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DC Conduction of Tsuga (*Tsuga sieboldii* CARR) in Cellulose I

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ABSTRACT: The absorption current and the steady-state current in a dc field have been measured in the temperature range from 140°C to 230°C for tsuga (*Tsuga sieboldii* CARR) of Cellulose I. The voltage-current characteristics at various temperatures follow the sine-hyperbolic law in the hopping model. The hopping distance is constant (2.8×10^{-6}m) at temperatures above about 140°C. The absorption current characteristics are also explained by the hopping model. Drastic increase in the dc conductivity above about 150°C seems mainly due to an increase in the mobility.

KEY WORDS Cellulose I / Absorption Current / Steady-State Current / Hopping Model /

In a previous paper,[1] it was found that the conductivity *vs.* temperature curve showed a break at about 150°C for Cellulose I (Cell I) and at about 80°C for Cellulose II (Cell II) in accord with the spacing *vs.* temperature curve.[2] These breaks are possibly associated with the second order transition at which the restricted motion of chain segments in the crystals begins to gain higher mobility. However, the conduction mechanism has not been discussed.

The present work has been undertaken to study dc conduction in detail and to clear the mechanism of dc conduction in cellulose, by measuring the absorption current and the steady-state current in a dc field in the temperature range from 140 to 230°C where the dc conductivity becomes relatively high.

EXPERIMENTAL

The samples of Cell I was prepared from soft wood tsuga (*Tsuga sieboldii* CARR), which showed clear X-ray meridional reflections. The crystallinities of the samples were almost the same.

The sample was parallelpiped in form (10 mm × 10 mm × 15 mm). The arrangement of electrodes and the method used for measuring the dc electrical current were the same as described in the previous paper.[1] The maximum applied voltage was 540 V. Prior to each measurement, the specimen was dried at 100°C for about 2 h under a pressure of 10^{-5} Torr.

RESULTS AND DISCUSSION

Figure 1 shows schematically the time characteristic of the current, after a dc voltage was applied at $t=0$. The dc current is denoted by i_d, and the absorption current is denoted by i_a. The temperature dependence of the dc electrical conductivity σ is shown in Figure 2. As has been reported,[1] a break is observed at temperature of about 150°C in both the fiber direction and the direction perpendicular to it (tangential direction).

To study quantitatively the dc conduction in Cell I, the voltage-current (steady-state) characteristics for two directions at various temperatures above 140°C were measured as

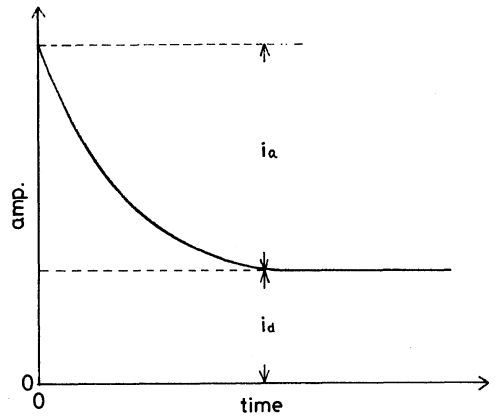

Figure 1. Schematic representation of current through sample.

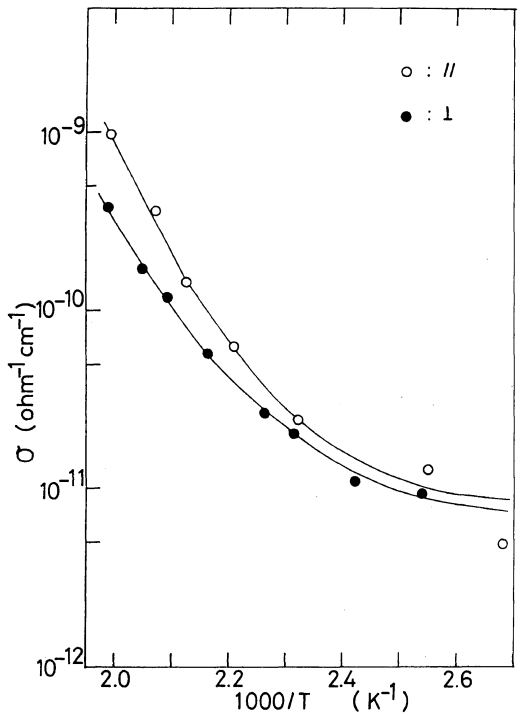

Figure 2. Temperature dependence of the dc conductivity in two directions; ∥, fiber direction; ⊥, tangential direction.

