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Effects of orange dye concentration on electrochemical properties of zinc/orange dye aqueous solution/carbon cells

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ABSTRACT

Electrochemical properties of a zinc/orange dye aqueous solution/carbon cells have been investigated for different concentrations of orange dye. In this cell, orange dye is used as an electrolyte and zinc and carbon rods serve as electrodes. As a cell compartment the cylindrical glass vessels of 4.0 cm in length and with a diameter 2.5 cm are used. Effects of concentration have been examined on the discharge voltage-current, charge voltage/current-time and discharge voltage/current-time characteristics. The open-circuit voltages and short-circuit currents of cells are observed as dependent on the orange dye concentration. The efficiency of current discharge/charge is found larger at higher concentration of the dye. The discharge voltage/current-time characteristics exhibit stable and constant behavior at all concentrations.

Keywords: Charge-discharge process; electrochemical sensor; orange dye; organic semiconductor; rechargeable cell.

INTRODUCTION

The study of electric and electrochemical properties of organic materials is attracting considerable interest. This is largely due to its low cost, ease of device fabrication, interesting electrical, electrochemical and optical properties, and that it is an environmentally harmless technology. Organic materials are promising candidates for future cost effective electric, electronic, and optoelectronic devices such as rechargeable batteries, fuel cells, electrochromic devices, sensors, light emitting diodes, lasers, photodiodes, solar cells, and field effect transistors (Rajendran *et al*. 2003, Sayyad *et al*. 2005). A wealth of information has been obtained on the behavior of different types of cells, employing organic electrolytes (Karimov *et al*. 2006, Wu *et al*. 2006, Park *et al*. 2007, Ye & Xu 2007).

There is a large range of organic materials which are semiconductors. Some of these organic semiconductors are very sensitive to humidity (Gutman & Lyon 1981, Gutman *et al.* 1983), temperature (Karimov 1982, 1994), infra-red, visible and ultraviolet radiation (Karimov *et al.* 2000), and different types of gases, such as ammonia (Fiodiorov 1999). Obviously, investigation of electrochemical behavior and fabrication of electrochemical cells and sensors with liquid and solid electrolytes based on organic materials is a very promising area (Stetter *et al.* 2003, Oh *et al.* 2003). For example, Panozzo *et al.* (2002) have described a high-efficiency light-emitting electrochemical cell on the base of organic salt, and Arnold *et al.* (1995) have reported an electrochemical glucose sensor. Organic-based transistors that are available to detect charged/uncharged chemical species in aqueous media via the electric field have been developed by Bartic *et al.* (2003). A number of ions selective electrode devices, semi-conductor oxide sensors and electrochemical ones based on liquid and solid electrolytes have also been described (Blythe 1979).

Very recently, we have studied electrical and optical properties of orange dye (Sayyad *et al.* 2005, Karimov *et al.* 2004, Moiz *et al.* 2005). It is a p-type organic semiconductor (Karimov *et al.* 2006) and is a potential candidate for use in electronic devices (Moiz *et al.* 2005). A heterojunction of Poly-N-epoxipropyl carbazole/orange dye exhibited rectification behavior (Karimov *et al.* 2002). Orange dye has excellent solubility in water, and shows good absorption in the visible region. It is also stable in normal conditions and harmless. Therefore, it would be useful to use this material in electrochemical devices that could be used for storage and conversion of energy. In an earlier study (Karimov *et al.* 2006), we reported a rechargeable zinc/orange dye aqueous solution/carbon cell. Zinc-carbon cells are the most popular primary cells. A rechargeable zinc/orange dye aqueous solution/carbon cell represents a very attractive and low cost battery with no environmental effect. This cell can be used as a source of electric power for low power applications, as an electrochemical sensor of moisture or water precipitation, and for measuring environmental parameters. The voltage and current generated by an electrochemical cell is directly related to the types of materials used in the electrodes and electrolyte.

In this work, we report the effects of orange dye concentration on open-circuit voltage, short-circuit current, discharge voltage-current characteristics, charge voltage/current-time characteristics and discharge voltage/current-time characteristics.

