

# SEMICONDUCTING PROPERTIES OF CHARGE- TRANSFER COMPLEX OF NATURALLY OCCURRING COMPOUND "PROTOPINE" WITH IODINE AND ITS APPLICATION IN SOLID - STATE BATTERIES

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## ABSTRACT

The charge- transfer (CT) complex based on protopine with electron acceptor iodine has been synthesized. The conductivity increases by several orders of magnitude and the activation energy decreases on formation of CT complex. Solid-state battery of configuration Zn protopine- I<sub>2</sub> / graphite has been developed using the CT complex as the cathodic material. The open- circuit voltage of the cell increases with the increase in temperature. The high open- circuit voltage and battery parameters indicate that the CT complex of natural occurring protopine can be used in fabrication of solid- state batteries.

**Key words:-** Fumaria indica, Protopine, Charge- transfer complex, Semiconductors, Solid- state battery.

## INTRODUCTION

Charge- transfer (CT) complex of bio-molecules possess certain properties, which could be used to explain the mechanism of electron transfer. The object of much intensive studies<sup>1</sup>. Many large bio-molecules become good semiconductors on preparation of their charge transfer complex. There is direct evidence that proteins are capable of forming charge transfer complexes<sup>2,3</sup>. In fact, in incorporation of Chloronil, a powerful electron acceptor, into cerum albumine arises its conductivity in its dry state by about 10<sup>6</sup><sup>4</sup>. Charge-transfer complex of vitamin B<sub>12</sub> and steroids with iodine has been reported earlier<sup>5</sup>.

In this communication, we report formation of charge transfer complex, of alkaloids "Protopine" isolated from Fumaria indica plant, with Iodine. Protopine shows 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<sup>6</sup>. It is known that low resistance CT complexes can be used in developing the solid- state electrochemical cell<sup>7</sup>. Recently solid -state batteries using vitamin A acetate - iodine<sup>8</sup> and lycopene - iodine<sup>9</sup> complexes have been developed. These types of battery based on biomaterials are potentially cheap and easily accessible low - power source. In this paper, the electrical characterisation (AC & DC) of the charge transfer

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complex based on protopine and iodine has been studied. Various electrochemical parameters like open circuit- voltage, short circuit current and their dependence on time and temperature have been studied. Impedance analyses of these batteries have been done in order to understand the electrode reactions.

### MATERIAL AND METHODS

The whole plant of *Fumaria indica* was collected from Varanasi district and identified by a Botanist. The specimen sample was kept in the department. Air-dried whole plant of *F. indica* (1Kg) was successively extracted from MeOH in soxhlet extractor. The methanolic extract was treated with 7% aqueous citric acid solution and filtered. The filtrate was basified with ammonia solution and extracted several times with chloroform. The combined extract on evaporation furnished crude base (9 gm). Chromatographic resolution of crude base over  $\text{SiO}_2$  column eluting with solvent of increasing polarity, eluent collected from  $\text{CHCl}_3$ -MeOH (95:5) yielded compound (A) protopine by crystallisation with MeOH.

Melting point was recorded over Toshniwal apparatus and uncorrected. IR spectra were recorded in Perkin-Elmer spectrophotometer model 221,  $^1\text{H-NMR}$  spectra were taken at 300 MHz in  $\text{CDCl}_3$  and TMS as internal reference. UV recorded on Elico spectrophotometer in MeOH. Mass spectrum was performed on Kratos M50 mass spectrophotometer operating at 70 eV. The electrical measurements were done on a Source Measure Unit (Keithley-236), Picoammeter (Keithley-485), LCZ meter (Keithley-3330) and temperature controller (Centure. India).

Compound A (Protopine): Crystallised from MeOH as colour needless crystals wt = 500 mg. m.p. = 204-205 °C Showed positive test for the alkaloids by Dragendorff's reagent. Rf. Values 0.56 [ $\text{CHCl}_3$ -MeOH (95:5)]. It exhibits UV  $\lambda_{\text{max}}^{\text{MeOH}}$  240 sh, 290 (log  $\epsilon$  -4.0) nm: IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{max}}$  : 1665, 1470, 1430, 1355, 1245, 1225. Its molecular

formula was found to be  $\text{C}_{20}\text{H}_{19}\text{NO}_5$  ( $\text{M}^+$  353.1244). The other peaks were at m/z 205 (100), 190 (35), 177 (10), 176 (10), 163 (75), 149 (25) and 148 (100).  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.0 (3 H, s), 2.70 (4 H, br), 3.70 (4 H, br), 5.92 (2 H, s), 5.95 (2 H, s), 6.66 (1H, s), 6.69 (2 H, d,  $J = 8\text{Hz}$ ), 6.92 (1 H, s). It was found to be identical with Protopine on comparison with authentic sample (mixed mp, co-TLC, superimposable IR)<sup>10,11</sup>.