shown in Figure 3(A) and (B). Below 140°C, it was difficult to obtain the reliable voltage-current characteristics, because of lower conductivity. The solid lines show the calculated

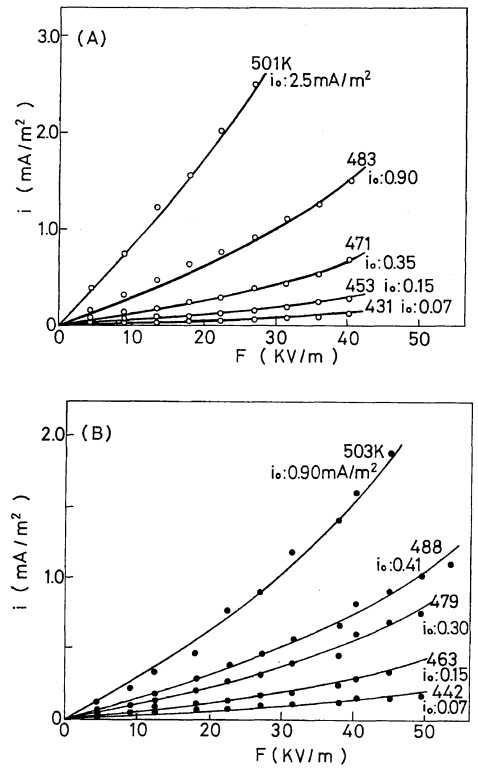

Figure 3. Voltage-current characteristics in two directions: (A), fiber direction; (B), tangential direction.

curves which are obtained by substituting the hopping distance $\lambda = 2.8 \times 10^{-6}$ m and each initial current density i_0 into the sine-hyperbolic equation in the hopping conduction model,[3] *i.e.*,

$$i = i_0 \sinh(e\lambda F/2kT) \qquad (1)$$

Here F is the electric field, k is Boltzmann's constant and T is the absolute temperature in K. As seen in the figures, the voltage-current characteristics can be well represented by the sine-hyperbolic equation and λ is found to be constant in both directions over the temperature range higher than about 140°C. Then, the possibility of the hopping conduction is expected. It has been stated by Murphy[4] that the conduction in dry cellulose involves the tunneling of proton between equivalent sites, the one in the ion and the other in an adjacent

neutral molecule. But the doubts about the correctness of this model above 40°C were pointed out by Tanaka,[5] since the dissociation energy calculated by Murphy's equation[4] was smaller than 1.72 eV estimated for the activation energy of thermal decomposition.[4] Our result[1] for activation energy is similar to Tanaka's result.

Figure 4 shows the initial current density i_0 in both directions plotted against $1/T$. The apparent activation energies $\Delta H^*_{i_0}$ are 1.2 eV in fiber direction and 1.0 eV in tangential direction. It should be noticed that $\Delta H^*_{i_0}$ is almost equal, in both directions, to the apparent activation energy ΔH^*_σ reported.[1]

The solid curve in Figure 5 shows an example of the time evolution of absorption current at 187°C for the tangential direction, which can be divided into two exponential functions as represented by two dashed lines. The frequency dependence of dielectric loss ε'' can be calculated by substituting the slopes α_i ($\alpha_1 = 0.457\ s^{-1}$, $\alpha_2 = 2.175\ s^{-1}$) and the current densities β_i ($\beta_1 = 50 \times 10^{-5}\ Am^{-2}$, $\beta_2 = 81 \times 10^{-5}\ Am^{-2}$) at $t=0$ into Whitehead's equation,[6] *i.e.*,

$$\varepsilon''(\omega) = \sum_i \omega\beta_i/(\omega^2 + \alpha_i^2) \qquad (2)$$

where ω is the angular frequency. Figure 6 shows the angular frequency dependence of dielectric loss ε'' obtained at 187 and 139°C for the tangential direction. The relaxation fre-

