Ferrite Based Room Temperature Negative Temperature Coefficient Printed Thermistors


Two screen printing inks were developed for the low-temperature fabrication of printed and flexible thick film negative temperature coefficient (NTC) thermistors able to operate at room temperature. The first of the two screen printing inks developed utilised cobalt ferrite (CoFe₂O₄) as the temperature sensing material with the second ink incorporating manganese ferrite (MnFe₂O₄). These were then screen printed onto lithographically printed silver interdigitated electrodes with a 200-micron track and gap using a synthetic paper (Teslin) as the substrate. The inks required a 10-minute curing step at 80°C. Pre-annealing of the ferrite powders before ink formulation enabled the avoidance of high-temperature processing post-fabrication typically required in industrial thermistor production. The printed thermistors were tested at a controlled constant humidity between 15 and 50°C. Both materials demonstrated typical natural logarithmic responses with high linearity and sensitivity.

Introduction: Temperature sensing is a crucial method of environmental monitoring for many industries including meteorology, medicine, smart packaging, and agriculture [1]. Meanwhile, developments in the printing industry now allow for low cost, high throughput fabrication of electronics, which can be achieved using traditional printing press equipment [2]. Recently, with an increased concern for environmental sustainability and low waste manufacturing, expanding the functionality of printed electronics has become of interest [3]. A main research area in this field has been printed sensing technology focusing on gas, humidity, and temperature sensing. The main focus of this research has been in enabling functional materials to be printable through dispersing the material in a vehicle to form an ink [4]. With regards to temperature sensors, traditionally these are manufactured through depositing a paste of material (typically a ferrite) onto electrodes and sintered at high temperatures before encapsulation [5]. However, these materials are difficult to print on flexible substrates due to the high processing temperatures required. This has led to research focusing on either 2D-materials such as the effect of thermal expansion on graphene or conductive polymers [6] [7]. However, these methods are difficult to integrate into high throughput printing processes or rely on high cost materials. Due to this, metal oxide materials provide an advantage in allowing for simpler manufacturing at a lower cost. Research using metal oxides has had some success with antimony tin oxide, however, little work has been performed into the materials traditionally used to manufacture commercially available thermistors, ferrites [8]. In this letter, we report the first fully printed ferrite based NTC thermistors which allow for highly linear temperature sensors to be manufactured through low cost, high throughput roll to roll printing methods.

Data and Methods: The interdigitated structures were printed via offset lithography using synthetic paper substrates (PPG Teslin) using a silver ink developed for the offset lithographic process described in previous authors work [9]. Use of such printed interdigitated structures were first reported as novel electrodes for 2D capacitive AC Electroluminescent Displays [10]. The silver was printed via offset lithography allowing for the interdigitation to have a 250 µm track and gap. This interdigitation is required to lower the overall resistivity of the thermistor due to the high resistivity of the ferrites. The ferrite nanoparticles were formulated through a previously reported method [11]. Briefly, CoCl₂·6H₂O (0.2 M) / MnCl₂·6H₂O (0.2 M) / FeCl₃·6H₂O (0.4 M) were dissolved in deionized water (18 MΩ) for CoFe₂O₄ and MnFe₂O₄, respectively. For both, 3 M NaOH was slowly added to the solution until a pH of 11-12 was reached, resulting in precipitation of a brown coloured solid. A few drops of oleic acid were added as a surfactant. The solution was then heated with stirring at 80°C for 1 h, after which the solution was allowed to cool to room temperature and the solid was filtered and washed thoroughly with water until the filtrate had a neutral pH to ensure complete removal of sodium and chloride species. The solid was finally washed in ethanol and allowed to dry in an oven at 100°C overnight. The solid was ground into a powder and annealed in a tube furnace at 600°C for 6 h for the CoFe₂O₄. The MnFe₂O₄ powder was annealed at 500°C for 6 h. These nanoparticles were then annealed at 600°C in order to convert the ferrites to their spinel phases. This phase is required in order to achieve the temperature sensing properties of the material. Typically, in traditionally manufactured thermistors, these materials are converted to their spinel phase after material deposition. However, to allow for the use of low temperature, flexible substrates, this step is performed on the powder only before ink formulation.

The ferrite inks were made by mechanically mixing the CoFe₂O₄ and MnFe₂O₄ with an organic based vehicle. The materials were mixed in a 50:50 wt.% ratio of powder to vehicle to provide two inks. The vehicle was comprised of a mixture of nitrocellulose resin, alpha-terpineol and methoxy-propanol. The mechanical mixing of this mixture was performed via the three-roll mill (EXACT 30L) method. Once these inks were formulated, they were printed via screen printing (DEK 1202) with a stainless-steel mesh screen (305 tpi, ASM) onto the interdigitated area of the printed electrodes to provide a 40x55 mm, thin and flexible thermistor as shown in Figure 1(a-b). Samples were then cured at 80°C for 10 minutes.

