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Electrical, thermoelectric and thermophysical properties of hornet cuticle

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Abstract
Seebeck effect (thermo-emf), thermal conductivity and electrical conductivity of social hornet cuticle were measured in a direction perpendicular to the cuticular surface. The obtained value of the Seebeck coefficient (S) was about 3 ± 0.5 mV K^{-1} and its sign corresponded to an n-type (electronic) conductivity. Hornet cuticle is shown to be a fairly good heat insulator, with recorded values of the heat conductivity as low as 0.1–0.2 W m^{-1} K^{-1}. The measured value of the electrical conductivity in the linear regime is $\sigma = 8.5 \times 10^{-5}\ \Omega^{-1}$ cm^{-1}. The thermoelectric figure of merit is computed. Implications for possible exploitation as a natural thermoelectric heat pump are discussed.

Introduction

Thermal photographs of hornets, taken with infrared camera, have indicated that hornet body temperature is sometimes lower than the ambient temperature [1]. A thermoelectric heat pump was suggested [1] as a possible mechanism for cooling of the hornet body. Electrical and thermoelectric properties of the Oriental hornet (*Vespa orientalis*) *along its cuticular surface* were investigated earlier [2–6]. In those studies, the so-called 'thermoelectric figure of merit Z' was estimated as $ZT = 0.002$ [1] (here T is the absolute temperature). The factor Z, which depends on material properties (transport coefficients) of the thermoelectric material, governs the efficiency of that material when it functions as a heat pump. However, it is well known [7, 8] that the microstructure of the vespan cuticle is extremely anisotropic, so that one might expect a different cooling efficiency in the direction *perpendicular to the cuticular surface*. Moreover, the largest temperature gradient in a live hornet is recorded in that direction, hence, the transport coefficients in the perpendicular direction are those that need to be used in calculating Z. The present study focuses on the transport coefficients of the Oriental hornet cuticle in the direction *perpendicular to its surface*.

Materials and methods

Test specimens were prepared from live hornets originally collected from nests in the field in the Tel Aviv area using the method previously developed by one of us (Ishay [9]). The transport measurements were performed at ambient temperatures pertaining to live hornet daily activity, namely, at 15–30 °C [9]. For thermoelectrical measurements (Seebeck effect), samples of fresh cuticle (about 1 h after dissection from a live hornet) were placed between two Cu discs, and a temperature gradient was induced between the discs by directly heating only one of the discs. The rate of the heating was regulated by changing the current through the heater and the temperatures of both discs were monitored by thermocouples attached to Cu discs. A measurement of the voltage drop (ΔV) and the temperature difference (ΔT) between Cu discs determines the Seebeck coefficient (S), *including its polarity*, namely $S = \Delta V/\Delta T$.

We used a modified axial heat flow method for measurement of thermal conductivity (κ) [10]. The properties of the cuticle did not allow us to carry out the measurement in a vacuum, therefore we used a specially designed set-up to minimize the heat flow arising from the thermal conductivity of the air. The test sample was mechanically clamped between two Cu discs (containing a heater and thermocouples) at a pressure of about 100 N cm^{-2}, and this construction was placed in the thermally insulated chamber. The shunting heat flux, through the surrounding air, was theoretically estimated to be less than 12%. This figure is taken to represent the measurement accuracy of κ. The thermal conductivity (κ) of the cuticle was calculated from the equation: $\mathrm{d}Q/\mathrm{d}t = -\kappa A\ \mathrm{d}T(t)/\mathrm{d}x$ [10], where $\mathrm{d}Q/\mathrm{d}t$ is the heat flow through the sample, A is the cross-section of the sample perpendicular to the direction of the heat flow, and $\mathrm{d}T(t)/\mathrm{d}x$ is the temperature gradient along the direction of the heat flow. The thickness of the cuticle (L) is about 0.06 mm and consequently $\mathrm{d}T(t)/\mathrm{d}x \approx \Delta T(t)/L$, where $\Delta T(t)$ is the temperature difference between the sides of the cuticle. The value of $\mathrm{d}Q/\mathrm{d}t$ was computed from: $\mathrm{d}Q/\mathrm{d}t = MC\ \mathrm{d}T/\mathrm{d}t + \mathrm{d}Q'/\mathrm{d}t$, where M is the mass and C is the specific heat capacity of the cooler copper disc, while T is its absolute temperature. The last term in the equation, namely, $\mathrm{d}Q'/\mathrm{d}t$ is the rate of heat loss from that disc to the surrounding air, which was estimated experimentally from the Newton cooling curve. The value of $\mathrm{d}Q'/\mathrm{d}t$ was about 15% compared to the first term ($MC\ \mathrm{d}T/\mathrm{d}t$). Moreover, we measured at the same conditions the thermal conductivity of polyester film samples with well-known κ (mylar, $\kappa = 0.08$ W m^{-1} K^{-1}). The obtained results agree with the tabulated value to within 10%.

The electrical conductivity was calculated as $\sigma = L/RA$, where R is the observed value of the cuticular resistance in the direction perpendicular to the surface, A is the cuticular surface area and L is the thickness of the cuticle.