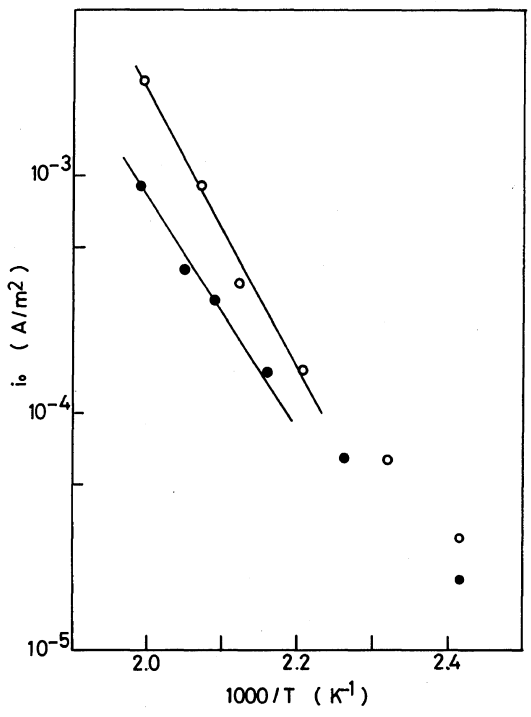

Figure 4. Temperature dependence of the initial current density in two directions; ○, fiber direction; ●, tangential direction.

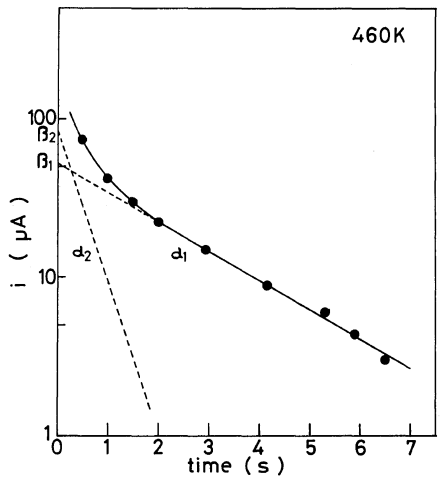

Figure 5. Time dependence of the absorption current in the tangential direction.

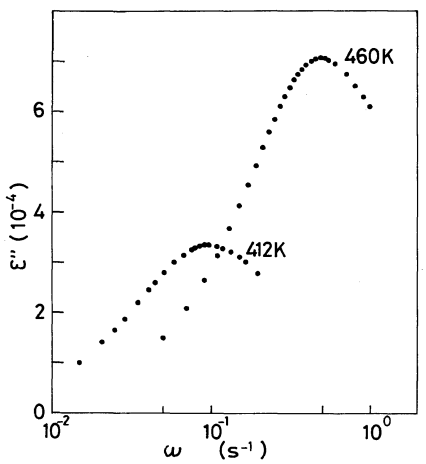

Figure 6. Angular frequency dependence of dielectric loss in the tangential direction.

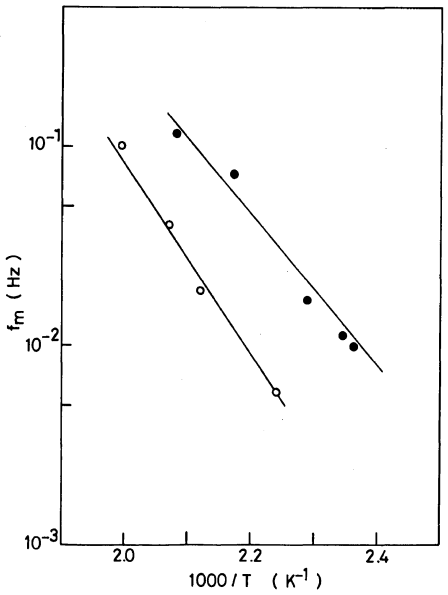

Figure 7. Temperature dependence of the relaxation frequency in two directions; ○, fiber direction; ●, tangential direction.

quency f_m at which ε'' has a maximum is plotted against $1/T$ in Figure 7. The apparent activation energies $\Delta H^*_{f_m}$ are 0.93 eV in the fiber direction and 0.75 eV in the tangential direction, as estimated from Figure 7. The values correspond to the activation energies in connection with mobility μ in the hopping conduction model. The values are shown in Table I, together with $\Delta H^*_{i_0}$. The activation energy in carrier formation is estimated as the difference of $\Delta H^*_{i_0} - \Delta H^*_{f_m}$. Then, the drastic increase in σ would be mainly due to an increase in μ.

