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Heat Transfer Engineering

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Experimental Study of Energy Exchange Attending Electron Emission from Carbon Nanotubes

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Phenomena based on nanoscale transport processes offer new possibilities for direct refrigeration by electron emission between opposing electrodes across a vacuum region. The average energy of emitted electrons depends upon the magnitude and shape of the potential energy barrier in the vacuum region, which is affected by the emission gap, emitter work function (potential barrier height), and emitter tip geometry. Emitted electrons are replaced by other electrons to maintain charge continuity, and the difference in energy between the emitted and replacement electrons produces a heating or cooling effect, known as the Nottingham effect, at the emitter surface. Theoretical studies indicate the possibility of very large (>100 W/cm²) cooling rates, but experimental confirmation is lacking due to challenging material and experimental requirements. To obtain the results discussed in this paper, the energy exchange attending electron emission from multi-walled carbon nanotube (MWNT) array samples is measured with an uncertainty of approximately 1 μW. The results are found to depend strongly on the adhesive used to bind the MWNT arrays to the substrate, and this effect is explored by using both silver and carbon paints as the adhesive material. An attempt to determine the effect of the emitter work function by intercalating the MWNT arrays with potassium was unsuccessful. Heating curves as a function of the emission current are presented for various sample groups, and these curves provide insight into the mechanisms involved in the energy exchange associated with field emission from MWNT arrays, including the Nottingham effect and Joule heating.

INTRODUCTION

Rapid technological advances in microscale and nanoscale devices offer intriguing possibilities in direct refrigeration through the emission of high-energy electrons across a vacuum barrier. Direct refrigeration is attractive for cooling applications because it involves no moving parts, and theoretical studies indicate the possibility of cooling powers exceeding 100 W/cm². Unlike solid-state thermoelectrics, electron emission across a vacuum gap eliminates undesirable solid-state heat conduction. The emission process can be divided into two regimes, thermionic emission and field emission, as shown in Figure 1a. Thermionic emission consists of electrons that have sufficient energy to overcome the surface potential barrier, known as the work function ϕ, while field-emitted electrons penetrate through the potential barrier by quantum tunneling. The emitted electrons are replaced by other electrons at the cathode to maintain charge continuity, and the net energy exchange at the cathode may produce heating or cooling depending on the average energy of the emitted electrons relative to that of their replacement counterparts (see Figure 1b). Refrigeration is attained by favoring the emission of high-energy electrons through filtering processes that depend upon geometric scale effects [1], Schottky depletion [2], or resonant-tunneling structures [3–5]. The present work measures the energy exchange attending field emission from multi-walled carbon nanotube (MWNT) arrays at room temperature. The results are found to depend strongly on the adhesive used to bind the MWNT arrays to the substrate, and this effect is explored by employing silver and carbon paints as the adhesive material.

Field emission was first considered theoretically in 1928 by Fowler and Nordheim [6], who derived the well known Fowler-Nordheim equation by linearizing the highly nonlinear electric field near the emission site. Later, the energy exchange attending field emission was discussed by Fleming, Henderson, and Nottingham, and has since become known as the Nottingham effect [7–9]. Subsequently, other studies have provided a clearer understanding of the thermodynamics associated with field emission [10–12]. The effect of tip geometry on electron emission has also been explored, revealing that sharper
Figure 1 (a) Vacuum electron emission model including thermionic and field emission; (b) device schematic showing heat source, emitter/cooler, and collector/heat sink. High-energy electrons carry energy from the emitter to the collector, and thus produce cooling at the emitter surface.

tips enhance the local electric field and thereby substantially increase the emission current [13]. In addition to the current enhancement that they provide, sharp emitter tips also favor the emission of high-energy electrons, making them attractive for cooling applications [14, 15]. Recently, an additional cooling benefit has been shown to exist for very narrow emission gaps, which lower the height of the potential barrier and reduce undesirable space-charge effects in the vacuum region [16].

