THE POWER OF THERMOELECTRICS

Duby S, Ramsey B. and Harrison D.
School of Engineering and Design, Brunel University,
Egham, Surrey, TW20 0JZ, UK
Sam.duby@brunel.ac.uk

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ABSTRACT: A novel process for the fabrication of thermocouples has been developed. Thermoelectric reactions of 22 μV/˚C per couple have been observed which are comparable to those of conventional thermocouples. This work outlines the potential for a rapid, low-cost, low-temperature manufacturing solution for the production of a renewable power generation device.

1. INTRODUCTION:

This paper presents a novel technique for the manufacture of thermoelectric generators via printing processes. The eventual goal is to produce a low-cost electricity generator that harvests energy from waste heat. The applications are wide-ranging, from boosting the efficiency and output of conventional solar panels, to providing power for small, embedded, autonomous sensing circuitry, to the practical and affordable electrification of rural areas both in the developing and developed world.

A number of European directives such as WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restrictions of the use of certain Hazardous Substances) have added to the increasing pressure from consumers on manufacturers to extend their responsibility and adopt more environmentally friendly production methods. Our current research capitalises on this need and builds on previous commercially successful work undertaken by this research group into environmentally sensitive electronics manufacture.

1.1 Context:

As we begin the 21st century, two billion people –one in three of us on the planet- have no access to electric lighting or decent cooking facilities. Getting people the clean and reliable energy necessary for essential needs such as clean water, health care facilities, heating and lighting is one of the most pressing problems facing humanity today [1].

According to a recent report published by Greenpeace and the World Wildlife Fund, there are 2 billion people in the world without access to basic energy services. Energy they argue is fundamental to economic and social development, both North and South. The solution in the past has been to invest in technologies dependant on fossil fuel. This is for a great many reasons an impractical, short-sighted and immensely damaging solution. Renewable energies offer an increasingly beneficial alternative.

We are becoming increasingly aware of the consequences of many years of burning fossil fuels. CO_2 emissions have been outlined as being particularly damaging. The International Energy Agency predicts a 60% increase in CO_2 emissions by 2020, one third of which would result from new electricity generation in developing countries.

In rural areas of many poorer countries, it is often unfeasible to provide a connection to a national grid, or to transport quantities of fuel such as Kerosene and diesel. Consequently the costs associated with providing power to people in these areas with conventional technologies is often more expensive than already available renewable energy solutions [2].

As the cost of oil steadily escalates, the real costs of renewable energies fall daily. Price is probably the most important factor for the dissemination and market penetration of renewable energies. According to the WWF, market surveys in Africa and Asia have shown that only about 5% of rural populations could pay cash for a solar home system. Costs of solar systems are dropping slowly and steadily, but they will always be limited by the fact that at approximately 50% of the costs associated with the manufacture of a solar cell are due to the raw material costs of silicon. Consequently, the potential for a low-cost electricity generating solution in terms of both potential market and potential humanitarian benefit are enormous.

The potential uses of renewable energies and particularly thermoelectric generators are virtually limitless. Mobile immunisation programs often require vaccines to be kept within a 0-8˚C temperature range. Electrically powered refrigerators are vastly more reliable than their kerosene fuelled counterparts, reducing the incidences of vaccines being spoiled [3]. Health centres need electricity for medicine refrigeration and blood storage as well as lighting, equipment sterilisation and telecommunications. Schools and education centres benefit hugely from access to basic facilities such as lighting, computers and audio-visual equipment. Small-scale electricity generators can also support income generating applications such as evening lighting in shops, charging batteries for local people, drying produce and running equipment such as sewing machines.

1.3 Background:

Previous work has been done at Brunel University into the printing of passive electronic components [4,5], from simple capacitors and resistors, to more complex integrated filter structures, microwave circuit components and humidity sensors [6]. A number of licenses to this technology have been sold and are being exploited for amongst other applications, the manufacture of RFID antennas.

There are many advantages that directly printed circuitry has over the more conventional printed circuit board. Printing is a high-speed, high-volume process which means that there are substantial reductions in production times that lead to large cost reductions. Printing is also an additive process that results in substantial environmental benefits over standard techniques. Traditional circuit board manufacture incurs raw materials loses of over 80% through the waste stream, as an entirely copper coated board is etched away leaving only a small amount of conductive material to form the tracks. Many toxic materials are used in the traditional process, from the photoresists to the etching chemicals, cleaners and fixatives. The only chemicals used directly in the printing of electrical components are the inks.

