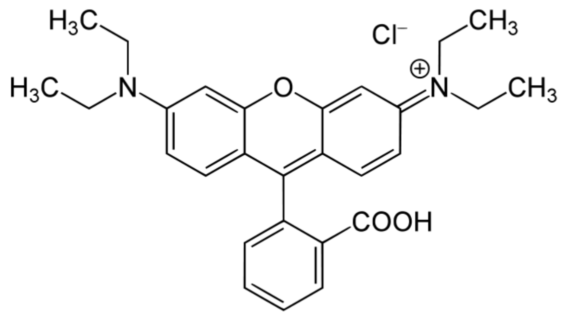

Figure 1 The chemical structure of Rhodamine B.

To prepare an aqueous solution of 0.01 M of Rhodamine B, distilled water dissolves the Rh.B under slow magnetic stirring for 10 minutes at 25 ±1 °C. A Philips model X'pert diffractometer with CuKα radiation operated at 40 kV and 25 mA was used for the structural investigation of Rh.B in powder form. Experimental electrochemical cell setup was constructed by using zinc electrode (5 mm in diameter) and carbon electrode (5 mm in diameter) in home-made special design cell. The spacing between the two electrodes was fixed at 1 cm. The current-voltage, the charge voltage/current–time and discharge voltage/current–time characteristics of cell were measured by digital multimeters and computer controlled UT71 digital multimeter via USB connection and a resistance box through a home-made design circuits. The Rh.B electrochemical cell was connected to the electrical circuit and left for one hour to reach the stability and equilibrium state of the studied cell before any measurements. A programmable automatic RLC bridge (PM 6304 Philips & Fluke) was used to measure both the impedance Z and the capacitance C directly. The RLC was connected to the PC through the GPIB cable and GPIB interface from National instrument and operated under windows 7 software. The automatic measuring mode for the investigated Rh.B cell was a resistance R connected in parallel with a capacitance C as appeared on the screen of the RLC bridge.

3.Results and discussion

3.1. Structure properties of Rh.B.

X-ray diffraction (XRD) of Rh.B in powder form was illustrated in Fig.2. As it can be seen from Fig. 1 that Rh.B is a single phase with a polycrystalline structure. The CRYSFIRE software was used for indexing the powder pattern with diffraction lines intensity larger than 5% corresponding to the highest maximum peak intensity. The lattice parameters of Rh.B were calculated based on TREOR90 (Trial-and-error program) [11-13]. The refinement of the lattice parameters was done by CHECKCELL program [11-13]. The values of Miller indices *hkl* for each diffraction peak are shown as the diffraction pattern as shown in Fig. 2.

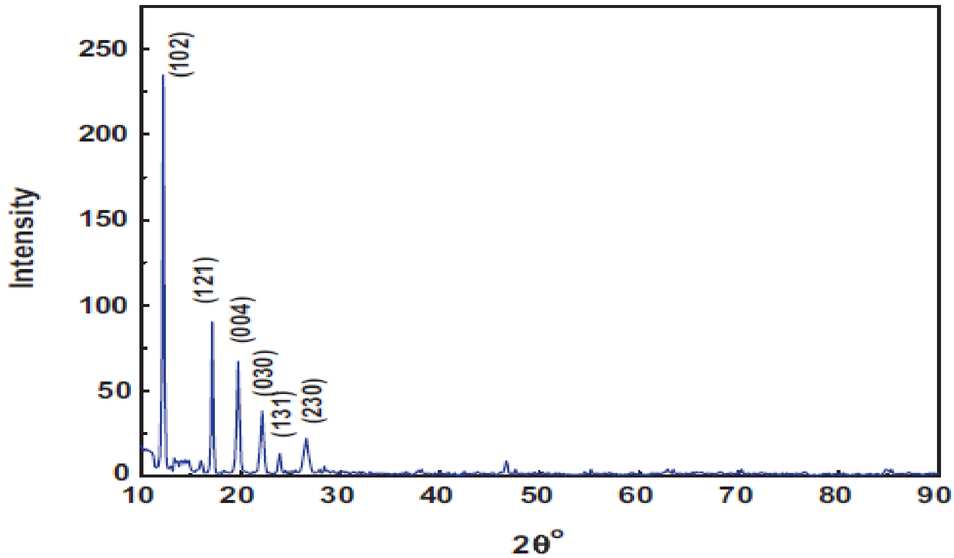

Figure 2 X-ray diffraction pattern of Rh.B in powder form [11].

The calculated system of Rh.B is tetragonal with space group P4.The lattice constants are given as: a = 12.0433 Å, b = 12.0433 Å, c = 17.9665 Å, $\alpha = \beta = \gamma$ = 90◦ [11].

