# Electrical Conduction Mechanism in Ferrocene

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Electrical conduction in ferrocene has been studied using a 'sandwich' type of cell in DC and AC fields. Space charge limited conduction in DC and orientation polarization in AC have been observed.

**Key Words: Ferrocene, Space-charge limited conduction, Relaxation effect, Bonding in ferrocene.**

## INTRODUCTION

The conduction behaviour of solids, specially of insulators, has been a subject of study for over 50 yrs. Mott and Gurney[1] predicted that the space-charged limited current in an insulator is directly proportional to the cube of the thickness of the material. Rose[2] formulated a theory of space-charge limited current in defect insulators. Current voltage characteristics in ferrocene carboxylic acid have been studied with the use of conventional sandwich type cells[3]. Lately, some interesting investigations on the effect of pressure on the conduction in ferrocene have been reported[4]. Ferrocene belongs to an interesting category of compounds called sandwich complexes, characterized by the presence of two cyclopentadienyl rings, one above and the other below the $Fe^{2+}$.

The authors report the results of their investigations on the conduction mechanisms in DC as well as in AC fields.

## RESULTS AND DISCUSSION

**(a) Direct current measurement:** Pellets of different thicknesses of the material were subjected to varying DC fields and the currents were recorded. The voltages were in the range of 50–1000 V, A log I-log V plot shows linearity with differing slopes at different voltage regions [Table-1], The region of Ohm's law is at the lower end followed by an abrupt change to a non-ohmic slope at a higher voltage, where the current was proportional to the cube of the applied voltages.

Experimental measurements were also carried out at different temperatures.

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The log I-log V characteristics for different temperatures show that the general nature of the plots remains practically unchanged. However, the transition in the slope takes place at 465 V at 70°C, whereas it takes place at 443 V and 403V at temperatures of 80° and 90°C respectively.

TABLE-1
CURRENT-VOLTAGE MEASUREMENTS OF DIFFERENT SAMPLE THICKNESSES OF FERROCENE

| Voltage (V) in volts | Current (I) in amperes | | |
|---|---|---|---|
| | Sample I | Sample II | Sample III |
| 50 | 0.027 | 0.013 | 0.012 |
| 100 | 0.055 | 0.023 | 0.023 |
| 150 | 0.082 | 0.036 | 0.035 |
| 200 | 0.140 | 0.105 | 0.040 |
| 250 | 0.234 | 0.060 | 0.058 |
| 300 | 0.337 | 0.072 | 0.061 |
| 350 | 0.535 | 0.094 | 0.089 |
| 400 | 0.799 | 0.116 | 0.093 |
| 450 | 1.136 | 0.131 | 0.109 |
| 500 | 1.559 | 0.165 | 0.137 |
| 550 | 2.074 | 0.197 | 0.178 |
| 600 | 2.993 | 0.258 | 0.245 |
| 650 | 3.420 | 0.308 | 0.241 |
| 700 | 4.997 | 0.350 | 0.326 |
| 750 | 5.248 | 0.452 | 0.412 |
| 800 | 6.396 | 0.537 | 0.486 |
| 850 | 7.649 | 0.644 | 0.594 |
| 900 | 8.040 | 0.757 | 0.603 |
| 950 | 10.691 | 0.899 | 0.815 |
| 1000 | 12.504 | 1.048 | 0.950 |
| Sample thickness(mm) | 0.920 | 2.100 | 2.170 |

Measurements of current were made at different temperatures at specific voltages of 100 V and 800 V. [Table-2]

The plots of log I *vs.* $T^{-1}$ were linear. The curves were linear at both 100 V and 800 V. An activation energy of 52.6 J $K^{-1}$ $mole^{-1}$ was obtained for both the ohmic and space charge conduction regions.

The current density J in a trap free insulator is given by the approximate relationship[3]

$$J = \frac{9}{8}\frac{\mu\varepsilon\varepsilon_0 V^2}{a^3}$$

where J = current density, $\mu$ = mobility, $\varepsilon$ = dielectric constant, $\varepsilon_0$ = permittivity of free space, V = applied voltage and a = thickness of the sample.

TABLE-2
VARIATION OF CURRENT TEMPERATURE AT CONSTANT VOLTAGE FOR FERROCENE

| Temperature (T) | Current in microamperes | |
|---|---|---|
| | 100 V | 800 V |
| 373 | 0.202 | 3.149 |
| 383 | 0.297 | 4.150 |
| 393 | 0.362 | 5.275 |
| 403 | 0.547 | 8.910 |
| 413 | 0.788 | 13.710 |
| 423 | 1.523 | 22.250 |
| 433 | 1.718 | 27.605 |

Sample thickness = 2.10 mm

This expression does not show the temperature dependence. The calculated values of current were higher than those obtained experimentally. However, the presence of traps modifies the current through insulators. Rose[2] showed that a larger fraction of the injected charge gets condensed in the traps, thus lowering the charge density. Traps lower the drift mobility of the carriers and hence the magnitude of the space charge limited current. The current density is given by

$$J = \frac{9\mu\varepsilon\varepsilon_0 V^2\theta}{8a^3}$$

where $\theta$ = ratio of the free to the trapped charges and given by the approximate relationship[5]

$$\theta = \frac{N_0}{N_\varepsilon}\exp\frac{-I}{kT}$$

For ferrocene, our results clearly establish the temperature dependence of $\theta$. The slopes of the curves obtained by plotting log I *vs.* log V are of the same order showing that $I \propto V^3$. The cubic dependance on the thickness of the sample was also observed with nearly equal values of $V^3/Ia^3$.