The charge transfer complex of the protopine with iodine has been prepared by the method described earlier<sup>12</sup>. The formation of 1 : 1 complex between protopine and iodine has been established by elemental analysis and conductimetric titration method<sup>5</sup>. The conductivity of the CT complex was measured in a sandwich configuration with graphite as a contact. For battery studies a cell with the configuration Zn/ protopine-  $\text{I}_2$ / graphite was developed.

### RESULTS AND DISCUSSION

#### Current-voltage characteristics

Current-voltage (I-V) curve of the charge transfer complex was plotted to learn whether the contact were ohmic or not and to assess the role of space charge limited current. The plot of I vs  $V^2$  is non- linear indicating that space charge limited current does not play any role in the conduction process at higher voltages.<sup>13</sup> The I-V characteristic was found to be linear showing ohmic in nature in the range of + 10 volt. The conductivity of the CT complex was found to be  $(9.41 \pm 0.15) \times 10^{-7} \text{ cm}^{-1}$  that was  $10^5$  times greater than the protopine. The conductivities were also studied as a function of temperature. The increasing trends of conductivity with temperature indicate that the material is semiconductor in nature. The activation energy of the compound was found to be 0.12 eV. These conductivity changes on complexation are explained by the removal of the electron from the donor to the acceptor leaving behind a 'hole' into which other electrons may flow. The decrease in

activation energy is explained, as less energy is required to promote the electron from donor to acceptor than is required to promote it into the conduction band of the donor<sup>5</sup>.

#### Time dependence of dc electrical conductivity:

The vast majority of bio-molecule shows ionic conductivity<sup>5</sup>. The invariance of electrical conductivity with time has been taken as a measure that most of the charge transfer materials are only electronic conductors rather than ionic ones. However the existence of mobile ion in ionic materials may leads to some or predominant ionic conduction as in super ionic conductors. The variation of electrical conductivity with time has been shown in fig. 1, indicate fast exponential type decrease in electrical conductivity and saturated latter to almost constant values, which could be separated as electrical and ionic part by extra plotting linear part to zero time for electronic and point wise subtracting for ionic conduction. It is clear that mobile ions are present in the material and it becomes a purely electronic conductor after two hours of electrolysis. Thus freshly prepared charge transfer complex of protopine showed mixed ionic electronic conduction. The relative magnitude of ionic conductivity to electronic conductivity was determined by extrapolation of linear portion and subtracting point wise. The ionic transport number ( $t_i$ ), determined from the ratio of  $\sigma_i/\sigma_{total}$ , has value of 0.18.

#### Alternate current studies :

AC conductivities were measured in the range of 40 Hz -  $10^5$  Hz, and then data were simulated in the range of  $10^{-3}$  Hz to  $10^{11}$  Hz using EG & G, CNLS fitting software. The complex impedance plot ( $Z_{real}$  vs  $Z_{imag}$ ) has been presented in fig. 2. Usually we expect the grain, grain boundary and electrode contribution to the overall measured electrical properties, so in general we expect the presence the three arcs. It is very likely that grain and grain boundaries processes are having time constant close to each other, giving rise to the left arc

which is very little depressed and the are appearing lower frequency corresponds to the electrode contribution. The equivalent circuit is found to be (RQ) (RC) ie one set of resistance and constant phase element (CPE) connected in parallel are further connected to another set of parallel set of resistance and capacitance. The CPE is some times used instead of pure capacitance because a (RC) circuit is not always sufficient for the analysis of AC response of a material<sup>14</sup>. The relaxation time ( $=RC$ ) for the two relaxation processes going on are found to be  $1.75 \times 10^{-4}$  s and  $9.60 \times 10^{-7}$  s. The presence of two peaks (one clear out & other a hump) corresponds to these two relaxation process can he observed in  $Z_{imag}$  vs frequency plane in 3D perspective plot (fig 2).

