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Large-Area All-Printed Temperature Sensing Surfaces Using Novel Composite Thermistor Materials

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Surfaces which can accurately distinguish spatial and temporal changes in temperature are critical for not only flow sensors, microbolometers, process control, but also future applications like electronic skins and soft robotics. Realizing such surfaces requires the deposition of thousands of thermal sensors over large areas, a task ideally suited for printing technologies. Negative temperature coefficient (NTC) ceramics represent the industry standard in temperature sensing due to their high thermal coefficient and excellent stability. A drawback is their complex and high temperature fabrication process and high stiffness, prohibiting their monolithic integration in large area or flexible applications. As a remedy, a printable NTC composite that combines a rapid and scalable all-printed fabrication process with performances that are on par with conventional NTC ceramics is demonstrated. The composite consists of micrometer-sized manganese spinel oxide particles dispersed in a benzocyclobutene matrix. The sensor has a B coefficient of 3500 K, with a 4.0% change in resistance at 25 °C, comparable to bulk ceramics. The selected polymer binder yields a composite exhibiting less than a 1 °C change in resistance to changes in humidity. The sensor’s scalability is validated by demonstration of a A4-sized temperature sensing sheet consisting of over 400 sensors.

Equipping the complex shapes found on objects, robots, or humans with a large number of sensors is necessary for realizing electronic skins.[1–5] For example, just to emulate the density of thermoreceptors on a human fingertip, an electronic skin would require ≈250 sensors per cm².[6] To work toward this goal, a scalable process for realizing a large number of sensors over large areas with mechanical flexibility is necessary. Printed flexible and stretchable electronics envisage a drastic change in production methods, but more importantly how electronics are perceived and implemented.[7] In applications where thin, flexible, and stretchable properties are required, printed sensors detecting a multitude of parameters represents an elegant solution.[8–12]

Accurate measurement of temperature is of critical importance. Measuring temporal changes in temperature or spatial temperature gradients is extensively used in industrial settings as well as for medical applications. Recently there is an increased interest in equipping complex surfaces and shapes with a large number of temperature sensors.[7,13,14] This requires a cost-efficient route to manufacture thermistor materials over large areas on flexible substrates.

Thermocouples are the classical instrument for measuring temperature, where changes in resistance of a metal is used to determine the temperature. The drawback of this method is the limited change in resistance (+0.1% °C⁻¹) and the need to compensate for the cold junction temperature, making accurate measurements challenging, costly, and sensitive to artifacts.[15] Resistance temperature detectors (RTDs) represent another
method, typically constructed of noble metals such as platinum, which have a stable resistance change over a wide temperature range but with relatively low sensitivity (~0.1% °C⁻¹).[16]

Positive temperature coefficient (PTC) composites consisting of a conductive filler (e.g., carbon, nickel) and a polymer binder (such as polyethylene) are an alternative technology. During heating, the PTC composite undergoes a phase transition centered around the melting point of the polymer binder, yielding an order of magnitude change in resistance. The main drawback of this technology is the poor stability and retention of the initial resistance under cycling.[12,17,18] Films sputtered or applied by chemical vapor deposition such as V₂O₅ or amorphous silicon may be used but exhibit a small response and are limited in their scalability due to the complex equipment required. Their application is limited to only high-end sensors such as uncooled microbolometers.

Traditional negative temperature coefficient (NTC) ceramics are the most widespread technology in industrial applications. This is because the sensors show a large resistivity change of ~4% °C⁻¹ over a large temperature range in combination with excellent stability.[19] The electrical properties of the sensors are characterized by their resistance at 25 °C, R₂₅, and the thermal constant, B. The B value is related to the activation energy for conduction, Eₐ, by:

\[ B = \frac{E_a}{k_b T} \]  

where \( k_b \) is the Boltzmann constant and \( T \) is the temperature in K. Realization of an electronic skin using this technology is only possible using a pick-and-place technique, incurring limits in cost, process speed, and substrate size. Until now, a reliable solution that maintains the advantages of ceramic NTC components is lacking. A large number of alternative methods for measuring temperature on foils have been suggested; however, stability has so far limited their widespread application.[20-23]

We demonstrate the development of a stable fully printed temperature sensor whereby the reliable performance of an NTC ceramic is combined with the flexibility and processability of a polymer binder.[18] Screen printing is a scalable printing technology that is fast and already well-established. Our printable temperature sensor ink can be processed on flexible plastic foils while fully retaining the performance of the bulk ceramic material, enabling applications which demand a high density of sensors on a flexible substrate.

The investigated system consists of two components: an electrically semiconductive metal oxide that is highly sensitive to temperature, milled to a micron particle size, and an insulating polymer binder. The electron transport in this system relies upon two transport processes, namely the bulk charge transport of the metal oxide and the hopping of charges between the ceramic particle domains. The bulk charge transport ensures that the high thermal coefficient, \( B \), of the ceramic is retained. Since we wanted to emulate as close as possible the bulk properties of the ceramic, a relatively large particle size (~µm) was chosen to limit the hopping of charges between particle domains.

