

# Semiconduction properties of some polyene–iodine charge-transfer complexes and their application in solid-state batteries

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The conjugated polyenes  $\beta$ -carotene, lutein, retinoic acid and  $\beta$ -apo-8'-carotenal are shown to form charge-transfer (CT) complexes with the electron acceptor iodine. The conductivity increases by several orders of magnitude and the activation energy decreases on CT complex formation. Using these complexes as cathodic material, batteries with the configuration Mg/(polyene–iodine CT complex)/graphite are developed. Different battery parameters are evaluated. The effects of ambient temperature and humidity on battery performance are also studied. Results show that a  $\beta$ -apo-8'-carotenal–I<sub>2</sub> based battery has the maximum power density and longest self-life and is suitable for use as a micro-electronic gadget energizer.

## 1. Introduction

Carotenoids which exist in close association with chlorophyll in plants and also in green-purple bacteria [1] are conjugated  $\pi$ -electronic systems. These materials in the solid state are well-known high-resistance semiconductors. Recently we have reported that these polyenes are capable of forming charge-transfer (CT) complexes with the electron acceptor iodine in the solid state [2]. A remarkable aspect of these materials is that they show an enormous increase in conductivity due to complex formation. This large enhancement in conductivity may be of much importance in relation to energy conversion and storage [3]. It is known that low-resistance CT complexes can be used as a new cathodic material in developing a solid-state electrochemical cell [4, 5]. CT complex based polyvinyl pyridine–iodine/lithium primary cells with a self-life of 10 years have been reported [6]. Recently, solid-state batteries using vitamin A acetate–iodine [7] and lycopene–iodine [8] complexes have been developed. These types of battery based on biomaterials are potentially cheap and easily accessible low-power sources. A comparative study of the performance of such batteries based on various carotenoids is of considerable importance in identifying the most efficient one for a specific application. In this paper we report the characteristics of solid-state batteries based on CT complexes of  $\beta$ -carotene, lutein,  $\beta$ -apo-8'-carotenal and retinoic acid and show that a  $\beta$ -apo-8'-carotenal–I<sub>2</sub> complex based battery has the maximum power density and self-life.

## 2. Experimental procedure

Ultra-pure polyenes used in this investigation were obtained as a gift from Hoffmann La Roche Co.,

Switzerland, and were used without further purification after checking the purity spectroscopically. Iodine was purified by vacuum sublimation. The electrode materials were degreased and surface oxides were removed by abrasion or acid-washing, followed by an acetone rinse and drying. For CT complex formation, polyenes in powder form were placed in iodine vapour at room temperature inside a dessicator. The vapour pressure of iodine inside the dessicator was maintained at 1 atm. The concentration of iodine in the complex would increase with the length of exposure time of the polyene in iodine vapour. After the formation of the complex the dessicator was evacuated to remove excess iodine. The conductivity measurements were made in a sandwich cell with stainless steel and SnO<sub>2</sub>-coated glass electrodes. For battery studies a cell with the configuration Mg/polyene–I<sub>2</sub> complex/graphite was developed. A schematic representation of the cell is shown in Fig. 1. The area of the cell was 1 cm<sup>2</sup>. Voltage and current were measured with a digital multimeter (Model 2100, HIL, India) and a Keithley 617 electrometer, respectively. Temperature measurement was performed using a copper–constantan thermocouple.

## 3. Results and discussion

### 3.1. Semiconductivity studies of polyenes and their CT complexes

In organic semiconductors, the temperature dependence of steady-state dark current generally follows the expression

$$I_d = I_{0d} \exp(-E_d/2kT) \quad (1)$$

and the slope of the linear plot of  $\log I_d$  versus  $1/T$  gives the dark activation energy  $E_d$ . In Equation 1 we

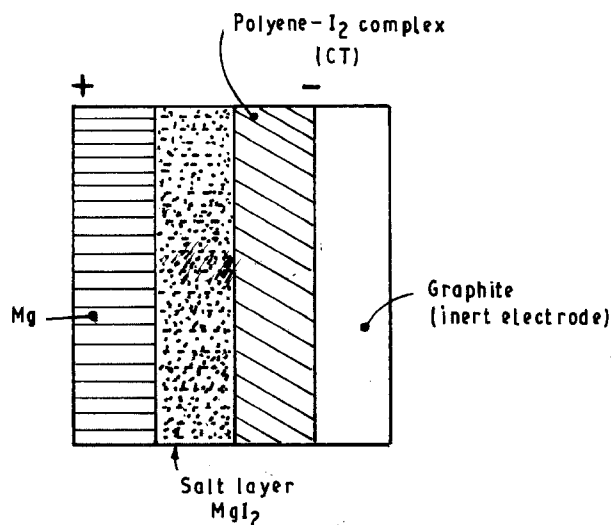


Figure 1 Schematic representation of the Mg/polyene-iodine complex/graphite cell.