MATERIALS AND METHODS

Organic semiconductor orange dye, $C_{17}H_{17}N_5O_2$ (Fig. 1) with a molecular weight 232 g, density 0.9 gcm^{-3} and p-type conductivity was used for preparation of the electrolyte for zinc/orange dye aqueous solution/carbon electrochemical cell. In order to examine, the effects of orange dye concentration on electrochemical properties of the cell, solutions of four different concentrations of the dye (10.0 wt.%, 5.0 wt.%, 2.5 wt.% and 1.25 wt.%) were prepared in distilled water. As cell electrodes, the rods and rectangular sheets of the carbon and zinc, respectively, were employed. The diameter of the carbon rods was 8.0 mm. Width and thickness of the zinc sheets were 1.2 cm and 1.0 mm, respectively. The length of both electrodes was 5.5 cm. For each cell, the separation between Zn and carbon electrodes was maintained at 4.0 mm and the volume of the electrolyte was 3.0 cm^3. The cells were assembled in cylindrical glass vessels (Fig. 2) with the length and diameter of each cell as 4.0 cm and 2.5 cm, respectively.

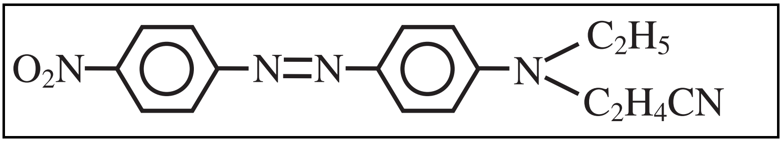

Figure 1: Molecular structure of orange dye (OD)

The discharge voltage-current, charge voltage/current-time and discharge voltage/current-time characteristics of all the cells were measured at room temperature by Keithley 196 Digital Multimeter.

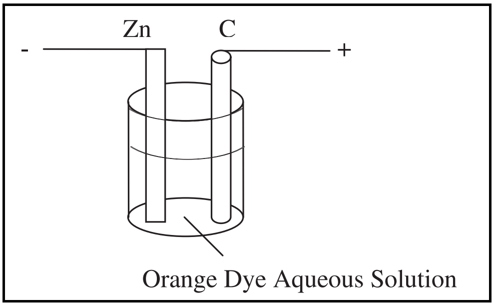

Figure 2: Schematic diagram of Zn/orange dye aqueous solution/carbon cell

Results and discussion

A comparison of discharge voltage-current (V-I) relationship of the zinc/orange dye aqueous solution/carbon electrochemical cells at different concentrations of orange dye is shown in Fig. 3. The zinc electrode's potential has negative polarity with respect to the carbon electrode (Karimov *et al*. 2006). The V-I relationship is typical for electrochemical cells (Hibbert 1993). The open circuit voltage/short circuit current-concentration of orange dye in aqueous solution is shown in Fig. 4 and their measured values are listed in Table 1. The increase of cell's output voltage and current are probably due to the increase of the concentration of orange dye molecules, involved in the reactions. At these processes, load resistance of the cell was changed accordingly. For the measurement of voltage-current discharge characteristics, the load resistance was variable. It was equal to "infinite" and "zero" for the measurement of open-circuit voltages and short-circuits currents, respectively. The current efficiency (E_i) for a fixed time (t) of 4 hours is calculated by the following formula (Crow 1988) and given in Table 1.

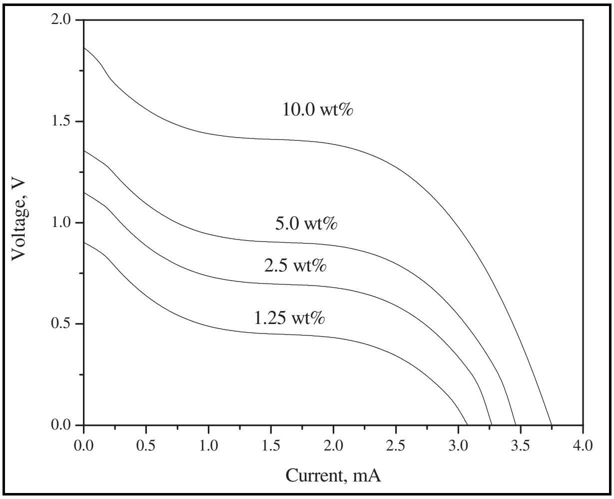

Figure 3: Voltage versus current discharge characteristic of zinc/orange dye aqueous solution/carbon cells for different concentrations

