

E1-19 The activation of electronic conduction in cobalt ferrocyanide by interstitial water

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Due to the unusually large unit cell structure, the crystals of heavy metal ferri- and ferrocyanides can accommodate water molecules and the electronic conductivity gets enhanced by several orders of magnitude. Studies on the above properties of cobalt ferrocyanide are reported. $(\text{Co}_2\text{Fe}(\text{CN})_6)$ was prepared and the conductivity of the polycrystalline powder was measured by pressing the sample between copper electrodes in a glass tube and immersing the sealed sample in a thermostatic oil bath to vary the temperature. DC and AC conductivities at different temperatures and at different H_2O concentrations (c) were measured. Electrolytic conduction was not observed in the sample.

The conductivity at 303 K increased from $\sim 10^{-8} \text{ } \Omega^{-1} \text{ m}^{-1}$ to $\sim 10^{-5} \text{ } \Omega^{-1} \text{ m}^{-1}$ when the H_2O concentration increased upto 17%. At a given value of c , a plot of $\ln \sigma$ vs T^{-1} gave a straight line satisfying the relation:

$$\sigma = \sigma_0 e^{-E/kT}$$

However, the activation energy decreases with c . A plot of activation energy vs concentration showed a linear relationship. E decreased from 0.8 eV to 0.4 eV when c increased from 1 to 17%. This result can be explained as due to the lowering of the activation energy of hopping electron transport by the high dielectric constant of water.

Interstitial water molecules activate the electronic conduction in cobalt ferrocyanide similar to the other ferri- and ferrocyanides. However, the observed decrease of the activation energy with the H_2O concentration is distinctly different from most of the similar heavy metal ferrocyanides, but have some similarities to that of Prussian blue when $T < 383$ K.

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