have used a half energy as was originally done by Rosenberg [9]. However, as localized states generally dominate in wide band-gap materials, it is more realistic for organic solids to write down the activation energy equation according to the convention of extrinsic semiconductors as

$$I_d = I_{0d} \exp(-E'_d/kT) \quad (2)$$

The  $E'_d$  value is now exactly half of that of  $E_d$ . In wide band-gap materials either dominant electron levels or dominant hole levels contribute to the conductivity and the material behaves as an extrinsic semiconductor. However, in some materials both the electron and the hole levels contribute equally and the material behaves as a non-extrinsic semiconductor [10]. In such a case the half energy consideration is more realistic and this is the situation we encounter in pure polyene. In CT complexes, however, the donor material is doped with acceptor molecules and it is realistic to apply the conduction equation relevant to extrinsic material.

We have measured the dark activation energy of  $\beta$ -carotene, lutein,  $\beta$ -apo-8'-carotenal, retinoic acid and their complexes with iodine. Fig. 2 shows the representative Arrhenius plots for dark conduction of the polyene-iodine CT complexes. All the results are summarized in Table I. The dark conductivity increases by several orders of magnitude on complex formation for all the polyenes we have studied. This may probably be due to the formation of excess free thermal carriers in the dark or due to the thermal removal of electrons from the donor to the acceptor, leaving behind a hole into which other electrons may flow [11].

From Table I we observe that the dark activation energy decreases on complex formation for all the polyenes. A trapping conduction mechanism can be used as the model to explain the dark activation energy for CT complexes. Charge carriers trapped in the polyene-iodine complex below the conduction level are thermally excited to the conduction band in the dark and the carriers thus generated can

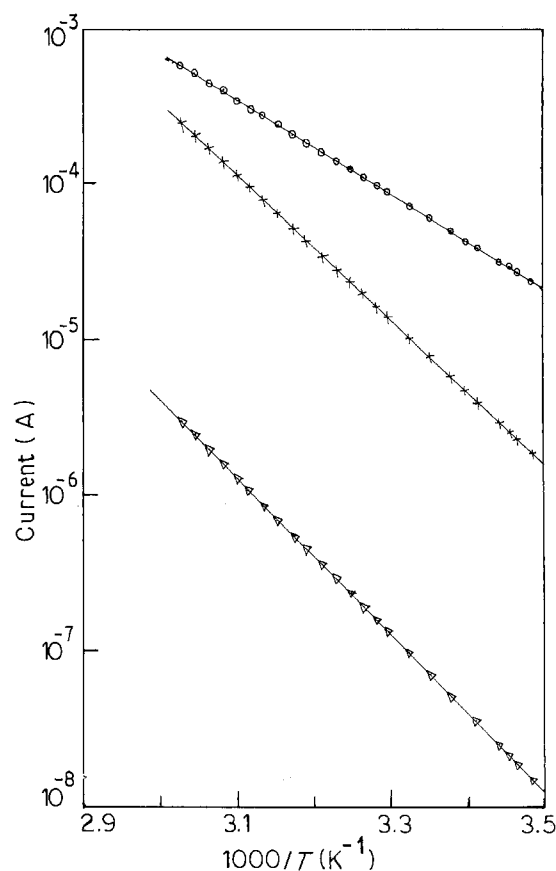


Figure 2 Arrhenius plots of different polyene-iodine CT complexes for (+) lutein, (O)  $\beta$ -apo-8'-carotenal, ( $\nabla$ ) retinoic acid.

TABLE I Conductivity enhancement ( $I_d^{CT}/I_d$ ) on complex formation and activation energy of pure polyenes and their CT complexes with iodine

Polyene	$E_d$ (eV)	$E_d^{CT}$ (eV)	$I_d^{CT}/I_d$
Retinoic acid	1.2	0.98	$7.5 \times 10^4$
$\beta$ -apo-8'-carotenal	1.1	0.6	$1.8 \times 10^8$
Lutein	2.19	0.93	$8.9 \times 10^7$
$\beta$ -carotene	1.5 <sup>a</sup>	0.55 <sup>b</sup>	—

<sup>a</sup> Data taken from Rosenberg [9].