The transition voltage ($V_t$) has a thermal activation energy equal to the difference of the activation energies in the ohmic and SCLC regions[3]. Activation involves the energies required to (a) raise the carriers from their dominant levels to the corresponding transport band and (b) to create carriers in the current levels. However, when enough carriers are injected, then the latter may be suppressed.

The similarity in activation energies for both the ohmic and SCLC regions shows that ferrocene is an extrinsic conductor.

**(b) Alternating Current Measurements:** Current frequency results are shown in Table-3 for three different voltages.

TABLE-3
CURRENT FREQUENCY MEASUREMENTS FOR FERROCENCE AT DIFFERENT VOLTAGES

| Frequency in kHz | Current in microamperes | | |
|---|---|---|---|
| | 1 volt | 5 volt | 10 volt |
| 0.5 | 0.120 | 0.206 | 0.311 |
| 1.0 | 0.169 | 0.330 | 0.602 |
| 2.0 | 0.243 | 0.481 | 0.952 |
| 3.0 | 0.278 | 0.596 | 1.120 |
| 4.0 | 0.298 | 0.679 | 1.221 |
| 5.0 | 0.298 | 0.723 | 1.317 |
| 6.0 | 0.328 | 0.741 | 1.385 |
| 7.0 | 0.327 | 0.759 | 1.390 |
| 8.0 | 0.328 | 0.765 | 1.399 |
| 9.0 | 0.324 | 0.758 | 1.398 |
| 10.0 | 0.322 | 0.757 | 1.395 |
| 15.0 | 0.321 | 0.757 | 1.386 |
| 20.0 | 0.320 | 0.750 | 1.373 |
| 25.0 | 0.319 | 0.742 | 1.342 |
| 30.0 | 0.308 | 0.730 | 1.281 |
| 35.0 | 0.307 | 0.721 | 1.242 |
| 40.0 | 0.297 | 0.709 | 1.181 |
| 45.0 | 0.290 | 0.699 | 1.152 |
| 50.0 | 0.281 | 0.684 | 1.121 |

Sample thickness = 0.79 mm

At low frequencies, current rises with an increase in frequency until the "relaxation frequency" is reached whereupon the current decreases[6]. For ferrocene the relaxation frequency was seen to be 6 kHz. Current frequency curves for samples of different thicknesses are of identical shape and the current rises with decreasing thickness of the ferrocene material. However, the current rises with increasing temperature.

Table-4 shows variation of current with temperature for ferrocene at a constant frequency and voltage.

TABLE-4
VARIATION OF CURRENT WITH TEMPERATURE FOR FERROCENE AT A CONSTANT FREQUENCY AND VOLTAGE

| Temperature (T) | Current in microamperes at 5 volts and 10 kHz frequency |
|---|---|
| 373 | 0.558 |
| 383 | 0.567 |
| 393 | 0.579 |
| 403 | 0.577 |
| 413 | 0.588 |
| 423 | 0.596 |
| 433 | 0.665 |

Sample thickness = 0.57 mm

A plot of log I *vs.* $T^{-1}$ for the above measurements was linear and the activation energy was found to be 2.96 J $K^{-1}$ $mol^{-1}$

The dipoles present in any dielectric tend to align themselves in the direction of the field. However, if the field is an alternating one, the dipoles will switch so as to orient themselves in the direction of the applied field. Resonance[5] occurs when the frequency of the applied field is the same as the frequency with which the dipoles switch. However, with increasing frequencies, the dipoles cannot switch as rapidly and the alternation of the polarization lags behind the field. In the region beyond the relaxation frequency, the field produces virtually no polarization of the dielectric. In the ferrocene molecule, considering its molecular orbital diagram[6], the ring orbitals and the corresponding 3d orbitals of the metal form two strong $\pi$ bonds[7]. These bonds are thought to be responsible for most of the stability in the ferrocene molecule. The $\pi$-electrons present in the cyclopentadiene rings appear to favour space-charge limited conduction.

## EXPERIMENTAL

The ferrocene sample was obtained from Aldrich (England) in a high state of purity. It was finely powdered and pellatized in a hydraulic press. All measurements were carried out in a dry nitrogen atmosphere.

### Direct current measurement

The stabilized mains voltage was stepped up beyond 1000 volts with the help of a DC power unit fabricated in our laboratory. For further smoothening, a series of Zener diodes were used. The output voltage was further calibrated using a digital Philips multimeter PM 2525. The experimental material in the form of a pellet was placed between the electrodes of a specially designed sandwich type cell[7]. The temperature of the experiment was varied using an electrically operated air oven.

**Alternating current measurement**

An AF signal generator (Type H, model I) manufactured by Advance Components, England) was used for applying alternating field to the experimental material. This gave an output voltage from 0–20V and the frequency ranged from 300 Hz to 50 kHz.

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## REFERENCES

1. N.F Mott, *Proc. Phys. Soc. (London)*, **62**, 416 (1949).
2. A. Rose, *Phys. Rev.*, **102**, 1648 (1955).
3. A. Bhattacharjee and B. Mallik, *Indian J. Phys.*, **66A**, 369 (1992).
4. ———, *Mater. Sci.*, **27**, 5877 (1992).
5. M. Deepak, A. Sharan, P. Srinivasan, K. Shahi and K.V. Srinivasan, *J. Indian Chem. Soc.*, **77**, 349 (2000).
6. J.C. Anderson, K.D. Leaver, R.D. Rawleigh and M. Alexander, Material Sciences, Chapman & Hall, London, 516 (1990).
7. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, p. 740 (2001).

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