1.4 History:

In 1780, the Italian Luigi Galvani demonstrated that when two different metals are used to form a circuit including the nerve muscle from a frog's leg, the muscle was shown to twitch. He ascribed this energy to inherent 'animal electricity'. Alessandro Volta, also an Italian, disagreed with this theory, stating that it was actually the joining of the two different metals that produced an electric charge. Unusually in the case of scientific debate, both men were later proved right, with Galvani demonstrating that bioelectric forces do in fact exist within living tissue, and Volta showing that a pile made from two dissimilar metals separated by a salt solution replacing the organic material, would also produce a charge. This invention won Volta much fame, and is said to be the first instance of a modern battery.

Ironically enough while replicating Galvani's experiments Volta noted that it was necessary to heat one end of the bimetallic junction connecting the muscle tissue in order to observe any twitching. When the metal had grown cold the twitching stopped. Somehow, Volta ascribed no importance to his own observation and it was not until 1821 that thermally generated electricity was discovered by a German physicist by the name of Thomas Seebeck.

In the early 1820s, Seebeck set out to prove that thermal processes could induce magnetism in metal ores directly without any flow of electrical current. His early experiments involved the removal of the electrolyte from Volta's basic cell and an investigation into different configurations of two bare metal contacts. In 1821, Seebeck observed that a magnetic needle could be deflected by a circuit made of two dissimilar metals, whose junctions were maintained at different temperatures. In dispute with fellow scientists, he maintained that the observed magnetic field was a result of the temperature difference and had nothing to do with a generated current. Despite further evidence produced though extensive research Seebeck was still reluctant to accept the theory of thermoelectric generation and argued his case until his death. None-the-less the discovery that by joining two ends of a pair of dissimilar metals in a closed loop and creating a temperature difference between the two junctions, an electromotive force would be created proportional to the temperature difference, is ascribed to him. This phenomenon is known as the Seebeck effect.

2. THERMOELECTRIC POWER:

The Seebeck coefficient is a value ascribed to a particular material at a particular temperature. It is an indication of the potential difference that will be generated for each degree difference in temperature between two points of the material and is expressed in volts per degree or more usually microvolts per degree (μV/K). For power generation calculations, factors such as thermal and electrical conductivities have to be taken into account and as a result, the dimensionless Figure of Merit (ZT) is more useful:

$$ZT = \frac{T\alpha^2}{\sigma\lambda}$$

Where: α is the Seebeck coefficient
σ is the electrical conductivity
λ is the thermal conductivity
T is the absolute temperature

2.1 Quantum explanation:

An understanding of these principals is impossible without careful consideration of the movement of electric charge carriers within the atomic structure of a material. Of equal importance is the fundamental principle endemic to the universe, implied by the Second Law of Thermodynamics suggesting that systems will always try to achieve equilibrium. The creation of a thermal gradient across a material implies the input of energy at one end of the material in the form of heat. This energy is manifested in the structure as excited charge carriers with increased kinetic energy, and phonons, which are basic quanta of vibrational energy similar to the photons that describe the fundamental quanta of light.

Analogous to the molecules in a gas, increasing the kinetic energy at one end of a conductor effectively increases the 'pressure' of the charge carriers. The imbalance of electron energies is redressed by the diffusion of those with higher energies towards the colder end of the conductor. This accumulation of electrons results in the build up of negative charge at the cooler end and the build up of positive charge at the other end where the positive ions are left with a shortage of electrons. The state of non-equilibrium results in the gradient of thermal potential being countered by an equivalent gradient of electrical potential (∂V balances ∂T). Kinetic energy is transferred into electrical potential. The rate and extent to which this occurs is dependant on a number of factors including the quantity of energy input into the system (Q) and the Fermi energy (E_f) of the material, defined as being the energy level of the highest occupied band at 0°K [7].

Substances with completely full atomic energy bands will not conduct. Substances with partially full bands will have electron-dependant conduction and those with almost full bands will display hole-dependant conduction. For practical purposes, holes can be considered to be positively charged particles moving though the lattice in much the same manner as an electron. In real terms, what is happening is that electrons are constantly shifting to fill a gap or hole, creating another hole in the space they have just left. Holes can be considered to have an equal and opposite charge to electrons but a slightly higher mass as they require more energy to accelerate.