Numerous experimental studies have been published that investigate the energy exchange associated with electron emission. Swanson et al. [17] conducted extensive experiments measuring the heat exchange involved in emission from high and low work function wires in the temperature range 300–1160 K and clearly observed the transition of the Nottingham effect from heating to cooling. Begeret et al. [18] measured Nottingham heating in the absence of Joule heating by utilizing niobium superconducting samples. Xu et al. [19] investigated the heat transfer between an STM tip and a sample surface by integrating planar thermocouples into the STM tips and reported Nottingham heating with a sensitivity of 10 nW. Recently, Hishinuma et al. [20] reported a cooling effect of 1–10 nW produced by thermionic emission across a nanometer gap at room temperature. To date, no experimental study has explored the effects of the adhesive material or the emitter work function on the energy exchange process attending electron field emission from carbon nanotubes. This work undertakes both these tasks by inducing field emission from both pristine and potassium-intercalated MWNTs arrays and using silver and carbon paints as adhesive materials.

EXPERIMENTAL METHODS

Direct measurement of the energy exchange associated with field emission is challenging because the heating or cooling effect expected from typical laboratory experiments lies in the microwatt range. For example, in typical experiments, emission from an array of MWNTs is limited to currents less than approximately 30 μA because currents above this value tend to be highly unstable and are often subject to sudden burnout. Moreover, to attain cooling, a relatively low applied potential is required, and this condition further limits the emission current and reduces the maximum cooling effect. For a typical array of MWNTs, the maximum cooling power is expected to range from one to a few microwatts. The apparatus employed in these experiments is capable of measuring such low cooling powers as discussed in the following paragraphs.

The temperature measurements in this study were obtained by measuring the resistance in a micro-BetaCHIP thermistor (Betatherm Corp.). To achieve the high thermal isolation required for the measurements in this study, the thermistor was suspended in vacuum by 0.05 mm diameter stainless steel wires extending from copper contact pads located approximately 6 cm from the thermistor (see Figure 2). The thermistor’s lead wires were connected to additional copper contact pads mounted approximately 6 cm behind the thermistor. To reduce radiation exchange between the lead wires and the surrounding vacuum chamber, the insulation on the lead wires was removed. The MWNT arrays were mounted on the flat end of the thermistor, which was placed approximately 1 mm from a molybdenum anode, as shown in Figure 2.

The total energy exchange at the thermistor (cathode) may be expressed in the form:

$$Q = Q_{\text{Joule}} - \frac{I_{\text{emit}} q_e}{\Delta \varepsilon}$$

where $Q_{\text{Joule}}$ represents Joule heating, $I_{\text{emit}}$ is the emission current, $q_e$ is charge per electron, and $\Delta \varepsilon$ is the average energy
difference between the emitted and replacement electrons. In Eq. (1), a positive value of $Q$ represents heating, and thus, to achieve maximum cooling, the emission current must be as large as possible, and Joule heating must be minimized by reducing the ohmic resistance experienced by the emitting electrons. Increasing the electric potential produces an increase in the emission current but also reduces the value of $\Delta \varepsilon$ because lower energy electrons are able to penetrate the vacuum barrier. Hence, at high applied potentials, $\Delta \varepsilon$ becomes negative, and the Nottingham effect produces heating at the emission site rather than cooling.

The heating or cooling effect produced at the thermistor by field emission to the anode was calculated by dividing the thermistor’s temperature change by the thermal resistance $\psi$ between the thermistor and the surrounding vacuum chamber. The following steps summarize the process used to measure the heating effect produced at the thermistor in these experiments.

1. thermistor calibration
2. mounting of the MWNT array
3. measurement of the thermistor thermal resistance $\psi$
4. measurement of the energy exchange attending field emission
5. determination of the uncertainty in the measurements

Each of these steps is discussed in the paragraphs that follow.

### Thermistor Calibration

The Steinhart-Hart equation provides an accurate relationship between temperature $T$ and thermistor electric resistance $R$ and is written as

$$\frac{1}{T} = A + B \ln(R) + C \ln(R)^3$$

where the coefficients $A$, $B$, and $C$ are determined for each thermistor by calibration. For this study, the calibration was performed by measuring the thermistor’s electric resistance $R$ at three temperatures determined by a thermocouple. The thermistor and thermocouple were placed in a 2 mm-diameter hole drilled axially in a copper rod, which was heated by sending an electric current through a heating wire wrapped around the copper rod. For each measurement, the copper rod was heated to the desired temperature and was allowed to reach steady state. Then, the electric resistance was measured by a National Instruments DAQPad 4350 system connected through an NI TBX-68T board, and the thermocouple temperature was measured with a Fluke 52 Thermometer. Typical temperature and electric resistance measurements recorded during calibration are shown in Table 1, from which values of $1.793 \times 10^{-3}$, $1.295 \times 10^{-4}$, and $1.257 \times 10^{-6}$ were determined for the coefficients $A$, $B$, and $C$, respectively.