Results

The thermo-emf has been investigated in 35 cuticular samples. Most of the emf curves exhibited hysteretic behaviour and an example of such a curve is displayed in figure 1(A). Some samples, however, showed very little hysteresis, as evident from figure 1(B). The average values of the Seebeck coefficient are summarized in table 1. For hysteretic graphs the Seebeck coefficient was calculated from the heating part of the emf curve. As seen from the table, the values of S were similar for both types of cuticle, that is: for yellow coloured cuticle $S_{\mathrm{yel}} = 3.5$ mV K^{-1} and for brown cuticle $S_{\mathrm{br}} = 3.0$ mV K^{-1} and this with an inward directed temperature gradient (i.e. inner side of the cuticle warmer than the outer side). However, both cuticle types (yellow and brown) exhibited much lower values of S when the gradient was applied in the opposite direction ($S_{\mathrm{in}}/S_{\mathrm{out}} \approx 2.5$). The sign of the Seebeck coefficient corresponded to n-type conductivity.

Thermal conductivity was assessed in 19 specimens of both types of cuticle. Results of the measurements are given in table 2. For both cuticle types the thermal conductivity was similar, with $\kappa = 0.15 \pm 0.05$ W m^{-1} K^{-1}.

At high voltage (about 0.5 V) the electrical conductivity (σ) was nonlinear and strongly dependent on the polarity of the applied voltage. In the linear regime ($V \to \pm 0$) its value approached $\sigma = 8.5 \times 10^{-5}$ Ω^{-1} cm^{-1}.

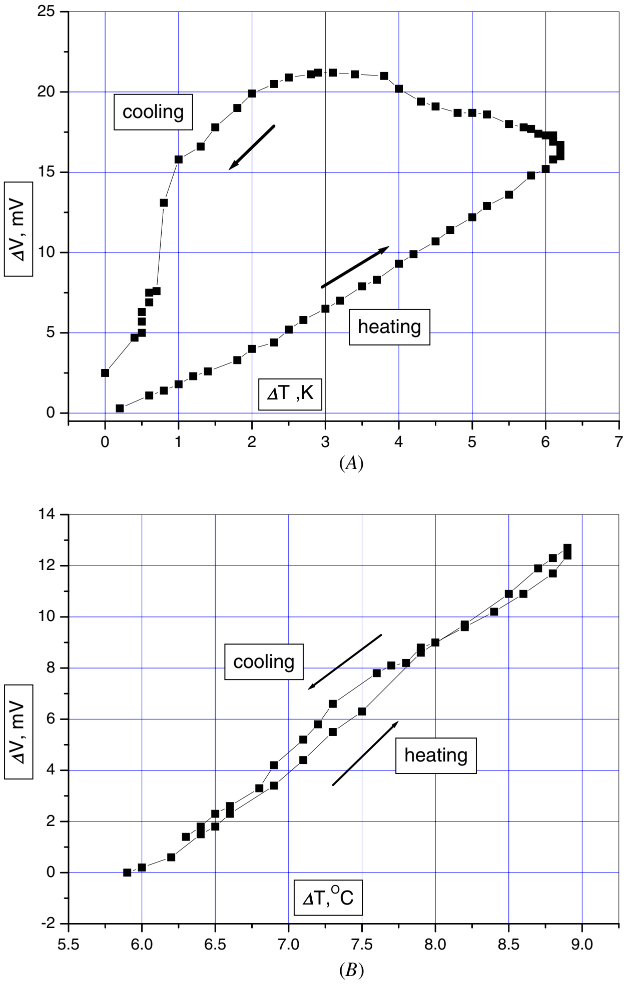

Figure 1. (A) Typical curve of emf in the direction perpendicular to the cuticle surface obtained during the heating and the cooling processes. The rate of heating was about 0.2 °C min^{-1}, the rate of cooling 0.15 °C min^{-1}. No correlation was found the between the hysteretic loop size and the type of cuticle (yellow or brown). The sign of $\mathrm{d}V/\mathrm{d}T$ corresponded to n-type conductivity. (B) Emf curve with very small hysteresis. Such dependences were observed in only about 5% of the samples.

Table 1. The Seebeck coefficient of hornet cuticle in the direction perpendicular to its surface.

Type of the cuticle	Hot side	S (mean) mV $grad^{-1}$	$S_{\max}$ mV $grad^{-1}$	SD	$S_{\mathrm{in}}/S_{\mathrm{out}}$
Yellow	Inner	3.5	10.0	1.8	2.6
Yellow	External	0.7	1.0	0.4	
Brown	Inner	2.95	5	1.2	2.1
Brown	External	1.4	2.7	0.86	

The Seebeck coefficient was calculated on the linear portion of the heating part of the thermo-emf curves. The ratio $S_{\mathrm{in}}/S_{\mathrm{out}}$ was determined from measurements of emf on the same samples with reversed sense of the temperature difference.

Discussion

In the present study, the obtained values of the Seebeck coefficient (S), measured in the direction *perpendicular to the*

Table 2. Thermal conductivity of the cuticle in the perpendicular direction.