Whether the material has holes or electrons as the majority charge carriers will define whether it is a *p* or *n*-type. Subjecting these materials to the same thermal gradient will cause their electrons to move in opposing directions creating opposite electrical potentials. Consequently connecting the two at one end will cause electrons to flow from one material to the other. This is the principal of a thermocouple.

3. METHOD:

In order to print a thermocouple, two thermoelectrically active materials with opposite bias need to be processed into inks. In this case, the inks developed consist of metallic particulates suspended in a variety of polyester, cellulose and conductive polyaniline *(Panipol M)* resins. The principal functions of the resin vehicle or matrix are to provide suitable flow-characteristics for the ink, to ensure that the final printed track has structural integrity, and ensure the active particulate is adequately adhered to the polyester substrate. There are a variety of factors that become critical at each stage of the process, and it is the optimisation and refinement of each of these that constitutes the majority of practical work carried out.

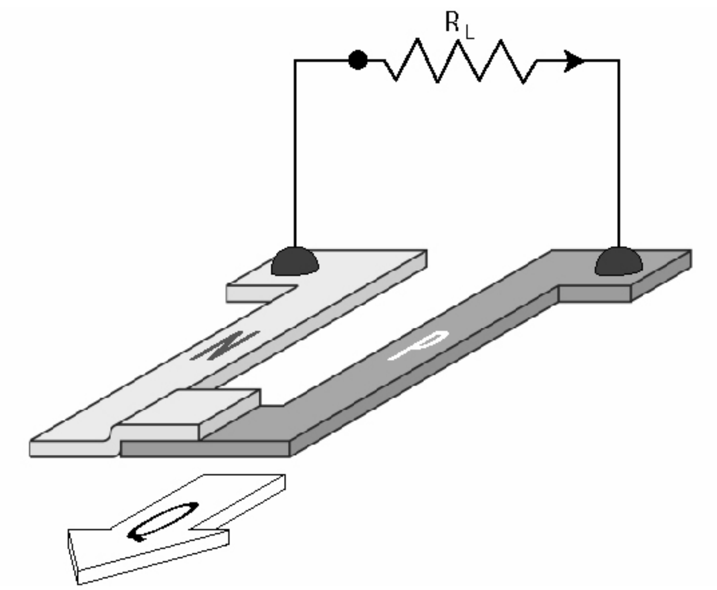

Figure 3.1 *The principle of a printed thermocouple*

In order to maximise the thermoelectric reaction of a printed sample, the proportion of thermoactive material to resin must be as large as possible. A small amount of matrix is necessary, as the particulate must remain adequately adhered to the substrate, however minimising the quantity of non-thermoactive material in the final dried printed sample is desirable. However, in order for an ink to be printable, it needs to have appropriate rheological properties. These characteristics will principally be derived from the resin vehicle, and not from the metal particulate itself. As a result, a balance must be sought between formulating an ink with enough resin vehicle to enable printing, and as little resinous material as possible in the final dried printed sample.

This balance is addressed through the careful selection of resins with an appropriate molecular weight. Very high molecular weight polymers will lend more viscosity to a stoichiometrically identical solution of lower molecular weight polymers. This is a function of chain tangling. Only a small quantity of a high molecular weight polymer will need to be added to a suitable solvent to give the resulting solution a relatively high viscosity and flow characteristics that enable printing. On drying, once all of the solvent has evaporated only a small amount of the polymer resin will remain adhering the particulate to the substrate, maintaining the highest possible particulate to matrix proportion.

The image below shows a 1000x magnified photograph of a printed NiCr track. It can be seen that the particles have been flattened into flake-like form. This is a result of having been ground in a three-roller mill as part of the production process. Flattened particles lie against each other with a greater amount of overlapping surface-area resulting in higher degree of inter-particle contact than nodular or granular particles. This means that the conducting electron does not have as much non-conductive matrix to tunnel through and can relatively easily hop from one particle to the next, facilitating conduction.