### Mounting of the MWNT Array

Mounting the MWNT array to the thermistor involves two significant challenges: securing the MWNT arrays to the thermistor, and providing an electrical contact to the MWNT array. The second challenge was overcome by covering the thermistor body with silver epoxy (M.E. Taylor Engineering, Inc.) and then applying several coats of silver (M.E. Taylor Engineering, Inc.) or carbon (Ted Pella, Inc.) paint after the silver epoxy had cured.

The MWNT films were grown by PECVD on silicon wafers using a process that has been described elsewhere [21]. Figure 3 shows an SEM image of a MWNT array cross-section exposed by breaking the silicon wafer along a line that contained the growth region. As shown in Figure 3, the MWNT arrays that resulted from the growth process are approximately 10 μm in length and are densely packed. Additional SEM images indicate the diameters of the MWNTs are approximately 30 μm. Typically, each growth process leaves a black layer containing the MWNTs on a silicon wafer. In order to mount the MWNT films on the thermistor, this black layer was removed from the silicon wafer with a razor blade and deposited on the end of the thermistor body with silver epoxy (M.E. Taylor Engineering, Inc.) or carbon (Ted Pella, Inc.) paint after the silver epoxy had cured.

The second challenge was overcome by covering the thermistor body with silver epoxy (M.E. Taylor Engineering, Inc.) and then applying several coats of silver (M.E. Taylor Engineering, Inc.) or carbon (Ted Pella, Inc.) paint after the silver epoxy had cured.

![Figure 3](image)

**Figure 3** SEM image of typical MWNT array sample. Description of growth process is given in [21].
Measurement of Thermistor Thermal Resistance $\psi$

The electric resistance of a thermistor is determined by passing a small current $I_{\text{excite}}$ (traditionally called the excitation current) through the lead wires and measuring the voltage drop $V$. The power dissipation in the thermistor $Q_{\text{self}}$ that accompanies this process is simply the product $V \cdot I_{\text{excite}}$, and is known as self-heating. This effect can be exploited to calculate the thermistor’s thermal resistance $\psi$ by determining the temperature rise caused by a specified increase in $Q_{\text{self}}$. $\psi$ may then be calculated as

$$\psi = \frac{T_2 - T_1}{Q_{\text{self}2} - Q_{\text{self}1}}$$  \hspace{1cm} (3)$$

where the subscripts ‘1’ and ‘2’ refer to measurements taken with electric currents $I_{\text{excite}1}$ and $I_{\text{excite}2}$ and corresponding voltage drops $V_1$ and $V_2$. For each measurement, a constant voltage is applied across the lead wires until a steady-state condition is reached, and then the electric current through the thermistor is measured in order to obtain the self-heating $Q_{\text{self}}$.

A Tenma power supply (model 72.6906) provided the electric potential bias, an Agilent 34401A multimeter measured the voltage across the thermistor leads, and a Keithley 8486 picoammeter measured the electric current. A 9.2 kW resistor was included in the circuit to bring the applied voltage into a suitable range for the power supply. The circuit configuration is shown in Figure 4. The thermistor’s electric resistance for each measurement was calculated by dividing the measured voltage drop by the current, and the thermistor temperature was calculated from Eq. (2). In order to determine $\psi$, steady-state conditions must exist during each measurement; however, a strict steady-state condition was not possible because of gradual drift (approximately 0.003°C/min) in the surrounding vacuum chamber’s temperature over time. To compensate for this effect, the background thermal drift was measured before and after the experiments, and the temperature changes were accordingly corrected.

The experimental data for three measurements are shown in Table 2, where the corrected temperature changes are labeled $\Delta T_{\text{corr}}$. The value of $\psi$ in the second row was calculated from the data in the first two rows of Table 2, and the value of $\psi$ in the third row was calculated from the data in the first and third rows.

