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# ELECTRODEPOSITION CHARACTERISTICS OF BISMUTH-TELLURIDE FILMS

**A. Prabhakar[1,3], E. J. Podlaha-Murphy[2,4], M.C. Murphy[2,3] & R.V. Devireddy[1,2,3]**
[1]Bioengineering Laboratory, [2]Center for BioModular Microsystems,
[3]Department of Mechanical Engineering, [4]Department of Chemical Engineering,
Louisiana State University, Baton Rouge, LA 70803.

## ABSTRACT
This work is a part of an on-going research effort to develop an array of micro thermoelectric coolers (TECs) for highly localized control of temperature at the cellular level. Prefabrication experimentation and modeling were carried out to understand the behavior of the proposed device. Mathematical models were used to identify important device parameters and optimal device dimensions. Preliminary experiments have shown that it is feasible to produce the TECs through electrodeposition of bismuth and telluride on modules produced using a modified multi-step LIGA (Lithographie, Galvanoformung and Abformung) technique. The development and characterization of the proposed TECs would enable the bioengineer highly localized control of temperature in a native or artificial tissue system. Thus enabling further usage of low temperatures in biological systems for both destructive (cryosurgical) and beneficial (cryopreservation) procedures.
*Keywords*: Cryobiology, Intracellular ice formation, Localized temperature control, Bi-Te thermo-electric cooler

## INTRODUCTION
Localized control of temperature at cellular level can be achieved by fabrication of a micro-thermoelectric cooler (TEC). The ability to control the temperature locally promises to pave way to many new areas of applications chief amongst which are low temperature banking (storage) of tissues (artificial and native) and organs. The precise temperature control and spot cooling features of the proposed TEC device make it an ideal choice for enabling temperature modulation of individual cells embedded in an extracellular matrix.

This study presents a method to fabricate an array of Peltier effect based thermoelectric (TE) modules using modified multi-step LIGA (Lithographie, Galvanoformung and Abformung) technique. The prototype device to be fabricated will consist of an array of 100 TECs that will be formed by electrodeposition of the proper materials (bismuth, Bi and telluride, Te). Within the array, the coolers will be interspersed to enable each one to be individually addressable and with each individual TEC having an n-type and p-type leg elements. These arrays of TECs will be embedded in polymethylmethacrylate (PMMA) matrix to improve insulation and will be situated under the tissue system to be cooled. PMMA sheet will provide an interface between the cooler and the embedded cells. PMMA was chosen as it is a commonly used X-Ray resist in microfabrication and is also biocompatible.

In recent years, efforts to fabricate the TEC with good figure of merit have been initiated. Microfabricated structures for the leg elements based on Peltier effect were produced via LIGA technique by Huang *et al* [1]. Bismuth telluride alloys were electrodeposited into patterns as deep as 750 μm. Miyazaki and Kajitani [2] have demonstrated a technique for deposition of Bi-

Te, which is used as leg elements in a thermoelectric cooler (TEC). Snyder *et al.* [3] fabricated and tested a thermoelectric microdevice using electrochemical MEMS technique, but the material optimization and the relationship among the deposition conditions, composition, electrical performance of the films and their performance as a device has not been reported.

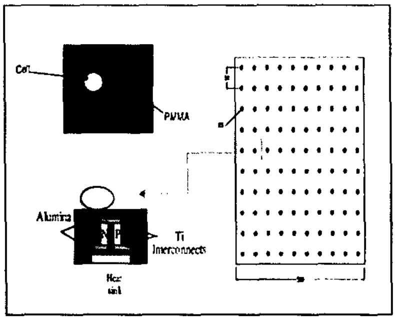


**Figure 1. Device Schematic.** The TECs will be staggered as shown, with spacing between the like devices of 50 microns. The entire device will be an array of 10x10 coolers.

## METHODS

### ELECTRODEPOSITION

Doped alloys of bismuth-telluride (Bi-Te) will be electrodeposited to form the branches of the TE actuators. The p-type Bi-Te alloy is bismuth rich whereas the n-type is tellurium rich [1]. These metals will be electrodeposited into recesses to form the needed geometry. The bath solution used for electrodeposition is a slight variation from the one pioneered by Miyazaki and Kajitani [2]. Initially, 10mM $Bi_2O_3$, 10mM $TeO_2$ were dissolved in pure $HNO_3$ (assay) with a concentration of 69.7%. It was found that at least 36h was needed to obtain a clear transparent solution as the dissolution of tellurium took longer time than bismuth, which dissolved immediately. DI water was subsequently added until the pH of the solution was close to 0.25. It was found that the lower the pH, the less time the tellurium took to dissolve. This result was further corroborated by an analysis of the Pourbaix diagram which showed that a pH 0.25 was optimal for the electrodeposition of $Bi_2O_3$ (at a concentration of ~70%).