3.2. The discharge current-voltage (I-V) and power-voltage Zinc/Rh.B aqueous solution/carbon electrochemical cell.

Zinc/Rh.B aqueous solution/carbon electrochemical cell was fabricated at 25 ±1 °C. The electrical properties of the cell measured by using home-made load circuit. The discharge current-voltage (*I*-*V*) and power-voltage characteristics of the measured electrochemical cell are shown in Fig.3.

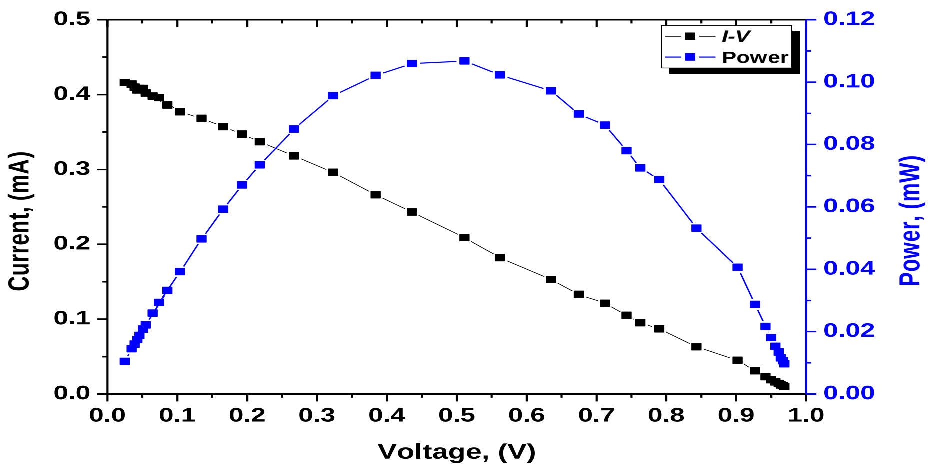

Figure 3 The load current-voltage characteristics and power versus voltage of zinc/Rh.B aqueous solution/carbon dye electrochemical cell.

It is clear that, zinc electrode's potential has a negative polarity with respect to the carbon electrode [5]. The current-voltage relationship is following the same behaviour for other electrochemical cells [14]. In the current case, this relationship is linear, which means that probably the Ohmic resistance dominates the system response. This is might be due to the low conductivity of the organic dye. The measured values of open-circuit voltage and short-circuit current of the studied cell are 0.969 V and 0.416 mA, respectively. The calculated power shows a maximum peak for zinc/Rh.B/carbon cell approaches 0.1068 mW at 0.511 V.

3.3. Charge/discharge, life cycles and impedance profile of Zinc/Rh.B aqueous solution/carbon electrochemical cell.

Charge/discharge profile of the voltage-time simultaneously with charge/discharge of the current are shown in Figs. (4 & 5), respectively.

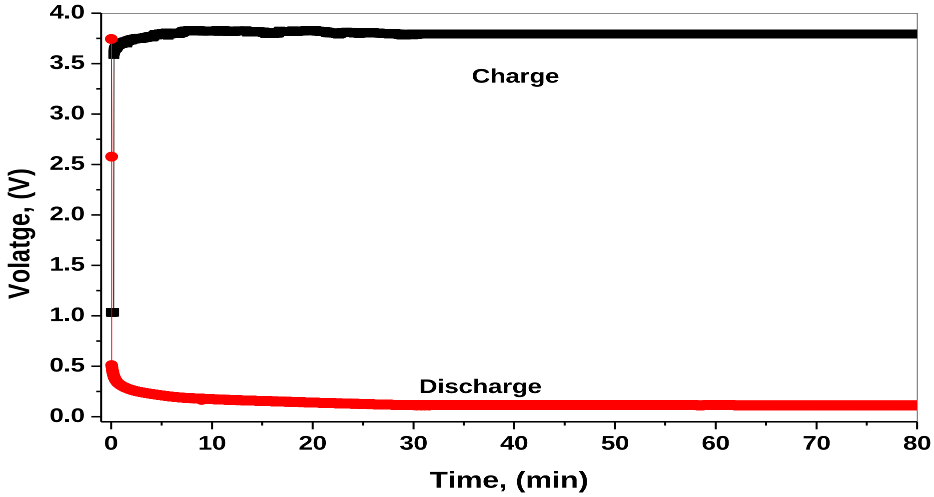

Figure 4 Charge/discharge of the voltage-time of zinc/Rh.B aqueous solution/carbon dye electrochemical cell.