### Measurement of the Energy Exchange Attending Field Emission

A National Instrument DAQPad 4350 system coupled to a TBX-68T was used to measure the thermistor’s electric resistance. The thermistor body and the MWNT array were held at zero potential by the support wires while a voltage was applied to the anode by a Spellman CZE1000R high voltage supply, capable of either constant current or a constant voltage operation. A Keithley 6386 picoammeter measured the field emission current, which was recorded through an IEEE-488 (GPIB) bus connected to a PCI-GPIB controller. Temperature and electric current measurements were taken 2 and 0.3 s apart, respectively. A 1.0 MΩ shunt resistor was included in the circuit to stabilize the field emission, and coaxial cables were used to connect the instrumentation to reduce EMI and RFI signals. A schematic of the electric circuit is shown in Figure 5. All measurements were taken in vacuum at a pressure of approximately 5.10⁻⁷ Torr.

Figure 6 shows typical data recorded during an experiment in which the applied voltage was held constant. The field emission current was produced by applying an electric potential of 1400 V to the anode at 80 s, and then removing the potential at 518 s. The rise in the thermistor temperature is presumably due to a combination of Nottingham heating and Joule heating, the total magnitude of which may be found by dividing the average thermistor temperature rise by the thermistor thermal resistance. In performing this calculation, the time interval 290–500 s was selected to estimate the average thermistor temperature rise. The background temperature was determined by taking temperature readings before and after the electric potential was applied, and it was found to have a nearly constant value of 26.02°C. The average temperature in the time interval 290–500 s was 26.08°C, yielding an average temperature rise of 0.06°C. Using a value of 2100 K/W for $\psi$, the total heating was estimated to be approximately 27 μW. As shown in Figure 6, a very precise value

### Table 2  Experimental data utilized in calculating the thermistor thermal resistance

<table>
<thead>
<tr>
<th>$V$ (V)</th>
<th>$I_{\text{excite}}$ (μA)</th>
<th>$R$ (Ω)</th>
<th>$Q_{\text{self}}$ (μW)</th>
<th>$T$ (K)</th>
<th>$\Delta T_{\text{corr}}$ (K)</th>
<th>$\psi$ (K/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15744</td>
<td>75.535</td>
<td>2084.3</td>
<td>11.89</td>
<td>299.07</td>
<td>0.00</td>
<td>—</td>
</tr>
<tr>
<td>0.30478</td>
<td>149.738</td>
<td>2035.4</td>
<td>45.64</td>
<td>299.81</td>
<td>0.72</td>
<td>21200</td>
</tr>
<tr>
<td>0.48540</td>
<td>251.278</td>
<td>1931.7</td>
<td>121.97</td>
<td>301.45</td>
<td>2.31</td>
<td>21000</td>
</tr>
</tbody>
</table>

$\Delta T_{\text{corr}}$ is the measured thermistor temperature change compensating for background thermal drift.
of the heating is difficult to determine because the emission current and thermistor temperature fluctuate significantly with time. This result is typical of constant voltage operation.

The total heating can be measured more accurately using a constant emission current. A typical example is shown in Figure 7, where a constant voltage was initially applied at 70 s, and then at 132 s the current was fixed at 4 mA. The background temperature was approximately the same as that in Figure 6, yielding a temperature rise of approximately 0.10°C, corresponding to a total heating of approximately 45 μW.

Uncertainty Analysis

Before presenting the complete set of experimental results, an uncertainty analysis is necessary to determine the significance of the results. The percentage uncertainty in the thermistor calibration is approximated by

$$U_{cal} = \sqrt{2} \frac{u_{tc}}{\Delta T_{tc}}$$  \hspace{1cm} (4)

where $u_{tc}$ is the thermocouple uncertainty, approximately ±0.4°C, and $\Delta T_{tc}$ is the calibration temperature range calculated from Table 1. With $\Delta T_{tc}$ equal to 31°C, $U_{cal}$ is approximately 2%. The uncertainty in the thermistor thermal resistance $u_{R}$ was estimated using the data in the first and third rows of Table 2 and is given by