Type of the cuticle	Number of the samples	Average values κ (W m^{-1} K^{-1})	SD	K_{max} (W m^{-1} K^{-1})
Yellow	13	0.15	0.05	0.25
Brown	7	0.14	0.05	0.22

Thermal conductivity (κ) was calculated from equation: $dQ/dt = -\kappa A \, dT/dx$, where $dQ/dt = MC \, dT/dt + dQ'/dt$ and $dT/dx \approx T/L$. (for details see 'materials and methods' section).

cuticular surface, were about five times higher than previously reported values of S measured *along the cuticular surface* [4]. Moreover, we have now also demonstrated that the values of thermo-emf strongly depend on the polarity of the applied temperature gradient, with S values about 2.5 times higher when the inner side of the cuticle is warmer than the outer side. Another noteworthy new finding is the hysteresis of the thermal emf during the heating and cooling cycle. In an earlier study [11] similar hysteretic curves were obtained in the variation of the cuticular resistance versus temperature. It was then suggested [12] that the hysteretic behaviour of the resistance could arise from some ferroelectric properties of the cuticle. It now seems plausible that such ferroelectric properties of hornet cuticle are reflected also in our present thermo-power measurements, evincing a hysteretic form of the thermo-emf curves. It would, however, require a separate investigation of the dielectric constant of the cuticle at low electrical fields to verify this conjecture.

The measured value of the cuticle's thermal conductivity (κ) is about the same as in many organic semiconductors [13–15], which is not surprising, considering that hornet cuticle is mainly comprised of chitin, a polymer of *N*-acetyl-ß-D glucose amine, various amounts of protein and lipids, and various pigments such as melanin, purines and pteridines, all of which are known to be organic semiconductors [16–19]. The cuticular structure contains an upper thin layer of epicuticle made of lipids and wax mainly. This is the layer with which the measuring electrodes make their contact [19]. Only behind this layer are there some 30 or more layers composed mainly of chitin and protein [6] arranged as in plywood that gives the cuticle added strength. The thickness of the cuticular layers is decreasing from the outermost one to the inner layers. Likewise, the measured values of the electrical conductivity (σ) are also typical for many organic semiconductors [20]. The observed nonlinearity and polarity dependence of σ lends plausibility to the idea of a bipolar semiconductor nature of the cuticle [21]. The value of $\sigma = 8.5 \; 10^{-5} \; \Omega^{-1} \; \mathrm{cm}^{-1}$ measured in the perpendicular direction is much smaller than the value $\sigma = 1.6 \times 10^{-3} \; \Omega^{-1} \; \mathrm{cm}^{-1}$ reported for the lateral conductivity of cuticle [4]. It should be pointed out that in both cases the measurements were made two terminally. The difference between the values could arise either from the anisotropy of the cuticle structure or from the contact resistance which makes a much higher contribution in the perpendicular direction. This issue is the subject of our ongoing research.

The 'thermoelectric figure of merit' is given by $Z = \sigma S^2/\kappa$ [22]. Substituting the obtained values of σ, S and κ for the cuticle, measured in the direction perpendicular to its surface, we get $ZT \approx 3.0 \times 10^{-3}$, which is about 1.5 times larger than previous estimates, which were based on measurements of σ and S, and a guessed value of κ, along the cuticular surface [1].

As far as we know, this is the first time anyone has attempted to measure the parameters σ, κ and S of fresh hornet cuticle (or any other cuticle, for that matter) in the direction perpendicular to the surface. Data on these parameters are essential for any serious discussion of the possibility that hornets activate a thermoelectric heat pump in the cuticle as a means of regulating their body temperature [1]. In this connection, the fact that S is considerably greater when the inner side of the cuticle is at the higher temperature may indicate that the main use of the thermoelectric heat pump is to cool the hornet body rather than to warm it up. On the other hand, the values found for the thermoelectric figure of merit Z are not large enough to achieve the negative temperature differentials which have been observed [1]. One should keep in mind, however, that the microstructure of the cuticle is heterogeneous along its surface and in fact is rather periodic, with a period of a few microns [7].

This is reminiscent of the structure of commercial thermoelectric modules, where bulkheads of p-type conductivity alternate with those of n-type. It is remarkable that the structure of the cuticle is similar. Our measuring set-up employed electrodes of 5 mm diameter, and the obtained values of S could possibly represent some average of different values along the surface. The signs of S for p-type and n-type conductivity are opposite, therefore the average value of S might be considerably smaller than the Seebeck coefficient of the p-type and n-type parts separately.

Our present findings indicate that the thermal and electrical transport properties of hornet cuticle are highly anisotropic, as might have been expected in view of the extremely anisotropic layered morphology of hornet cuticle [7, 8].

The hysteretic nature of the thermoelectric response, as well as its dependence on polarity of the applied temperature gradient, support the notion that the cuticle may undergo some kind of phase change (ferroelectric or other) within the relevant temperature range. It will be interesting to pursue this possibility and its implications.

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