

E1-11 The influence of interstitial water on electronic conduction and activation energy in zirconium ferrocyanide

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Electronic conduction properties and crystal structures of many heavy metal ferri- and ferrocyanides are well known. The activation of electronic conduction due to interstitial water is a common property to all. The activation energy of most of them are reported to be independent of H₂O concentration.

The electronic conduction properties of zirconium ferrocyanide, prepared by double decomposition of potassium ferrocyanide with a large excess of zirconium sulphate, is investigated. The temperature variation of polycrystalline powder, compressed between copper electrodes in a glass tube, is studied. DC and AC conductivities at different temperatures and at different H₂O concentrations are measured.

At a given H₂O concentration (c), the conductivity (σ) varies according to the relation. $\sigma = \sigma_0 e^{-E/kT}$. The variation of activation energy (E) with c is approximately linear. E decreases from 0.6 eV to 0.3 eV when c increases by 12%. The conductivity at 303 K increases by 8 orders of magnitude ($\sim 10^{-21} \Omega^{-1}m^{-1}$ to $\sim 10^{-13} \Omega^{-1}m^{-1}$) when the H₂O concentration increases upto 12%.

Like many ferri- and ferrocyanides, the interstitial water molecules enhance the conductivity of zirconium ferrocyanide. The decrease in activation energy with c makes this sample distinctly different from most of the ferrocyanides but the results are very similar to that of cobalt ferrocyanide. According to these results it is reasonable to believe that there exist a new class of ferrocyanides with distinctly different electronic conduction properties. For this new class, the activation energy decreases with H₂O concentration while for the previously reported class the activation energy is independent of the H₂O concentration. A simple theoretical model, which describes the data qualitatively, is discussed.

Financial assistance by University of Ruhuna (Research grant RU/SF/RP/94/2) is acknowledged.