$$u_{\psi} = \frac{1}{\Delta Q_{self}} \sqrt{u_{I_{excite}}^2 + \left(\frac{\Delta T_{cor}}{\Delta Q_{self}}\right)^2 (u_{Q_{self3}}^2 + u_{Q_{self1}}^2)}$$  \hspace{1cm} (5)

where $u_{\psi}$ is the uncertainty in a temperature measurement, $U_{Q_{self}}$ is the uncertainty in a power dissipation (thermistor self-heating) measurement, and $\Delta Q_{self}$ is difference between $Q_{self3}$ and $Q_{self1}$. The subscript ‘1’ refers to data in the first row of Table 2, while the subscript ‘3’ refers to data in the third row.

In order to evaluate Eq. (5), each of the terms $u_{T3}$, $u_{T1}$, $u_{Q_{self3}}$, and $u_{Q_{self1}}$ must be estimated individually. $u_{T3}$ may be approximated as

$$u_{T3} = \sqrt{u_{T3_{resist}}^2 + u_{T3_{cal}}^2}$$  \hspace{1cm} (6)

where $u_{T3_{resist}}$ is the temperature uncertainty associated with the measurement of the thermistor’s electric resistance, and $u_{T3_{cal}}$ is the uncertainty associated with the thermistor’s temperature calibration. To determine $u_{T3_{resist}}$, first the uncertainty in the thermistor’s electric resistance $u_{R3}$ must be estimated; then, the upper bound on the uncertainty in the thermistor’s electric resistance $R_{3+}$ is calculated by summing $R_3$ and $u_{R3}$. Next, the upper bound on uncertainty in the thermistor’s temperature $T_{3+}$ is calculated by substituting $R_{3+}$ into Eq. (2), and $u_{T3_{cal}}$ is found by subtracting $T_3$ from $T_{3+}$. This method is necessary because Eq. (2) is nonlinear, and is valid because both the uncertainties $u_{R3}$ and $u_{T3_{cal}}$ are approximately symmetric and because the uncertainties $u_{T3_{resist}}$ and $u_{T3_{cal}}$ are independent. $u_{R3}$ is estimated from

$$u_{R3} = \frac{1}{I_{excite3}} \sqrt{u_{V3}^2 + \left(\frac{V_3}{I_{excite3}}\right)^2 u_{I_{excite3}}^2}$$  \hspace{1cm} (7)

where $u_{I_{excite3}}$ and $u_{V3}$ are the uncertainties in $V_3$ and $I_{excite3}$, respectively. The electric current and voltage measurement
uncertainties corresponding to the first and third rows in Table 2 are given in Table 3, from which a value of \( \pm 0.2 \, \Omega \) is calculated for \( u_R \). Summing \( R_1 \) and \( u_R \) gives a value of 1931.9 \( \Omega \) for \( R_3 \), which when substituted into Eq. (2) yields a value of 301.45 K for \( T_3 \). This is the same value as that shown for \( T_3 \) in Table 2, and indicates that \( u_{T3resist} \) is less than 0.01 K. For future calculations, \( u_{T3resist} \) is estimated as \( \pm 0.005 \) K. The last step to determine \( u_{T3} \) is to find \( u_{T3calc} \), which may be done using

\[
 u_{T3calc} = U_{calc} \cdot \Delta T_{corr3} 
\]

(8) where \( \Delta T_{corr3} \) equals 2.31 K from Table 2 and \( U_{calc} \) is 2% as calculated previously. Inserting these values into Eq. (8) yields a value of \( \pm 0.05 \) K for \( u_{T3calc} \). \( u_{T3} \) is then calculated from Eq. (5) and has a value of \( \pm 0.05 \) K, \( u_{T1} \) is calculated following the same pattern using the data in Tables 2 and 3, except that \( u_{T1calc} \) is zero because the uncertainty in the thermal resistance depends only on the difference between the temperatures \( T_1 \) and \( T_3 \).