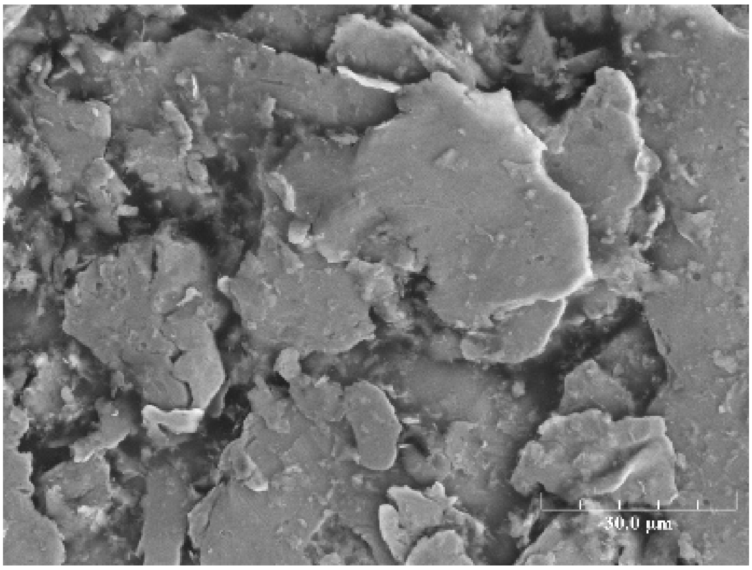

Figure 3.2 *Printed NiCr track -1000x magnification*

Enabling better dispersion of the particulate in the resin was another technique that effectively reduced the quantity of resin that was needed to create a viable ink. This was done using ‘dispersion’ or ‘wetting’ agents. This is common practice in the ink industry, where a wetting agent is often used to disperse solid dye particles. There are a number of different ‘wetting-out’ mechanisms. The most effective wetting agent for these purposes was found to be heptanoic acid, a carboxylic acid that exploits the fact that it is a polar molecule. This means that in terms of electron density, it is heavily biased towards one side, and a dipole moment is created between the two ends of the molecule. In the case of carboxylic acids, the dipole moment is created by the presence of a carboxyl group (-COOH) on one side of what is otherwise a simple, predominately saturated hydrocarbon. The length of this carbon chain differentiates the various carboxylic acids from each other. The polar nature of a carboxylic acid means that one end of the molecule will often be attracted to the molecules in a solvent whereas the other end will be repelled. This mechanism is known as hydrophobic and hydrophilic action. Practically what this will mean is that one end of the molecule will be repelled by the solvent and attach to the solid particulate leaving behind a 'tail' that is attracted to the solvent. In this way the solid particulates are effectively separated from one another and dispersed in the solution.

The addition of NaCl was found to improve the wetting of the n-type NiCr inks. Chloride ions in solution will penetrate and destabilise a passive chromium oxide layer. The chemistry of this mechanism has been closely scrutinised and carefully documented because of the corrosive effect that chloride ions have on the chromium in stainless steels. Although usually viewed as an unfortunate, destructive reaction, in this context, it is thought that the NaCl would break down the protective oxide layer of the chromium, leaving the metal exposed and open to an attractive reaction with a wetting agent, thereby enhancing this wetting mechanism.

One of the more interesting additives was Panipol M, a polyaniline based conductive polymer. Panipol M is a solution of polyaniline salt in 1-Methyl 2-Pyrrolidinone, and is an example of a commercially available conductive polymer. Most conductive polymers suffer from being very unstable, breaking down in ambient conditions very readily. Doping atoms are often added to improve the stability of conductive polymers. These added atoms have the effect of attracting the otherwise highly mobile disassociated electrons and consequently render the polymer a hole-based conductor. As a result, these materials can only be used as part of a *p*-type formulation. To date there is no readily commercially available *n*-type conductive polymer.

4. TESTING:

Inks were formulated to conform to the required rheological criteria, screen printed into single-leg thermoelement and two-leg thermocouple configurations, and electrically assessed for thermoelectric performance. The Seebeck coefficients of the samples were obtained using test apparatus that held the ends of the thermoelement or thermocouple at two stable and different temperatures (maintaining a ∂T of approximately 150˚C) while measuring the generated emf. The technique was in accordance with prior methods as described by Kayadanov [8] and Yang [9]. Results were obtained for printed samples of single legs containing various material combinations and solid samples of standard thermoelectric materials. Results were also obtained for the reaction of printed thermocouple configurations and standard thermocouples.