Furthermore, it has been suggested[7] by the hopping conduction theory that σ should be proportional to $2\pi f_m \varepsilon_0 \Delta\varepsilon$, where $\Delta\varepsilon$ is the intensity of the dielectric absorption and ε_0 is the dielectric constant of vacuum. Figure 8 shows the relationship between $\log\sigma$ and $\log(2\pi f_m \varepsilon_0 \Delta\varepsilon)$. The experimental points in both directions locate approximately between two straight lines, the dashed line drawn through the origin ($m=1$) and the solid line drawn through the point of 1.9 times as the

Table I. Apparent activation energies

	$\Delta H^*_{i_0}$	$\Delta H^*_{f_m}$
	eV	eV
∥[a]	1.2	0.93
⊥[b]	1.0	0.75

[a] Fiber direction.
[b] Tangential direction.

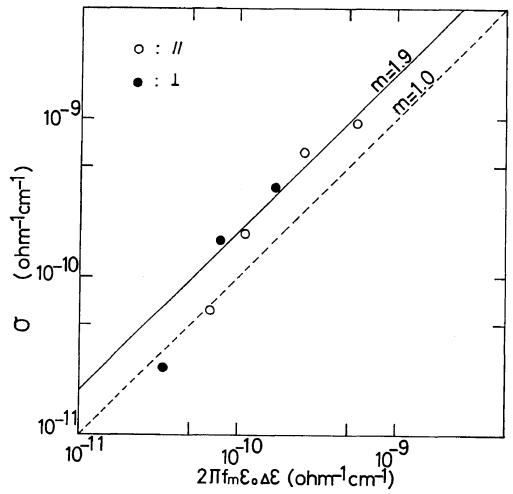

Figure 8. Relationship between σ and $2\pi f_m \varepsilon_0 \Delta\varepsilon$ in two directions; ∥, fiber direction; ⊥, tangential direction.

origin ($m=1.9$), with slope of 1. Therefore it can be concluded that

$$\sigma \simeq 2\pi f_m \varepsilon_0 \Delta\varepsilon \tag{3}$$

for Cell I. The result also supports the hopping conduction mechanism in cellulose. The carrier in cellulose may be ion such as proton or protonhole detected by Murphy.[4]

According to the hopping conduction theory,[7] the mobility μ and the concentration n of the charged particle are given by

$$\mu = 2\pi e f_m \lambda^2 / 12kT \tag{4}$$

$$n = 12kT\varepsilon_0 \Delta\varepsilon / e^2\lambda^2 \tag{5}$$

respectively, where e is a protonic charge. The calculated values of μ and n at 140—230°C are $\sim 10^{-12}$ m^2/Vs and $\sim 10^{22}$ m^{-3}. These values

of μ and n agree approximately with those obtained by Tanaka.[5] The concentration n_0 of hydroxyls in cellulose is 1×10^{29} m^{-3}. Then, the ratio of n to n_0, n/n_0, is $\sim 10^{-7}$. Therefore, the protons of a very small part of the hydroxyls contribute to the carrier.

CONCLUSION

The voltage-current characteristics for two directions of Cell I at various temperatures are explained in terms of the sine-hyperbolic law in the hopping model. The hopping distance is constant (2.8×10^{-6} m) above about 140°C in both directions. Absorption currrent characteristics are also explained by the hopping model.

Drastic increase in σ above about 150°C may be mainly due to an increase in μ. The ratio of carrier density to the concentration of hydroxyls in cellulose is $\sim 10^{-7}$.

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