The last two terms needed to evaluate Eq. (5) are \( u_{Qself3} \) and \( u_{Qself1} \). \( u_{Qself3} \) can be estimated from

\[
 u_{Qself3} = \sqrt{(I_{excite3} \cdot u_{V3})^2 + (V_3 \cdot u_{Iexcite3})^2} 
\]

(9) Substituting the appropriate values from Tables 2 and 3 yields a value of 6.9 nW for \( u_{Qself3} \). A similar calculation may be performed for \( u_{Qself1} \), yielding a value of 1.0 nW. Finally, from Eq. (5), a value of 400 K/W is calculated for \( u_{T} \). Comparing the uncertainty values in Table 3, it may be observed that for temperature changes above approximately 0.1 K, the percentage uncertainty in the thermistor calibration, \( U_{calc} \), dominates the uncertainty; however, for temperature changes below this value, the uncertainty due to the electric resistance measurement, \( u_{Tresist} \), dominates the uncertainty. Notably, the uncertainties calculated above are theoretical and do not account for fluctuations in the background vacuum chamber’s temperature or the physical limitations on the thermistor itself. For example, it has been assumed that spatial temperature variations within the thermistor itself can be neglected under steady-state conditions. This assumption can be verified and is valid as long as the measured temperature rise is much greater than the temperature variation along the thermistor length. In order to verify the accuracy and repeatability of temperature measurements taken with the thermistor, it is necessary to perform a number of controlled experiments with known heat inputs. For this purpose, a series of experiments was conducted in which a measured current flowed through the thermistor stainless steel support wires while an Agilent 34401A multimeter measured the corresponding voltage drop. A schematic of the circuit would appear the same as that shown in Figure 4, except that a 62.2 k\( \Omega \) resistor was used in place of a 9.2 k\( \Omega \) resistor. The total heat dissipation \( Q_{self} \) (thermistor self-heating) for each of the experiments is listed in Table 4, along with the thermistor’s temperature rise. The dissipated power \( Q_{self} \) in each of the last five rows of Table 4 is 13.02 \( \pm 0.01 \) \( \mu \)W. The uncertainty in \( Q_{self} \), may be calculated as in Eq. (9) and is less than 1%, indicating that the variations in the measured temperature rises are due principally to random errors in the temperature measurements. With this observation, the precision interval for measuring a temperature rise of 0.04°C can be estimated based on the data in Table 4. Assuming the standard student-t distribution with four degrees of freedom, the 95% probability precision interval is calculated to be \( \pm 0.002 \)°C, which agrees well with the theoretical uncertainty in temperature rise \( u_{T} \) calculated earlier (compare with \( u_{Tresist} \) in Table 3). As noted by Figliola [22], a small statistical sample size with only four degrees of freedom can give erroneous results; however, additional experiments have been conducted and yield similar results, though they are not presented here for the sake of brevity.

Having established that small temperature rise measurements (<0.05°C) are repeatable, the question arises if they are accurate. A comparison of the last five rows of Table 4 with the first two rows, where the temperature rise was much larger, indicate that small temperature rise measurements are indeed precise to at least better than 10%. Additional analysis of the data in Table 4 reveals that thermistor heating increases with the square of the current, as expected for heating in an ohmic resistor.

### Experimental Results

#### Thermistor Heating-Emission Current Relationship

Thermistor heating as a function of electron emission current was measured for six different growths of MWNT arrays. From...
Figure 8  Current-voltage curves of a MWNT array. The diameters of the MWNTs are approximately 30 nm, and the emission gap is approximately 1 mm. Inset shows the corresponding Fowler-Nordheim plot. Data points (a) and (b) mark the last and largest emission currents measured in data sets 1 and 2, respectively. Silver paint was used to attach the MWNT array to the thermistor.

Each MWNT growth, several samples could be prepared, and for this study, a total of over 20 samples were tested, although only representative results are included here. The diameters of the MWNTs from all growths were approximately 30 nm, and all arrays were mounted on the thermistor using silver paint, except as specifically noted otherwise. Figure 8 shows three different current-voltage curves obtained from the same sample. Each data point represents the mean of at least 200 measurements taken 0.3 s apart at a constant applied voltage. The inset in Figure 8 displays the corresponding Fowler-Nordheim plot, in which \( I/V^2 \) is plotted as a function of \( 1/V \) on a semi-logarithmic scale. The resulting curve is usually linear with a negative slope for metallic emitters as in Figure 8, which confirms that the measured current was produced by field-emitted electrons. As discussed previously, for emission currents above approximately 5 \( \mu \)A, MWNT array emitters typically become unstable and are subject to sudden degradation and burnout. In Figure 8, data collected in the first two data sets may be combined to create a nearly smooth curve; however, after the last and largest current measurement in the second data set (data point labeled b), the emitter appears to have become degraded, as indicated by the lower current measurements in the third data set.