Since achieving the proper composition of the deposit for Bi-Te is a function of both solution composition and current (or potential) used in deposition process, a modified Hull cell device (Autolab HT Rota-Hull®, Eco-Chemie B.V.,Utrecht, Netherlands) was used to facilitate the process of solution optimization. The working electrode (WE) for the Rota-Hull® is a rotating cylinder, and the counter electrode (CE) is shielded from the WE to create a calibrated ratio of current density along the length of the sample (Figure 2). In a single experiment, a range of current densities can be tested for a chosen solution.

The composition of the deposits along the length of the rod were analyzed using an Energy Dispersive X-Ray Fluorescence (ED-XRF) Spectrometer (Kevex Omicron). Using the calibration curve, the composition measured at each point can be associated with a current density. A polarization curve (Figure 3) shows the relationship between potential and current under identical deposition conditions. Because the composition and thickness at each point is known, the partial current densities of each species can be determined. From these graphs (Figs. 2 and 3) the deposition characteristics of Bi-Te can be determined *a priori.*

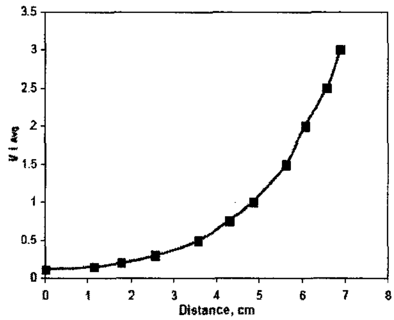


**Figure 2.** Calibration curve of current along the WE.

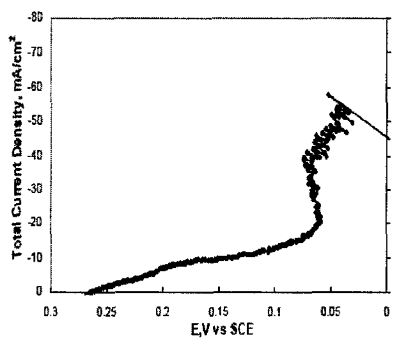


**Figure 3.** Polarization curve of Bi-Te electrodeposition on a RCE, dia. 0.6 cm, and 450 rpm.

## MATHEMATICAL DESIGN

An analytical model was developed following Yamanashi's approach [4-5] to establish the relation between the required cooling parameters and the TEC structure. In this preliminary model, all of the material properties were assumed to be independent of temperature and heat balance equations were calculated for each interface. Design parameters and conditions were varied to obtain a range for the expected cooling power. A closed form solution was also obtained to describe the transient temperature distribution within the device. To examine the validity of the analytical model, a system design methodology involving finite element analysis (FEA) was adopted [6]. In the FEA model the temperature dependence of the material properties was taken into consideration, utilizing the characteristic curves of $Bi_2Te_3$ given in the CRC Handbook of Thermoelectrics [7].

For both the analytical and numerical models described above certain common assumptions were made. Firstly, because of the symmetric design of the TEC, analysis was done considering a single thermoelectric element sandwiched between two substrates. Based on the size of the region that requires localized temperature control in a typical tissue system (~10 μm) we chose to restrict the width of the TE leg element to 10 μm. As a further simplification of the device analysis, we neglected the temperature distribution along the width of the TE leg element.

## RESULTS

To determine the electrodeposition characteristics of Bi-Te the current densities ranging from 0.2 to 13.88 mA/cm$^2$ were studied. It was observed that at the lower values of these current densities the growth rate of the deposit was slow, whereas at the higher values in spite of having a good growth rate the material had black colored grit formation and did not adhere to the electrode. The deposited films displayed desirable characteristics of metallic, regular pearl-gray deposition for current densities in the range of 0.3 to 7.5 mA/cm$^2$ with corresponding growth rates of 0.34 to 3.9 μm per half hour.

