

Electronic Conduction in Solid Potassium Permanganate Excited by Water Molecules

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Received April 18, 1983; in revised form August 10, 1983

Water molecules present as an interstitial impurity are found to induce electronic conduction in solid KMnO_4 with an activation energy of ≈ 0.28 eV. It is suggested that when ionic sites are surrounded by water molecules the high dielectric constant of the water lowers the activation energy associated with transfer of electrons between the donor-acceptor states involved in the hopping conduction.

The study of electrical transport phenomena in low mobility solids has received much attention (1-6). Most earlier investigations in this field were limited to study of metallic oxides (3, 4). Recently, more elaborate compounds, especially inorganic and organic charge transfer complexes, were also widely studied (5). In this note we report our observations on a novel type of electronic conduction in solid potassium permanganate containing water molecules as an impurity.

Experimental

Analytical grade KMnO_4 was further purified by recrystallization in deionized water free from organic matter. The crystals were dried in vacuum at 40°C , pulverized, and compacted between stainless steel electrodes in a pyrex glass tube (diameter ≈ 4 mm and pellet length ≈ 2 mm) at a pressure of 10^6 Pa. The desired amount of moisture was introduced by exposing the pellet to the humid atmosphere in a desiccator containing water, before sealing the ends of the tube with epoxy resin. The samples

tested contained 2% water by weight. ac conductivities (40 Hz, 4 kHz) at different temperatures were determined. Thin disks of the material pressed between stainless steel electrodes were used to pass large currents for very long intervals of time, to see whether electrolytic effects were present. Single crystals of KMnO_4 containing 2% H_2O were also tested; the conductivity characteristics were found to be isotropic and the same as that of compressed pellets.

Results and Discussion

The electrical conductivity of anhydrous potassium permanganate (7) at room temperature (30°C) is $\approx 10^{-8} \Omega^{-1} \text{m}^{-1}$. Introduction of 2% H_2O (KMnO_4 has no fixed quantity of bound water of crystallization) increases conductivity by a factor of $\approx 10^3$. Conduction in samples containing water is entirely electronic. When several faradays of charge was passed through small quantities of the material (pellets 0.05 cm thick and diameter 0.2 cm) no changes in conductivity characteristics were observed (if ionic conduction is present, electrolysis

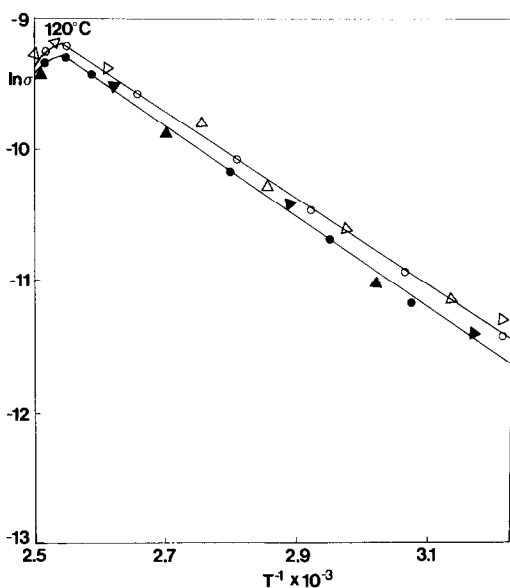


FIG. 1. The plot of $\ln \sigma$ (σ in $\Omega^{-1} \text{ m}^{-1}$) vs $1/T$ (T in $^{\circ}\text{K}$): \circ —ac measurement at 4 kHz (compressed pellets), \bullet —ac measurement at 40 Hz (compressed pellets), \triangle —ac measurement at 4 kHz (single crystal), \blacktriangle —ac measurement at 40 Hz (single crystal).

will change I–V characteristics, increasing the resistance with time).

The plots of $\ln \sigma$ vs T^{-1} are found to be linear until a critical temperature $T_c \approx 120^{\circ}\text{C}$ is reached, i.e., below T_c , the relation

$$\sigma = \sigma_0 e^{-E/kT} \quad (1)$$

is satisfied. The activation energy E and σ_0 are slightly dependent upon frequency of the current, i.e., $E = 0.31 \text{ eV}$, $\sigma_0 = 0.8 \Omega^{-1} \text{ m}^{-1}$ at 40 Hz, and $E = 0.28 \text{ eV}$, $\sigma_0 = 0.4 \Omega^{-1} \text{ m}^{-1}$ at 4 KHz. E is independent of the percentage of H_2O in the compound; however, σ_0 is sensitive to concentration of H_2O and the values given above corresponds to KMnO_4 containing 2% H_2O by the weight (Fig. 1).

The electronic transport in low mobility materials can result from hopping or polaron mechanism (1, 2, 8). Because of the availability of donor–acceptor sites (MnO_4^- and MnO_4^{2-} in the case of KMnO_4) the

charge transfer complexes are ideal materials where this mechanism can operate. When MnO_4^- , MnO_4^{2-} ionic sites are surrounded by water molecules, the activation energy associated with the donor–acceptor electron transfer process is lowered, as the electric field around the ions is reduced by the high dielectric constant of water, i.e., when ions are surrounded by water molecules, they are in an environment similar that in the aqueous solution and the electron transfer becomes easier. The fact that the electrical conductivity decreases very rapidly when the temperature exceeds $T_c \approx 120^{\circ}\text{C}$ can also be explained very easily. For water molecules to act as an effective dielectric medium around the ions, the hydrogen bonding between water molecules is important. These bonds are broken at the critical temperature T_c ($kT_c = 0.034 \text{ eV}$, \sim strength of a hydrogen bond).

H_2O excited electronic conduction is also observed in other charge transfer solids, e.g., ferrocyanides and ferricyanides; here again the conductivity decreases very rapidly once a critical temperature $T_c \approx 118^{\circ}\text{C}$ is exceeded (9).

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