<sup>b</sup> Data taken from Huggins and Leblanc [12].

migrate through the crystal by a repeated trapping-detrapping process. The depth of the trap level below the conduction level is the energy required for detrapping the carriers, which shows up as the thermal activation energy in the dark.

### 3.2. Polyene-iodine CT complex based solid-state battery

Primary solid-state electrochemical cells have been developed using CT complexes [4-6]. Batteries based on vitamin A acetate-iodine [7] and lycopene-iodine [8] CT complexes have been reported. In the CT complexes of  $\beta$ -carotene, lutein,  $\beta$ -apo-8'-carotenal and retinoic acid with iodine, the electrochemically active iodine is weakly bonded and can find its application in developing a CT-based solid-state battery.

The open-circuit voltage (OCV) of the cell with configuration Mg/(polyene-iodine CT complex)/graphite increases with time and attains a final value of 1.65 to 1.7 V in about 3 h after construction of the cell. The short-circuit current density for different polyene-iodine complexes is different and is shown in Table II. Fig. 3 shows the current-voltage characteristics of different polyene-iodine complex based batteries. The overvoltage (difference between OCV and the voltage after drain) is negligible for low current drainage. The value of overvoltage increases abruptly for current values greater than 100  $\mu$ A. It is found that for  $\beta$ -carotene and  $\beta$ -apo-8'-carotenal based batteries the voltage drop is very slow up to 100  $\mu$ A (corresponding voltage drops are 1.35 and 1.25 V, respectively). Above this current value a sharp voltage drop occurs. However, for lutein and retinoic acid based cells the value of current after which the voltage drop changes very rapidly is low (60  $\mu$ A) and corresponding voltage drop is 1.3 V. Assuming the cell weight to be equal to 0.2 g, a maximum power density of these cells has been calculated and values are given in Table II.

The cell was completely discharged through a load. The value of discharge current was maintained at 4  $\mu$ A for all the cells except for lutein-based cell where

TABLE II Short-circuit current ( $I_{sc}$ ), maximum power density ( $P_{max}$ ) and energy density ( $ED$ ) of different polyene-iodine complex based batteries

Polyene (complexed with $I_2$ )	$I_{sc}$ (mA)	$P_{max}$ ( $W\ kg^{-1}$ )	$ED$ ( $W\ h\ kg^{-1}$ )
Retinoic acid	0.19	0.45	0.6
$\beta$ -apo-8'-carotenal	20	1.47	25.6
Lutein	0.8	0.48	1.1
$\beta$ -carotene	0.63	1.25	1.6

0.5  $\mu$ A was the discharge current. The discharge characteristics are shown in Fig. 4. In the initial stage each cell shows a discharge with time after which a stable voltage is attained in spite of the drain. This cell stability continues for a significant length of time after which the cell voltage falls very rapidly with time. For  $\beta$ -apo-8'-carotenal- $I_2$  the stable voltage is about 1.31 V and the corresponding period is 750 h. For other cells these values are much lower. For cells with  $\beta$ -carotene- $I_2$ , lutein- $I_2$  and retinoic acid- $I_2$  these values are 1.05 V 30 h; 1.25 V, 190 h and 1.15 V, 8 h, respectively. From graphical integration of the discharge curve, a useful energy density is obtained for different polyene-iodine cells and values are given in Table II. It is found that these values are different for different polyene-iodine complexes and are in the order  $\beta$ -apo-8'-carotenal >  $\beta$ -carotene > lutein > retinoic acid. The decrease in energy density may arise from the lower iodine contents in the respective polyene-iodine CT complexes.

The operational mechanism of this type of cell is very simple [3, 4]. Here no salt is physically included in the cell assembly but is allowed to form at the surface of the anode in the form of a layer during operation. The CT complex works as a cathode and graphite as an inert electrode. The salt layer works as a separator between cathode and anode because it is electronically insulating but ionically conducting [3]. During operation, iodine is released from the complex and it enters the layer in ionic form. The iodine ion then reacts with magnesium and produces energy. Thus the formation of salt seems to be related to the energy generation. The reaction mechanism is as follows:

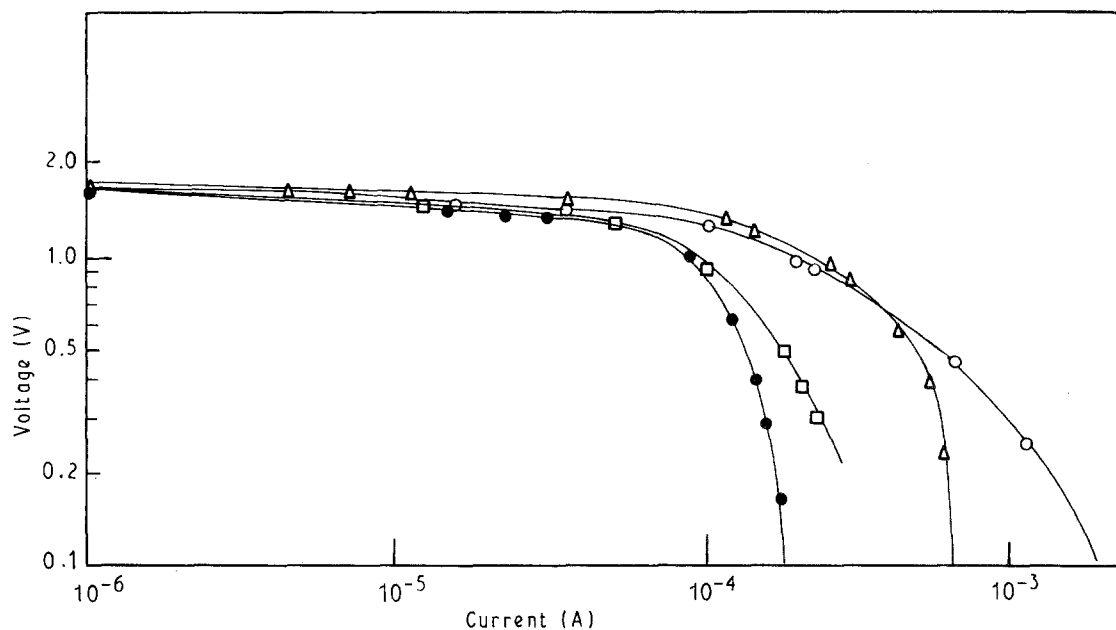
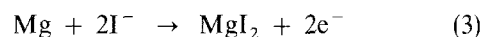


Figure 3 Current-voltage characteristics of cells with different polyenes-iodine CT complexes for ( $\Delta$ )  $\beta$ -carotene, ( $\square$ ) lutein, ( $\circ$ )  $\beta$ -apo-8'-carotenal, ( $\bullet$ ) retinoic acid.