#### Cell Characteristics :

Primary solid- state electrochemical cells based on CT complexes have been reported<sup>7</sup>. Batteries based on vitamin A acetate- iodine<sup>8</sup> and lycopene- iodine<sup>9</sup> CT complexes have been developed. The variation of  $V_{oc}$  and  $I_{sc}$  as a function of time against  $10\text{ K } \Omega$  external load for the cell of configuration Zn/ protopine-  $I_2$ / graphite has been shown in fig. 3. The variation of initial cell voltage  $V_c$  with current density  $J$  at different temperatures is shown in fig. 4. It can be observed that  $V_c$  remains almost constant for  $J = 200\text{ } \mu\text{A cm}^{-2}$  but decreases afterwards with an increase in the value of  $J$ . Initial cell voltage was measured as soon as the current was drawn, and the internal resistance of the freshly prepared cell was very small, hence the decrease of the cell voltage is due not to resistance polarization but probably to anodic and cathodic polarizations. In this cell the CT complex works as cathode and graphite as an anode electrode. The salt layer deposited at anode works as a separator between cathode and anode because it is electronically insulating but ionically conducting<sup>6</sup>. During operation, iodine is released from the complex and it enters the layer in ionic form. The released

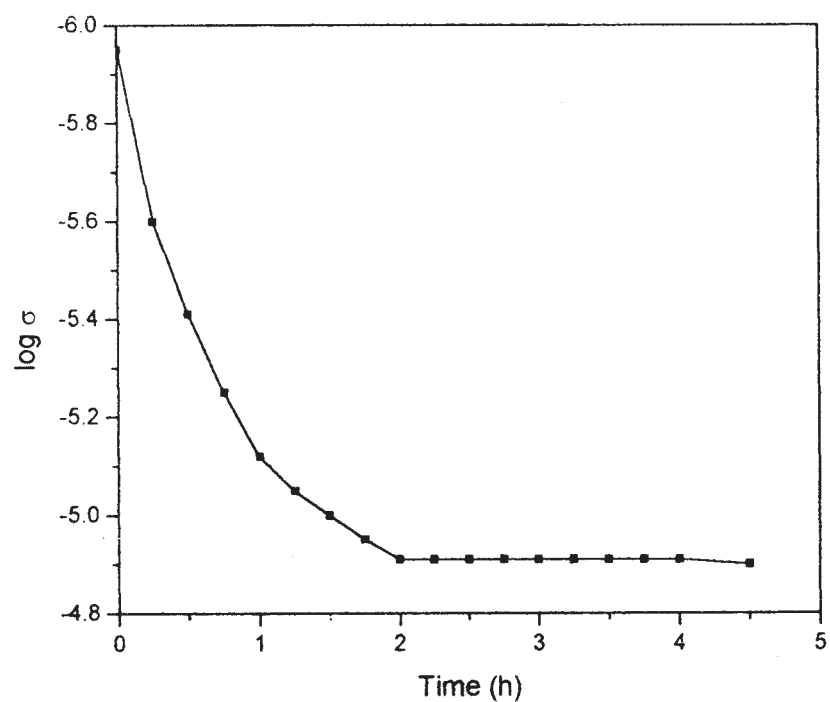


Fig. 1. log (sp. conductance) Vs time plot for CT complex.

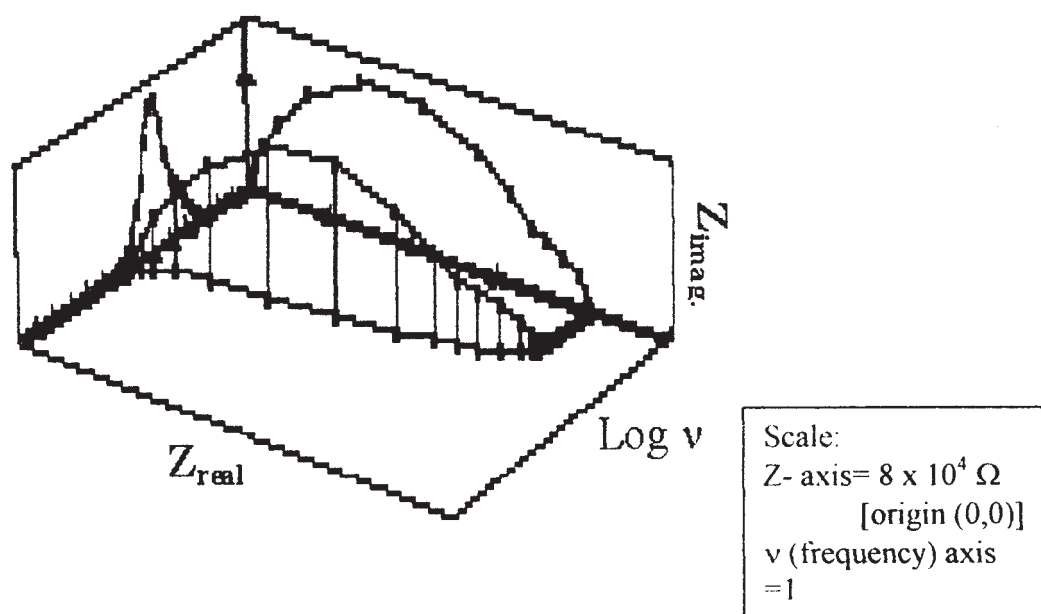


Fig. 2. Three-dimensional perspective plots for CT complex.