The apparatus was designed such that one end of the thermocouple was held between two air-cooled Peltier modules capable of maintaining a closely controllable temperature of down to –20˚C, while the other was held between two flat-plate resistance heaters powered by a *Zenith* 240V a.c. variable transformer capable of maintaining a stable temperature of between ambient and 170˚C. The sample was only otherwise in contact with the air, ensuring that heat flow was predominately through the printed track with a negligible amount through the polyester substrate. Three mineral-insulated k-type thermocouples probes continually monitored the ambient, cold-junction and hot-junction temperatures through a *Pico TC-08 8-Channel Thermocouple Data Logger* connected to a PC. The *TC-08* data logger was capable of measuring absolute potential difference with a resolution of unitary microvolts and was also used to monitor the generated emf of the sample. Results from the testing of standard thermocouple legs using this set-up correlate with theoretical data (within 5% variance) [10].

5. RESULTS:

The thermoelectrically generated potential differences of the printed couples are comparable to that of conventional couples. The sum of the experimental results for Seebeck voltages of the separate thermoelements of a standard couple is in close accordance with the theoretical data for the complete couple.

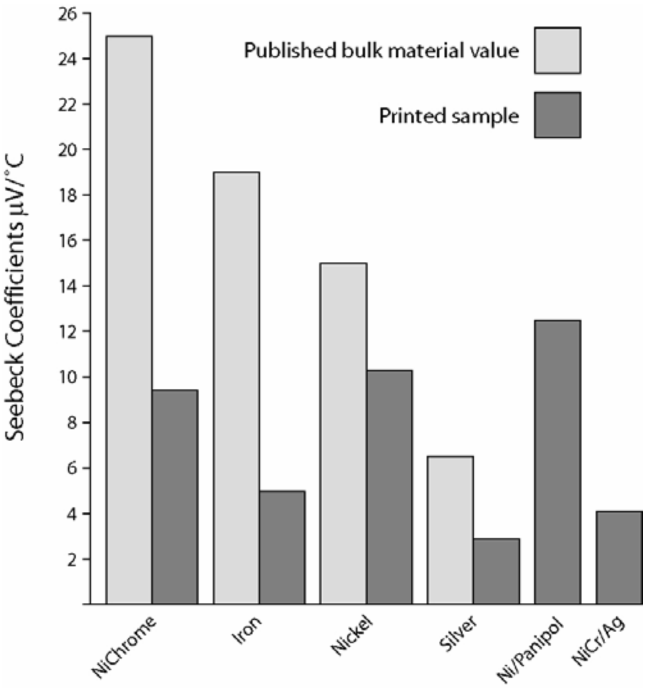

Figure 5.1 *Published bulk material Seebeck coefficients compared to those of printed samples*

Results indicate that generated Seebeck emf was more dependant on the type and quantity of the principle thermoelectric material used than on the intrinsic electrical resistivity of the material. The amount of thermoelectrically active material in the formulation, which in this instance is analogous to the particulate loading of the ink, was defined by the required physical characteristics of the ink.

Particulate loadings of 96% by volume in the dried deposited sample have been achieved. These provide a greater per degree potential difference, but the constraints of adequate adhesion mean that lower particulate loadings are more suitable. The inks were deposited onto a flexible polyester substrate so the binder system had to be compatible with this type of material.

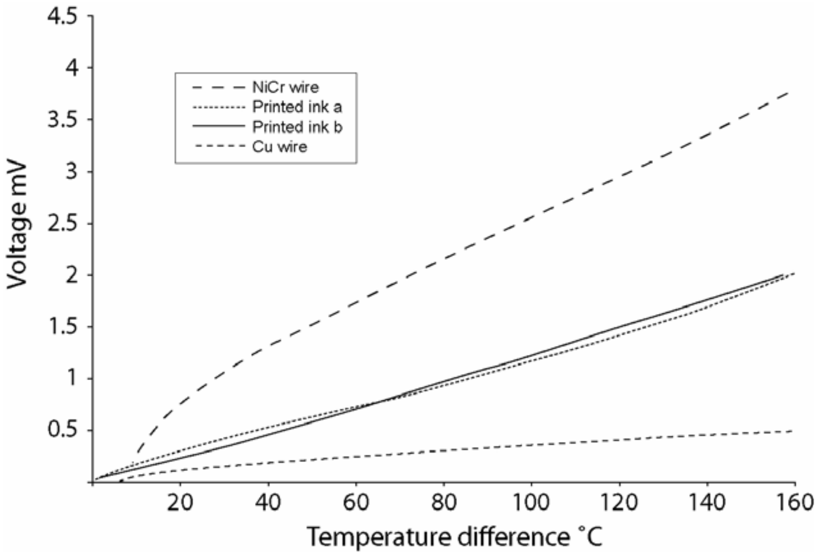

Figure 5.2 *Generated Seebeck voltages of two printed and two standard thermoelements*