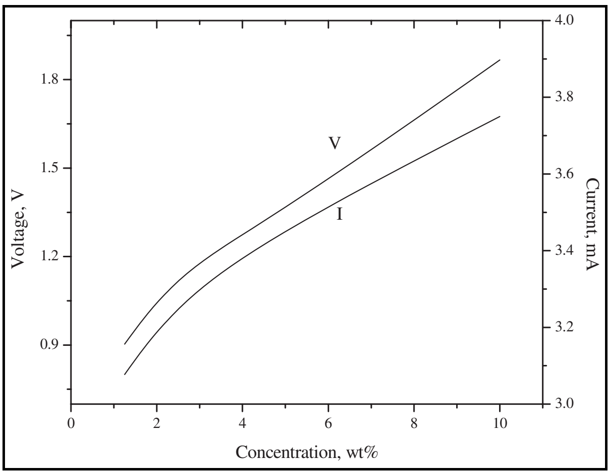

Figure 4: Open circuit voltage/short circuit current versus orange dye concentration curves for zinc/orange dye aqueous solution/carbon cells

$$E_i = \frac{\int_0^t I_d dt}{\int_0^t I_c dt} \quad (1)$$

where I_d is the discharging current and I_c is the charging current.

Optimal curves for charging and discharging at an orange dye concentration of 10.0 wt% are shown in Figures 5 and 6. The discharge voltage/current-time characteristics exhibit stable and constant behavior (Fig. 6). As a cell is charged, its voltage increases and as this voltage is opposite to the voltage of the supply, the current of the cell decreases (Fig. 5). The discharge characteristics were measured under constant load. These characteristics show that power is practically constant in the observed interval of time. Thus, charges produced by the cell in the unit of time are equal to the charges supplied to the load.

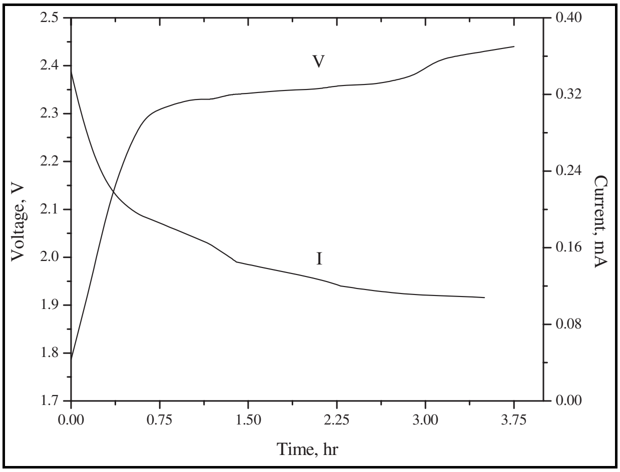

Figure 5: Charge voltage/current-time curves for 10.0 wt% concentration of orange dye in aqueous solution

The reactions taking place in this cell can be represented as (Karimov *et al.* 2006):

$$\text{At anode}: Zn \rightarrow Zn^{2+} + 2e^- \quad (2)$$

$$\text{At cathode}: 2(C_{17}H_{17}N_5O_2) + 2H_2O + 2e^- 2(C_{17}H_{17}N_5O)(OH) + 2OH^- \quad (3)$$

The over all cell reaction is

$$2(C_{17}H_{17}N_5O_2) + 2H_2O + ZnZn^{2+} + 2(C_{17}H_{17}N_5O) + 2OH^- \quad (4)$$

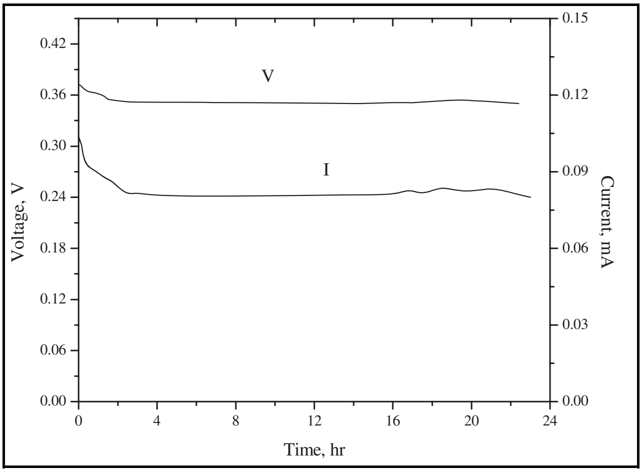

Figure 6: Discharge voltage/current-time behavior for 10.0 wt% concentration of orange dye in aqueous solution

As seen from Eq. 4, zinc is involved in chemical reaction, therefore it may be considered that the zinc electrode is active with respect to the carbon electrode in the zinc/orange dye aqueous solution/carbon electrochemical cell (Karimov *et al*. 2006). The electrical energy of each cell as a change of standard Gibbs free energy (ΔG^0), given in Table 1, is calculated by using following expression (Hibbert 1993).

$$\Delta G^0 = nFE^0 \tag{5}$$

where n is the number of electons transferred per mole (equal to 2); F is the Faraday constant (96487 C); and E^0 is the standard electromotive force of the cell.