In order to determine the quality of the coating and to determine whether the material retained its particle size post mechanical milling, field emission gun scanning electron microscopy (FEGSEM, Jeol 7800F) images were taken. The uniformity of the printed films can be seen in Figure 2(a), which displays the overall uniformity of the MnFe₂O₄ film. The three-roll mill used for mechanical mixing has a 5μm gap between rolls which can damage large particles. In order to determine whether the ink formulation step led to agglomerates which can therefore be damaged in the milling process, SEM images were taken at higher magnification. As shown in figure 2(b), it can be seen that the nanoparticles remain unaltered from their pre-ink form and therefore the temperature sensing properties remain intact.

For the measurement of the temperature sensing properties of the printed thermistors, an environmental control chamber (HygroRotronic) was used. This chamber allows for the alteration of relative humidity between 15 and 50% and for control of the temperature between 15 and 50°C. For these experiments, the relative humidity of the chamber was kept constant at 50% and the temperature was altered between 15 and 50°C. Each sensor was placed in the chamber with wires connected to each side of the printed sensor electrode, these wires then connect to a digital multimeter (Fluke 189), enabling the resistance to be measured. Each sample was provided with 1 hour in the chamber at 15°C to acclimatise before experimentation. The temperature in the chamber was then increased by 5 degrees at a time, with resistance measurements being taken once the temperature had stabilised. This was performed for increasing and decreasing temperature in order to determine whether the response was reversible or just a thermal degradation effect of the material.

Fig. 1 Images demonstrating a printed MnFe₂O₄ thermistor showing (a) a top down view with thermistor dimensions and (b) a side view highlighting the printed inks used

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Temperature response measurements regarding the CoFe$_2$O$_4$ thermistors can be seen in Figure 3. As can be seen from the decreasing resistance with respect to an increasing temperature, the CoFe$_2$O$_4$ thermistor can be regarded as a negative temperature coefficient (NTC) type thermistor. For an increasing temperature, the logarithmic response provides a high linearity with an $R^2 = 0.9845$. However, with a decreasing temperature it is clear that while it has a definite resistance increase, there is hysteresis in the device. The initial starting resistance at 15°C was 68.9 MΩ whereas the thermistor final resistance at 15°C was 35.6 MΩ. The thermistor had a high sensitivity which was calculated to be 1.91 MΩ/°C. This shows that although the sensor has a higher resistance than most off the shelf thermistors, it also provides a much higher signal per °C. This provides an advantage, considering a printed thermistor is most likely to be integrated with printed electronics this high signal response removes the need for amplification.

**Fig. 3 Temperature response graph of a printed CoFe$_2$O$_4$ thermistor**

Temperature response data for the MnFe$_2$O$_4$ printed thermistor can be seen in Figure 4. Upon analysis, it can be seen that it provides a similar NTC response to the CoFe$_2$O$_4$. The initial starting resistance is 23.8 MΩ at 15°C with a 3.41 MΩ resistance at 50°C. This provides a lower sensitivity of 0.58 MΩ/°C. However, the final resistance at 15°C was measured to be 23.1 MΩ demonstrating that MnFe$_2$O$_4$ is less prone to hysteresis than the CoFe$_2$O$_4$ printed thermistor. The manganese ferrite-based sensor also provides a higher degree of linearity with $R^2 = 0.9998$ suggesting this material functions better as a thermistor than its cobalt based counterpart.

**Fig. 4 Temperature response graph of a printed MnFe$_2$O$_4$ thermistor**

**Conclusion:** We have demonstrated that by performing the high temperature processing of ferrite materials before paste formulation, it is possible to print room temperature functioning NTC thermistors onto flexible polymer substrates. This allows for high performance temperature sensors to be printed in high volume, roll to roll manufacturing processes, and integrated into smart packaging and embedded into devices for environmental monitoring. Adding to the environmental sustainability of this manufacturing process, the curing step only requires 80°C for 10 minutes. The manganese ferrite was found to be the highest performing material with a high degree of linearity, a sensitivity in the KΩ/°C region and was less prone to hysteresis than the CoFe$_2$O$_4$. Future work will be focused at determining if composites of ferrites could provide better performance. It will also comprise of research into the long-term stability of the thermistors compared to traditionally manufactured counterparts and whether the sensing properties function under flex.

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**References**