Total thermistor heating as a function of emission current is plotted in Figure 9 for the first two emission current data sets shown in Figure 8. Thermistor heating for the third data set in Figure 8 was not calculated because the emission current was not sufficiently stable. The inset shows the total measured heating for the five lowest measured currents. Interestingly, the thermistor heating-emission current relationship appears to be nearly linear over the entire emission current range, with approximately 0.92 eV of heating per electron. Preliminary calculations, following the work of Fisher and Walker [23], indicate that Nottingham heating is well approximated as a linear function of emission current; however, emitter heating due to the Nottingham effect is not expected to exceed 0.1 eV per electron except for very large emission current densities. Therefore, it is more likely that Joule heating is responsible for the emitter heating shown in Figure 9, although Joule heating is typically characterized by a quadratic dependence on current. The relatively large applied electric potential (approximately 1.5 V/\( \mu \)m) could affect electrons traveling in the MWNTs, particularly if there are non-metallic states near the MWNT surface, and this effect could alter the quadratic relation that typically exists between Joule heating and electric current. This possibility is discussed further below.

Another possible source of thermistor heating is the anode, and great care has been taken in these experiments to ensure that the electron beam striking its surface did not produce a temperature rise sufficient to affect the cathode. The molybdenum anode is a 15 mm diameter rod embedded in a 10 cm diameter aluminum shaft. Analytical models as well as a 2-D numerical simulation with commercial software indicate that the anode temperature rise in the experiments reported here is approximately one-tenth that of the thermistor. Thus, anode heating is not likely to have a significant effect on the thermistor heating.

A further issue that must be addressed is experimental uncertainty. The minimum resolvable change in thermistor heating can be estimated by dividing the temperature measurement’s least-count uncertainty (approximately \( \pm 0.002^\circ \) C as determined above) by the thermistor thermal resistance, which has a value of 19350 \( \pm 400 \) K/W for the sample shown in Figure 9, resulting in a thermistor heating resolution of approximately 0.1 \( \mu \)W. Of course, instability in the emission current further degrades the thermistor heating resolution, as shown previously in Figures 6 and 7; nevertheless, the experimental uncertainties in Figure 9, if shown, would be approximately the same magnitude as the
Figure 10 plots thermistor heating as a function of emission current for three samples prepared from the same MWNT array growth. The MWNT arrays were mounted on the thermistor using silver paint for all samples, yet the heating per electron was different for each of the samples, varying from approximately 0.5 to 1.0 eV. Because each of the samples originated from the same growth process, it seems probable that differences in the slopes of the heating curves is a result of varying conditions at the interface between the silver paint and the MWNT arrays. As described earlier, the process by which the MWNT arrays are embedded in silver paint on the thermistor surface does not guarantee that the electric resistance between the silver paint and the electron emission sites located within the MWNT array is the same for all experiments, and this difference may explain the variation in the slopes of the heating curves. Another interesting feature of Figure 10 is that the second and third data sets of the sixth sample are shifted approximately 0.4 eV above the first data set. Although the difference is quite small, the larger heating per electron in the latter experiments could be due to a change in the pathway of the emitting electrons that occurred after the first data set was collected. A clearer example of this phenomenon is discussed in the next section.

In fitting the data of Figure 10 to linear curves, the possibility of a non-zero offset has been allowed to account for the possibility of a non-zero emission current producing zero emitter heating. Depending on the shape of the emission energy barrier profile, the Nottingham effect is expected to produce cooling for low emission current densities [23]. Thus, a critical emission current can be defined at which Nottingham cooling exactly balances Joule heating to produce a net energy exchange of zero at the emitter. Therefore, in order to allow for emitter cooling, the linear fits in Figure 10 include statistically significant non-zero offsets. It must be noted that the linear fits only apply in the emitter heating regime. Emitter cooling as a function of emission current must curve in order to assure zero cooling when the emission current is zero. Therefore, for very low values of emitter heating (<1 μW), the linear relationship between emitter heating and emission current as seen in Figures 9 and 10 may break down. Due to experimental error and equipment limitations, the present study is not capable of resolving thermistor heating in this very low emitter heating regime, and subsequently, the data in Figure 10 do not necessarily demonstrate that the heating curves have a non-zero intercept. Nevertheless, a non-zero intercept has been allowed to preserve the possibility of cathode cooling and to improve the linear fit.