The capacity of the cell (C), that is the proportional to energy accumulation by the cell, was calculated using the expression (Hibbert 1993).

$$C = \frac{nFW}{(MW)} \tag{6}$$

where W is the weight of the active electrode material (zinc in this case). Its weight is equal to 2.136 g; MW is the molecular weight of the material (zinc = 65.37). The calculated value of C is 6.31 kC = 1.75 Ah.

Table 1: Measured and calculated parameters of zinc/orange dye aqueous solution/carbon cells

Orange dye Concentration (wt.%)	Open circuit Voltage (V)	Short circuit Current (mA)	Current Efficiency (%)	Free energy Change, (kJ/ mol)
10.0	1.87	3.75	74	-724
5.0	1.36	3.46	69	-668
2.5	1.15	3.27	64	-631
1.25	0.90	3.08	60	-594

As a rule, an increase in the dimension of the cell and electrodes has an effect on the electrochemical properties and in particular, results in an increase in the output current.

CONCLUSIONS

For different concentrations of orange dye in aqueous solution, electrochemical zinc/orange dye aqueous solution/carbon cells have been fabricated and their electrochemical properties have been investigated. The cells are rechargeable. The value of open circuit voltage and short circuit current are found to be dependent on orange dye concentrations. At higher concentrations of orange dye, values of open circuit voltage and short circuit current are also observed high.

The current discharge/charge efficiency is also observed to be concentration dependent and higher with higher concentrations of orange dye. The stable and constant behavior is observed for discharge voltage/current-time characteristics for all concentrations of orange dye in aqueous solution. Higher concentration of orange dye can be used for better efficiency in zinc/orange dye aqueous solution/carbon electrochemical cells.

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REFERENCES

Arnold, E. In: Petty, C. M., Bryce, M. R. & Bloor, D. (Eds.) 1995. An introduction to molecular electronics. St. Edmundsbury Press Limited, London.

Bartic, C., Campitelli, A. & Borghs, S. 2003. Field-effect detection of chemical species with hybrid organic/inorganic transistors. Applied Physics Letters **82**: 475-477.

Blythe, R. 1979. Electrical properties of polymers. Cambridge University Press, USA.

Crow, D. R. 1988. Principles and applications of electrochemistry. Third Edition, Chapman and Hall, London.

Fiodiorov, M.I. 1999. Patent # 21244719, Moscow Russia 3.

Gutman, F. & Lyon, L. E. 1981. Organic semiconductors, Part A, Krieger Robert E. Publishing Company. Malabar, Florida, USA.

Gutman, F., Keyzer, H., Lyons, L. E. & Smoano, R. B. 1983. Organic semiconductors, Part B, Krieger Robert E. Publishing Company. Malabar Florida, USA.

Hibbert, D. B. 1993. Introduction to electrochemistry. Macmillan Press Ltd. London, UK.

Karimov, Kh. S. 1982. Electric properties of quasi-one dimensional crystals of tetracyanoquine dimethane complexes. Ph.D. thesis, A. F. Ioffe Physical Technical Institute, St. Peterburg, Russia.

Karimov, Kh. S. 1994. Electric properties of organic materials under uniaxial tension and complession. D.Sc. thesis, Department of Heat Physics, Academy of Sciences, Tashkent, Uzbekistan.

Karimov, Kh. S., Akhmedov, Kh. M., Dzhuraev, A. A., Khan, M. N., Abrarov, S. M. & Fiodorov, M. I. 2000. Organic-on-inorganic Ag/n-GaAs/p-CuPc/Ag photoelectric sensor. Eurasian Chemico-Technological Journal **2**: 251-256.