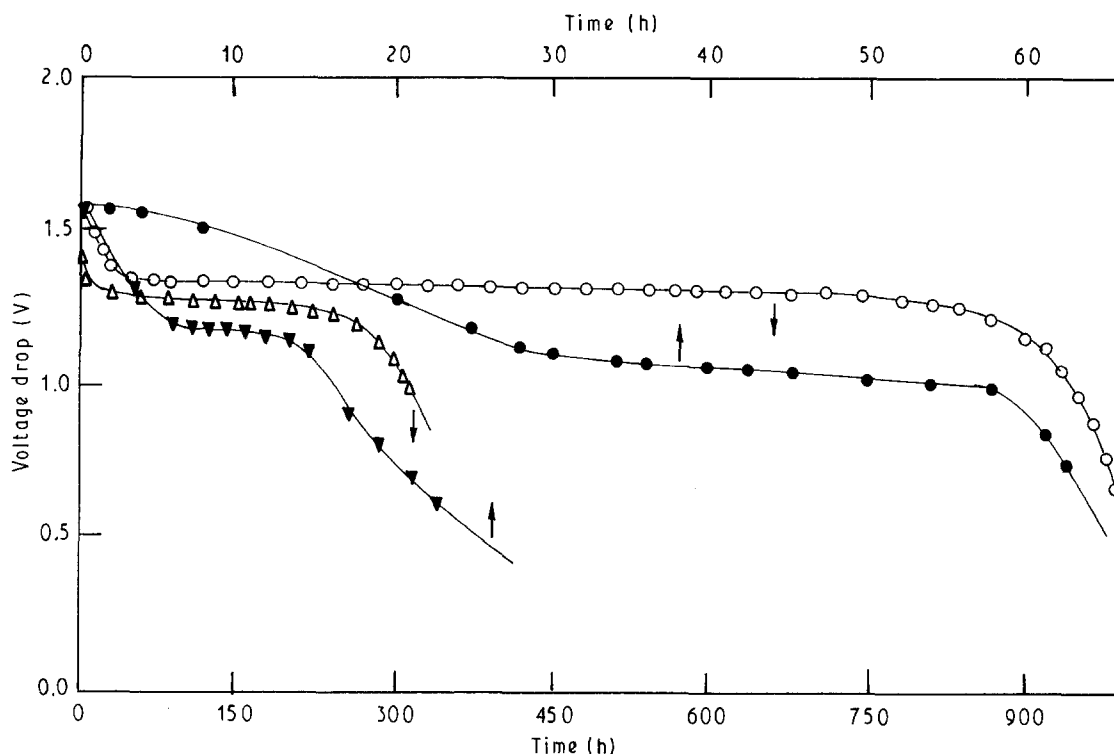


Figure 4 Discharge characteristics of cells with different polyenes-iodine CT complexes. The discharge current is maintained at  $4 \mu\text{A}$  for all the cells, except for lutein. (●)  $\beta$ -carotene, ( $\Delta$ ) lutein ( $0.5 \mu\text{A}$ ), (○)  $\beta$ -apo-8'-carotenal, ( $\nabla$ ) retinoic acid.

Using free energy or the heat of formation ( $H = 86 \text{ cal mol}^{-1}$ ) of the  $\text{MgI}_2$  salt in a simplified Gibbs-Helmholtz equation

$$E = \frac{H}{zF} + T \left( \frac{dE}{dT} \right) \quad (5)$$

where  $z$  is the number of electrons involved in the reaction,  $F$  the Faraday constant and  $T$  the absolute temperature, one can obtain the open-circuit voltage  $E$  theoretically. The value of  $E$  for  $\text{MgI}_2$  salt formation at room temperature ( $27^\circ\text{C}$ ) is thus found to be 1.87 V. The experimentally observed value of 1.6–1.7 V is close to the theoretical value. The slight deviations from this value are thought to be caused by imperfect formation of the  $\text{MgI}_2$  layer, resulting in a small degree of internal short-circuiting.

Fig. 5 shows the temperature dependence of open-circuit voltage of the  $\beta$ -apo-8'-carotenal based cell. It is found that the open-circuit voltage increases linearly with increasing temperature as expected from Equation 5. The value of  $dE/dT$  obtained from the slope is  $3.8 \times 10^{-3} \text{ V deg}^{-1}$  for  $\beta$ -apo-8'-carotenal and is very small. The effect of humidity on open-circuit voltage and on short-circuit current has also been studied. For all the batteries no appreciable changes in these parameters with humidity (from 0 to 90% at room temperature) have been observed.

#### 4. Conclusions

1. Due to the formation of a CT complex the conductivity of the polyenes increases by several orders of magnitude and the dark activation energy decreases. A trapping conduction mechanism seems to be operative.

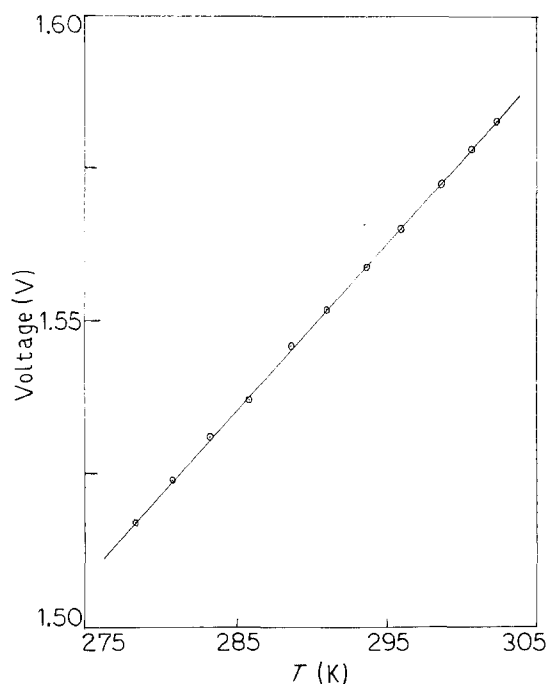


Figure 5 Temperature dependence of open-circuit voltage of the cell with configuration  $\text{Mg}/(\beta\text{-apo-8'-carotenal-I}_2 \text{ CT complex})/\text{C}$ .

2. Primary solid-state batteries with the configuration  $\text{Mg}/(\text{polyene-iodine CT complex})/\text{C}$  have been constructed. All the battery parameters have been measured and a maximum energy density of  $25.6 \text{ W h kg}^{-1}$  is obtained for the  $\beta$ -apo-8'-carotenal based battery, which also shows long-term stability of the voltage. The open-circuit voltage increases with increasing temperature. The battery parameters

indicate its prospective use as a micro-electronic gadget energizer.

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