Figure 4 shows the final deposition characteristics observed from the analysis of the Rota-Hull® data. Using this figure specific range of potential values to fabricate p-type or n-type can be determined using eq. (1). From the literature it is known that Bi-Te with the stoichiometric composition ratio $Bi_2Te_3$ (Bi% - 40.065, Te% - 59.935%) is electronically neutral. In Figure 4 as the potential decreases, the percent composition of bismuth increases, indicating a progression from n-type to p-type. It also indicates that p-type material would be obtained for values of E < 0.23V and n-type for values of E>0.23V.

$$X_i = \frac{\frac{i_j}{n_j F}}{\frac{i_j}{n_j F} + \frac{i_k}{n_k F}} \qquad (1)$$

The deposited concentrations of Bi at a particular voltage were determined from the values of the partial currents (Figure 5) by eq. (2). The curves were produced from the combined data of the Rota-Hull and the RCE polarization curve results as explained earlier. It is seen from the Figure 5 that the side reactions in the experiments increases as the current increases and initially the side reaction partial current is the much higher than those of Bi and Te. Therefore the current efficiency, which describes how much current is lost in deposition to side reactions, is low. The data from the Rota-Hull® gives results for a particular rotation rate. The rotation rate can be related to the same limiting current conditions as those found in a corresponding recess depth, through the well established Eisenburg Equation shown below, assuming that the boundary layer thickness is approximately equal to recess depth [8].

$$\delta = 99.62 d^{0.4} v^{0.344} D^{0.356} S^{0.7} \quad (2)$$

It is established from the Rota-Hull® data that the Bi-Te system is kinetically controlled, i.e. they do not reach a point of limiting current. Fortunately, this will yield deposition that is independent of recess depth. Also, from the ED-XRF data analysis, Te was always observed to be of higher concentration than Bi. Further testing is under way to supplement these results.

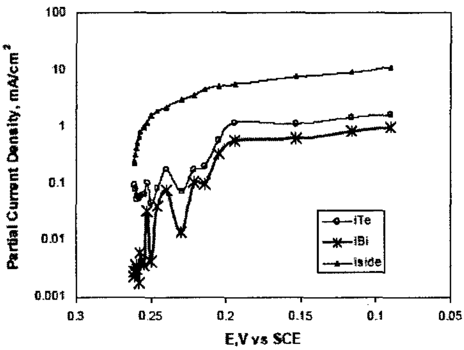


**Figure 4.** Deposition characteristics for Bi-Te, 450 rpm

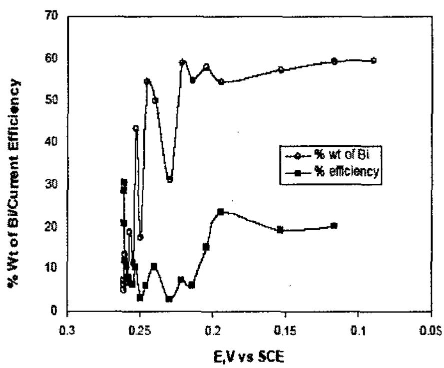


**Figure 5.** Partial currents for the Bi-Te deposition along with side reactions, rotation rate of 450 rpm, and avg. current density of 2.9mA

The modeling is done assuming an array of array of 100 microscale TECs with each of its leg element having a fixed width of 10 μm, placed 20 μm apart. The microdevices are separated by a distance of 50 μm center-to-center and dimensioned so that each device will measure or modulate the temperature within the neighborhood of a single cell. The length dimensions of the leg element of the micro TEC was varied to get an analytical solution of the expected temperature profiles. The numerical model resulted in values that were in accordance with the values obtained by the analytical model, for a commercial cooler. But the model is limited in that it does not include radiation or the use of a heat sink, and thermal contact and spreading resistance, thereby causing model breakdown at the microscale level. Further work is in progress to refine the model.

## CONCLUSION

The n-type and p-type leg element deposition can be achieved by varying the cathodic potential while maintaining the same bath composition. Hence the material deposition development can focus on a singe material system, which will yield both n-type, and p-type pellets of TEC. The deposition of bismuth-telluride with the proper doping is being studied experimentally. Flat plate experiments are underway which would establish the relationship between the electrical and thermal properties of the films with the composition and deposition conditions. Further work to refine the present FEA model is being done. The wiring and the associated control system are currently being finalized to initiate preliminary testing of the device with an artificial tissue system [9,10].

## ACKNOWLEDGMENTS

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