Karimov, Kh. S., Ahmed, M. M., Gul, R. M., Mujahid. M., Ahmedov, Kh. M. & Valiev, J. 2002. Proceedings of Advance Materials-2001, Dr. A. Q. Khan Research Labs., Rawalpindi, Pakistan.

Karimov, Kh. S., Sayyad, M. H., Ahmed, M. M., Khan, M. N., Karieva, Z. M., Shah, M., Zakaullah, Kh., Moiz, S. A. & Turaeva, M. A. 2004. Effect of temperature and humidity on electrical properties of organic orange dye complex films. Eurasian Chemico-Technological Journal **6**: 145-150.

Karimov, Khasan S., Sayyad, Muhammad H., Ali, Mukhtar, Khan, Muhammad N., Moiz, Syed A., Khan, Khurram B., Farah, Humera & Karieva, Zioda M. 2006. Electrochemical properties of Zn/ orange dye aqueous solution/carbon cell. Journal of Power Sources **155**: 475-477.

Moiz, Syed A. Ahmed, Mansoor M. & Karimov, Khasan S. 2005. Effects of temperature and humidity on electrical properties of organic semiconductor orange dye films deposited from solution. Japan Journal of Applied Physics **44**: 1199-1203.

Oh, B., Vissers, D. R., Zhang, Z., West, R., Tsukamoto, H. & Amine, K. 2003. New interpenetrating network type poly(siloxane-*g*-ethylene oxide) polymer electrolyte for lithium battery. Journal of Power Sources **119**: 442-447.

Panozzo, S., Armand, M. & Stephan, O. 2002. Light-emitting electrochemical cells using a molten delocalized salt. Applied Physics Letters **80**: 679-681.

Park, Cheol-Wan, Ryu, Ho-Suk, Kimb, Ki-Won, Ahn, Jou-Hyeon, Lee, Jai-Young & Ahn, Hyo-Jun 2007. Discharge properties of all-solid sodium-sulfur battery using poly (ethylene oxide) electrolyte. Journal of Power Sources 165: 450-454.

Rajendran, S., Sivakumar, M., Subadevi, R. 2003. Effect of salt concentration in poly(vinyl alcohol)-based solid polymer electrolytes. Journal of Power Sources **124**: 225-230.

Sayyad, M. H., Karimov, Kh. S., Ellahi, A., Moiz, S. A., Karieva, Z. M., Turaeva, M. A., Zakaullah, Kh. 2005. The photo-electrical behavior of n-Si and p-Si/orange dye/conductive glass cells. Eurasian Chemico-Technological Journal **7**: 133-138.

Stetter, J. R., Penrose, W. R. & Yao, Sh. 2003. Sensors, chemical sensors, electrochemical sensors, and ECS. Journal of The Electrochemical Society **150**: S11-S16.

Wu, G. M., Lin, S. J. & Yang, C. C. 2006. Alkaline Zn-air and Al-air cells based on novel solid PVA/PAA polymer electrolyte membrane. Journal of Membrane Science **280**: 802-808.

Ye, Hui & Xu, Jun John 2007. Zinc ion conducting polymer electrolytes based on oligomeric polyether/PVDF-HFP blends. Journal of Power Sources **165**: 500-508.

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تأثير تركيز الصبغة البرتقالية على الخواص الكهروكيميائية للزنك/ المحلول المائي للصبغة البرتقالية/ خلايا الكربون

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خلاصة

لقد تم التحقيق في الخصائص الكهروكيمياوية للزنك/ المحلول المائي للصبغة البرتقالية/ خلايا الكربون وذلك باستخدام تراكيز مختلفة من الصبغة البرتقالية. في هذه الخلايا تم استخدام الصبغة البرتقالية كمحلول الزنك والكربون كأقطاب كهربائية. وكان طول الأوعية الزجاجية 4 سم وقطرها 2.5 سم. لقد تم فحص آثار التركيز على خصائص تفريغ الجهد – التيار، الشحنة جهد/التيار – الزمن وتفريغ الجهد/التيار – الزمن. كما تمت ملاحظة جهود الدائرة الكهربائية المفتوحة وتيارات خلايا الدائرة القصيرة معتمدين على تركيز عالٍ من الصبغة. لقد وجد أن كفاءة تفريغ التيار/الشحنة تكون أكبر عند تركيز أعلى للصبغة. كما أظهرت خواص وقت التيار/ جهد التفريغ سلوك مستقر وثابت عند جميع التراكيز.