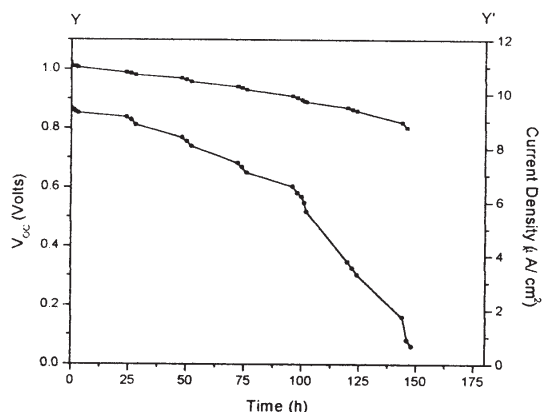


Fig. 3. Variation of open circuit voltage ( $V_{oc}$ ) and current density with the time at  $10K \Omega$  load

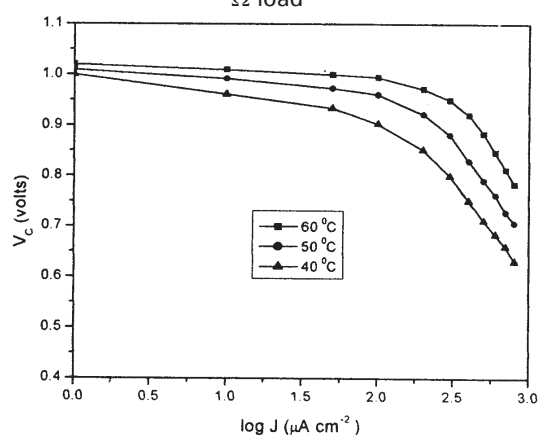


Fig. 4. Current- voltage characteristics of the cell at different temperatures

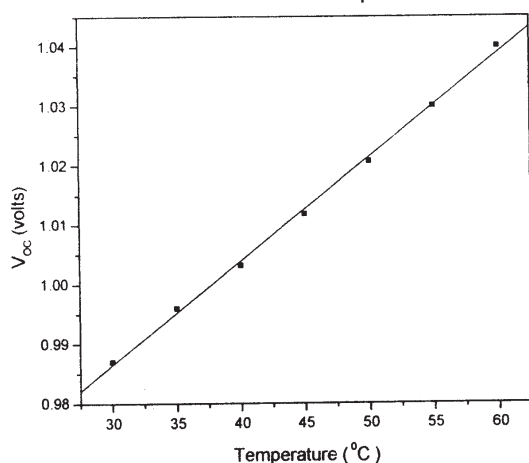


Fig. 5. Temperature dependence of open- circuit voltage of the cell

iodine then reacts with zinc and produces energy. The operational mechanisms of such type of cells have been reported earlier<sup>6,7</sup>. The reaction mechanism is as follows

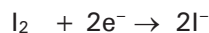
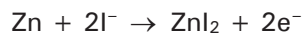


Fig. 5 shows the temperature dependence of open- circuit voltage of the cell. It is found that the open- circuit voltage increases with increasing temperature. Thermodynamic parameters for the cell are calculated by using the following equations

$$\Delta G = -nEF \quad (1)$$

$$E = -\Delta H/nF + T [dE/dT] \quad (2)$$

$$\Delta G = \Delta H - T\Delta S. \quad (3)$$

The Gibbs free energy for the cell was found to be 190.5 kJ/ mol. The enthalpy and entropy values were found to be 292.2 kJ/ mol and 347.1 J/K respectively, from the temperature dependence of the cell<sup>15</sup>.

## CONCLUSION

The CT complex based on protopine and iodine has been synthesized. Due to the formation of CT complex the conductivity of the protopine increases by several orders of magnitude and the activation energy decreases. The open- circuit voltage of the cell with configuration  $\text{Zn} / \text{protopine- I}_2 / \text{graphite}$  increases with the increasing temperature. The high open- circuit voltage and battery parameters indicate that the CT complex of natural occurring protopine can be used in fabrication of solid- state batteries.

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