Effects of Adhesive

Figure 11 shows the total thermistor heating as a function of the emission current for two MWNT array samples taken from the same growth. One sample was mounted using silver paint as the adhesive to attach the MWNTs to the thermistor, while the other sample was mounted using carbon paint. Similar to the other samples, the thermistor heating-emission current relationship is nearly linear, although the heating associated with the carbon paint appears much greater than that measured using the silver paint. Also, one data point taken for the sample with carbon paint is far below the others and, for this reason, was not included in the linear fit. That data point was the first taken, and then immediately after that, the heating per electron more than tripled. At present, this effect has not been explained; however, it is very unlikely that the large jump in thermistor heating seen in Figure 11 could be produced by Nottingham heating. One explanation for the increase in heating that occurred after the first data point is that as emission current increased, the electron path through the MWNT array burned out, forcing the electrons to travel through a path of greater resistance. If the emitter site remained the same, the emission current-applied voltage curve...
would change very little, although the emitter heating could increase greatly.

**Potassium and Cesium Intercalation**

Alkali metal intercalation is known to reduce the work function of carbon nanotube arrays and, consequently, decreases the potential barrier seen by the emitting electrons, resulting in an exponential increase in the emission current \[10\]. Potassium intercalation of several MWNT samples was attempted in situ at room temperature following the basic procedure described in \[24–26\]. A potassium metal dispenser (SAESGETTER) was placed approximately 1 cm beneath and slightly forward from the end of the thermistor to which the MWNTs were attached. Then, after conducting a series of experiments using non-intercalated MWNTs, an electric current of 5.5 A was run through the potassium source for approximately 20 min. to intercalate the MWNT arrays with potassium. However, emission current curves and thermistor heating curves obtained from the MWNT arrays after intercalation did not differ significantly from curves obtained before intercalation, indicating that potassium atoms did not intercalate into the carbon lattice. Similar intercalation procedures were followed using cesium metal dispensers, in which a current of 5.5 A was passed through cesium dispensers for various times ranging from one to several hours. Subsequent field emission experiments, however, indicated that cesium atoms also failed to intercalate into the MWNT lattice.

**CONCLUSIONS**

Interestingly, the emitter heating-emission current relationship associated with room-temperature field emission from MWNT arrays appears to be linear and not quadratic, as is usually the case for situations dominated by Joule heating. Yet the emitter heating is much larger than that expected from the Nottingham effect alone. Emitter heating depends strongly on the adhesive used to bind the MWNT arrays to the thermistor. Experiments further suggest that emitter heating depends more strongly on the path the emission electrons travel through the MWNT array than on conditions at the emitter site(s). Both of these observations indicate that Joule heating is the dominant heating effect in the experiments.

The linear relation observed between emitter heating and emission current could be a result of electric field penetration within the MWNTs that carry electrons toward the emission site(s). In this case, non-metallic states near the MWNT surface could be affected, and the quadratic relation that typically exists between Joule heating and electric current would be altered. To determine the exact cause of the linear heating-current relationship, additional experimentation and analytical modeling will be necessary. Also, in these experiments, alkali metal intercalation failed to reduce the emitter work function. Future experiments will further investigate the effect of the work function on the energy exchange associated with field emission by improving the alkali metal intercalation process.

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**NOMENCLATURE**

### Greek Symbols

- \( \Delta \varepsilon \) : average difference between the emitted and replacement electrons, eV
- \( \Delta T_{corr} \) : corrected temperature rise, K
\[ \Delta T_{tc} \] range of thermocouple temperature calibration with thermocouple, K

\[ \theta_{\text{heat}} \] average cathode heating per electron, eV

\[ \phi \] work function, eV

\[ \psi \] thermistor thermal resistance, K/W

REFERENCES


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