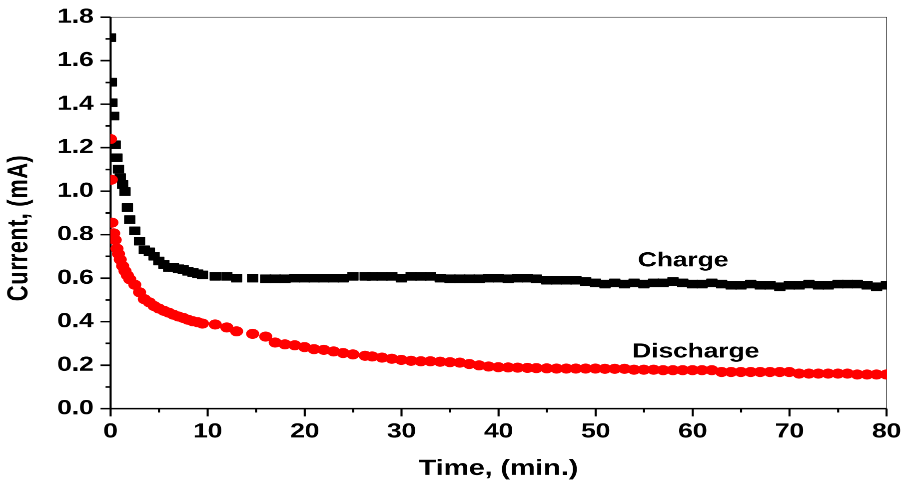

Figure 5 Charge/discharge of the current-time of zinc/Rh.B aqueous solution/carbon dye electrochemical cell.

The charge of the cell was measured through a constant voltage larger than the open circuit voltage as the standard method for the electrochemical cell [5]. Charge/discharge characteristics of the voltage/current versus time were measured through a load resistance of 500 Ω. It is found that the Rh.B cell is rechargeable. The cell charging voltage is higher than the cell discharging voltage and there is a sharp decrease in the discharge voltage ensuring the high sensitivity of the Rh.B cell for the charge and discharge conditions. The initial drop observed in the voltage can be attributed to the polarization of the cell, which arises from the concentration gradient of the reactants and products at the electrode Surface [18]. Both the charge/discharge of the current versus time decrease with increasing the measuring time until it reached the stable conditions. It can be concluded that both charge/discharge of the voltage/current-time characteristics illustrate the rechargeable process of the studied cell and their stability.

Life cycles of charge/discharge characteristics of voltage-time for zinc/Rh.B aqueous solution/carbon electrochemical cell were measured and plotted in Fig.6.

During the conditions of charge/discharge of the Rhodamine B electrochemical cell, it showed some stability. The voltage range through the charge/ discharge process was limited to 3.557– 0.116 V. The charge voltage of the cell drops very fast through the discharge cycle showing the response of the Rh.B electrochemical cell for continuous charge and discharge process and vice versa. It is evident from the above results that the Rh.B electrochemical cell is rechargeable.

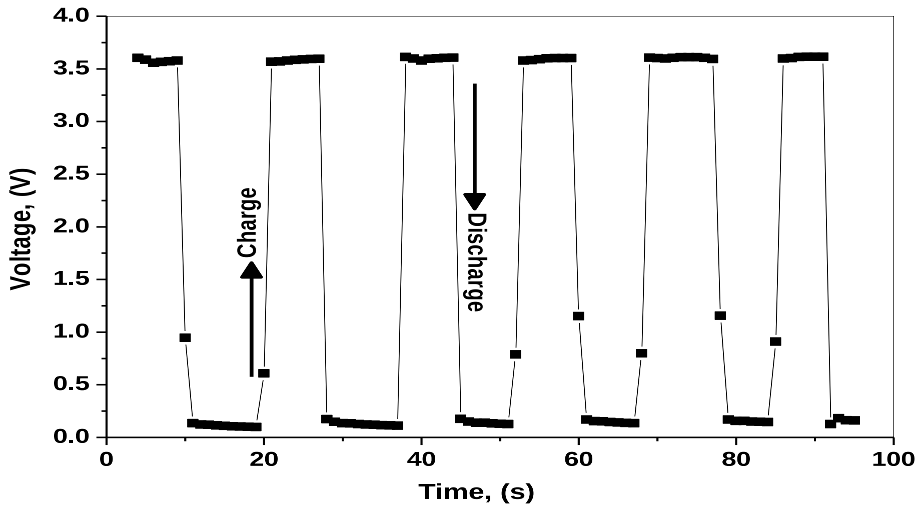

Figure 6 Life cycles of charge/discharge of the voltage-time of zinc/Rh.B aqueous solution/carbon dye electrochemical cell.

The chemical reaction inside the Rh.B electrochemical cell can be expressed as follows:
-At the anode: $Zn \rightarrow Zn^{2+} + 2e^{-}$
-At the cathode: $2(C_{28}H_{31}ClN_2O_3) + 2H_2O + 2e^{-} \rightarrow 2(C_{28}H_{31}ClN_2O_3)(OH) + 2OH^{-}$
-Total cell reaction: $2(C_{28}H_{31}ClN_2O_3) + 2H_2O + Zn \rightarrow Zn^{2+} + 2(C_{28}H_{31}ClN_2O_3)(OH) + 2OH^{-}$
The impedance (*Z*) and capacitance (*C*) were measured for Rh.B electrochemical cell at different frequencies in the range 100 Hz-1 MHz were illustrated in Fig.7.