The graph above shows how the electrical reactions of two printed thermoelements compare with those of copper and Nichrome wire, both of which are thermoelements from standard commercially available thermocouples. Data has been gathered over the range of 0-160˚C. The reaction is stable and demonstrates a reasonable hysteresis, typical of standard thermocouple configurations. The best printable thermocouple configurations were found to be a combination of a Nichrome based ink and a Nickel/Panipol blend. This is not a standard thermocouple combination. Data has been gathered that demonstrates that different batches of samples printed with inks of the same formulation perform consistently with a standard deviation of <0.01.

6. CONCLUSIONS AND DISCUSSION:

Thick film manufacture processes have been employed to fabricate thermoelectric generators. Separately developed *p* and *n*-type materials have been used in conjunction in a thermocouple arrangement. Thermoelectric reactions of 22 μV/˚C per couple have been observed which are comparable to those of conventional thermocouples. At present, the internal resistances of the devices are such that the generated current is in the order of microamps per degree temperature difference.

The experimental results indicate a potential for this approach to offer a rapid, low-cost, low temperature manufacturing process for effective electrical temperature monitoring devices or sensors, overcoming the need to place and solder components and the requirement to 'fire' and laser trim ceramic systems.

One of the more exciting potentials that this work has allowed is the use of new materials as elements in a thermoelectric device. The inclusion of conductive polymers in specific ink formulations had a positive effect on the thermoelectric performance of the device and as such represents an interesting avenue of research.

For the first time thermocouples have been manufactured using high-speed printing processes. This constitutes an important step towards thermoelectric power generation becoming a serious contender in the burgeoning field of renewable energies. With their lack of moving parts, non-toxic nature, scalability, ease of manufacture, reliability and rapidly decreasing costs, thermoelectric generators provide the potential for a viable and widely applicable solution to the energy crises.

REFERENCES:

[1] United Nations Development Program (2000) **World Energy Assessment: Energy and Challenge of Sustainability**

[2] The International Association for Energy-Efficient Lighting (2000) 'Fuel Based Lighting in the Workplace' **IAEEL Newsletter**

[3] J. Gwillim (2002) 'The Feasibility of a Battery-less PV-Powered Vaccine Fridge' **DTI Pub. Urn No. 02/1376**

[4] P.S.A Evans, B.J. Ramsey, P.M. Harrey and D.J. Harrison (1999) 'Printed analogue filter structures' **Electronics Letters**, Vol 35, (4), pp. 306-308

[5] P.M. Harrey, P.S.A Evans, B.J. Ramsey and D.J. Harrison (2000) 'Interdigitated Capacitors by Offset Lithography' **Journal of Electronics Manufacture**, Vol. 10 No.1, pp 69-77.

[6] P.M. Harrey, B.J. Ramsey, P.S.A Evans and D.J. Harrison (2002) 'Capacitative-type humidity sensors fabricated using the offset lithographic printing process', **Sensors and Actuators**. B6361, 1-7.

[7] M.J. Clugston (1998) 'The New Penguin Dictionary of Science' **Penguin Books**, ISBN 0-14-051271-3

[8] V.I. Kayadanov and T.R. Ohno (1999) 'Process Development and Basic Studies of Electrochemically Deposited CdTe-Based Solar Cells' **Annual Technical Report –Colorado School of Mines**, pp. 11-12

[9] B. Yang, J.L. Liu, K.L. Wang and G. Chen (2002) 'Simultaneous measurements of Seebeck coefficient and thermal conductivity across superlattice' **Applied Physics Letters**, Vol. 80, No. 10, pp 1758-1761

[10] 'Guide to Thermocouple and Resistance Thermometry',**TC Limited**, Issue 6.0.