Protonic Conductivity along Lattice Defects in Sucrose

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IN formulating mechanisms of energy transfer for systems of biological interest, it is necessary to consider[1,2] the feasibility of proton as well as electron transport. But in studies of the electrical conductivity of proteins and related solids, it is, in practice, difficult[3] to decide unequivocally the nature of the charge carriers. Since it is now accepted that adsorbed water affects the magnitude[4] and nature[5] of the conductivity, the necessity to study single-crystal rather than polycrystalline samples has been sharply emphasized. It does not, however, seem to be appreciated that the dislocations inevitably present in single crystals may provide ionic conduction paths of magnitudes comparable with surface conduction in polycrystalline materials, even when good vacuum conditions are maintained. This Communication deals with such conduction in sucrose; and it draws attention to a simple technique for determining whether electronic or protonic conductivity prevails.

Studies of the electrical and defect properties of single-crystal and polycrystalline sucrose (prepared[6] and measured[7] as previously described) suggested that the d.c. conductivity along all three crystallographic directions [100] sin β, [010] and [001] were probably ionic. Thus, at a fixed temperature, the current decayed rather slowly with time;[3] and, more significantly, over a range of temperature the specific conductivity, σ, was best represented by an equation known[8] to be indicative—for certain values of the energy terms—of an intrinsic ionic, together with an impurity ionic, conduction:

$$\sigma = \sigma_1 + \sigma_2 = \sigma_{01} \exp\left(-\frac{W_1}{RT}\right) + \sigma_{02} \exp\left(-\frac{W_2}{RT}\right)$$

For example, the values of W_1 and W_2 for the [100] sin β direction were 16·5 and 10·0 kcal. mole^{-1} respectively. Water impurity (up to 0·4 per cent) has been shown[6] to be accommodated along dislocations, it being possible to have essentially cylindrical columns of water, of diameter as much as 10 μm, situated in the cores of screw dislocations of the type (001)[100], which emerge at (100) faces (see Figs. 15 to 17 of ref. 6 for micrographs of such columns). From the absolute magnitude of σ (3×10^{-14} ohm^{-1} cm.$^{-1}$ at 30°), and the values of W_1 and W_2, it is highly likely[8] that protonic conductivity dominates, and that the second term in the above equation represents the contribution of the water impurity.

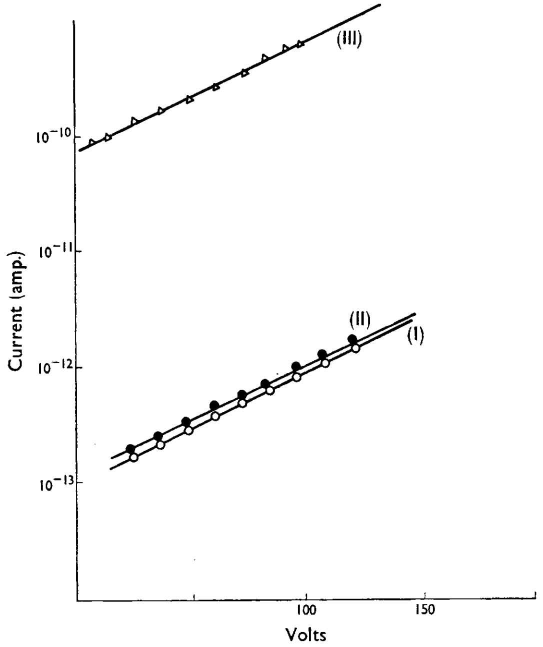

FIGURE. *Current-voltage characteristics of a sucrose crystal* (thickness 1 mm.) *in the* [100] sin β *direction using* (I), evaporated Au electrodes under dry N_2; (II) evaporated Pd electrodes under dry H_2; and, (III) powdered Pd electrodes saturated with H_2 (guard rings used throughout).

The protonic conductivity was confirmed using an injector electrode similar to that which has been used[2,9] to demonstrate the protonic character of the bulk conductivity of ice. The injection of protons at a palladium anode saturated with H_2 results in a roughly thousand-fold increase in the conductivity. As seen from the Figure, the palladium must be saturated with H_2 (*e.g.* from a previous electrolysis of aqueous acid) before injection becomes efficient.

Since most single crystals of biochemical importance are usually prepared by crystallization from protonic solvents, and since there is a pronounced[6,10] tendency for solvent to be occluded along dislocations, it would be advisable to utilize techniques such as proton injection or possibly[11] ^{1}H n.m.r. to assess the importance of such effects.

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