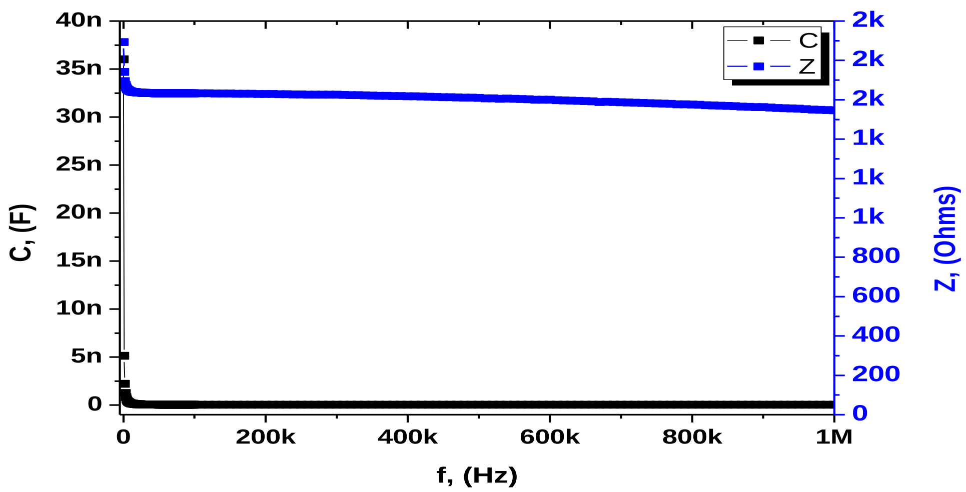

Figure 7 Capacitance and impedance as a function of the applied frequency of zinc/Rh.B aqueous solution/carbon dye electrochemical cell.

For the impedance, at the higher frequency region; the impedance is independent on the applied frequency due to the resistance of the electrolyte between the sample and the reference electrode. But, at the lower frequency region, the impedance is attributed to the polarization resistance of the sample in the electrolyte[15]. The capacitance is showing an ideal decrease with increasing the applied frequency, which attributed to the interaction between the electrode/electrolyte.

3.4. The electrical energy and the capacity of Zinc/Rh.B aqueous solution/carbon electrochemical cell.

The electrical energy of the cell as a change of free energy (*ΔG*) was calculated according to the following equation [14, 16]:

$$\Delta G = -nFE, \tag{1}$$

where *n* is the number of electrons transferred per mole (2 electrons), *F* is the Faraday constant (96487 Columb) and *E* is the electromotive force (0.969 V) of the cell. The calculated value of electrical energy equals -186.991 kJ/mole.

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The capacity of the cell (*C*) that is the proportional to the energy accumulation by the cell was calculated according to the given equation as [14, 16]:

$$C = \frac{nFW}{M_W}, \quad (2)$$

where *W* is the weight of the active electrode material (zinc in this case) which is equal to 8.650 g whereas M_W is the molecular weight of the material (for zinc it is equal to 65.37). The calculated value of the C is 25.535 kC (7.093 Wh).

Comparing between the obtained results Rh.B rechargeable electrochemical cell and orange dye ($C_{17}H_{17}N_5O_2$) measured by Khasan S. Karimov [5], it is found that the open circuit voltage for orange dye is larger than Rhodamine B dye electrochemical cell (1.5 V > 0.969 V). Also, the short circuit current for orange dye is approximately approaches from each other (0.45 mA > 0.416 mA). The difference between the two cells may be due to the molecular structure of the studied dyes, the conductivity of the dye in aqueous solution, the cell design, concentration of the organic dye, and the measuring conditions.

Conclusion

The main conclusions of the present study can be summarized as follows:

- Electrochemical cell based on Rhodamine B as an organic dye was fabricated for the first time.
- Polarization curve charge/discharge characteristics of the voltage/current versus time and life cycles measurements showed that the Rhodamine B as organic dye-electrochemical cell is rechargeable and stable throughout these measurements.
- The measured values of open-circuit voltage and short-circuit current of the studied cell are 0.969 V and 0.416 mA, respectively. The calculated power shows a maximum peak approaches 0.1068 mW at 0.511 V. The electrical energy and the capacity of the Rhodamine B cell are -186.991 kJ/mole and 25.535 kC (7.093 Wh), respectively.
- The impedance measurements showed how the interaction between the resistance of the electrolyte and the reference electrode.
- The Rhodamine B (organic dye-electrochemical cell) can be used as a source for low power applications, electrochemical sensor and electronic applications.
- More investigation are needed on the organic dye-electrochemical cell

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