A number of well-known NTC oxides such as CuFe₂O₄, MnO, and V₂O₅ were considered.[19,24] The dependence of their bulk electrical properties on processing conditions, dopant composition, and environmental stability has been the subject of extensive studies.[19,24] A doped Manganese spinel oxide is used in this study, having the composition Mn₁.₇₁Ni₀.₄₅Co₀.₁₅Cu₀.₄₅Zn₀.₂₄O₄. This composition was reported to exhibit superior stability and resistivity when compared to other NTC ceramics.[25-27] The spinel composition was synthesized according to published procedures and its composition was verified using X-ray fluorescence (XRF) (Supporting Information).[25,26] The crystal structure of the as-prepared powder was analyzed using X-ray powder diffraction (XRD) which shows a cubic spinel as the main phase with traces of a tetragonal spinel, NiO, ZnO, and Mn₂O₃ (Supporting Information). Following the sintering process, ceramic pellets were ball milled and sieved to ensure that a particle distribution between 100 nm and 10 µm is obtained. As a final step, a self-assembled monolayer was formed onto the surface of the microparticles by submerging them in a solution of octadecylphosphonic acid. The formation of the monolayer was confirmed by X-ray photoelectron spectroscopy (XPS) (Supporting Information).[28]

Whereas the electrical properties are defined by the ceramic particles, the environmental and mechanical stability is defined by the polymer binder. The most critical factor dictating the applicability of a printed temperature sensor is its stability to changes in temperature and humidity. Most printed sensors fail in this aspect, mainly due to changes in resistance arising from swelling of the films from humidity or irreversible chemical or morphological changes during heating and cooling cycles.[29,30] Selection of a suitable binder is therefore crucial for obtaining stable electrical characteristics of a composite material in various environmental conditions. Benzocyclobutene (BCB)-based resins are a good candidate, since they are revered for their low moisture uptake and excellent dielectric, chemical, and thermal stability.[31,32] Other polymer binders that were evaluated enabled functional devices but suffered from poor stability upon changing humidity, poor adhesion to substrates and electrodes, or extremely low conductivities (Supporting Information).

To form a screen-printable ink, the processed Mn spinel oxide powder was blended with a commercially available cyclotene resin, which upon curing forms a polycrystalline composite film of BCB. We note that composites using CuFe₂O₄ as the ceramic were also functional, demonstrating the universality of the approach (Supporting Information). The electrical characteristics of the composite were obtained using a planar interdigitated electrode arrangement. Ag electrodes were screen printed onto a 75 µm thick polyimide substrate, with a channel width and length of 30 mm and 250 µm, respectively (\( W/L = 120 \)) (Figure 1). Subsequently, the ink was screen printed atop the electrodes and then cured. The total sensor area was 1.13 cm² (based on a 6 mm in diameter circle). To protect the sensor from direct condensation and other environmental contaminations, a polyethylene naphthalate (PEN) foil was laminated atop the sensor using a thermoplastic polyurethane film as an adhesive.

The surface of the composite films was analyzed using scanning electron microscopy (SEM). The images for 2500 x magnification at 1 and 10 kV accelerating voltages are shown in Figure 1c and 1d, respectively. At 1 kV, the surface features of the film are shown with mainly the polymer phase visible. The composite film has a smooth structure with a few
voids. The ceramic particles are well dispersed and are completely enveloped by the polymer binder, indicating good adhesion of the BCB precursor to the particles. When visualized at 10 kV (Figure 1d), the polymer phase becomes transparent and the heavy ion–based ceramic elements of the film are probed, showing mainly the distribution of ceramic particles. It is evident that no large or isolated aggregates are formed. Images at lower and higher magnifications are available in the Supporting Information.

To probe the thermal activation of the charge transport characteristics, the temperature-dependent current–voltage ($I$–$V$) behavior was measured in a cryostat (Figure 2a) in a vacuum of $\approx 10^{-5}$ Pa. The sensors were swept from $-10$ to $+10$ V in temperatures ranging from 340 to 180 K. No hysteresis was observed during the $I$–$V$ sweeps and upon heating and cooling. The characteristics were fit to Ohm’s law to extract the steady-state resistance of the sensor. In this temperature range, the sensor resistance drops about 4 orders of magnitude as a result of a 160 K temperature change. It is also observed that as the temperature decreases, a nonlinearity of the $I$–$V$ characteristics can be observed, reminiscent of a carrier density–dependent or electric field–dependent charge transport mechanism. The extracted resistances as a function of temperature follow an Arrhenius law, with an activation energy of 302 meV with a $B$ coefficient of 3512 K (Figure 2b). Despite being a composite material, the $B$ coefficient obtained is on par with commercially available surface-mount temperature sensors composed of bulk ceramics, which have values typically in the range of 2500–4500 K.

The dependence of the electrode dimensions on the resistance of the sensor was also evaluated (Supporting Information).
The sensor width was fixed at 10 000 µm while the length was varied from 200 to 5 µm. The scaling follows the reciprocal of the electrode’s width over length, indicative of a scalable device with a low contact resistance even for short channel lengths. Additionally, after normalizing the current and voltage characteristics according to the electrode geometries, the electrical characteristics collapse to a single curve, validating the scalability of the sensor (Supporting Information).

To ascertain the performance of our printed temperature sensor under varying environmental conditions, we placed the sensor in a climate chamber. Initially, the thermal cycling of the sensor was investigated. The sensor was subjected to a temperature profile that held the temperature at 40 °C for 1 h, ramped up to 140 °C in 1 h, and then returned to 40 °C in 1 h. The relative humidity of the chamber was not controlled in this test. The printed sensor was evaluated in comparison to a commercial NTC thermistor (Figure 3a). The resistance of the printed

![Figure 3. Characterization of temperature sensors in a climate chamber. a) Cyclical heating and cooling of a commercial NTC thermistor (solid black line), our printed temperature sensor (solid red line). The climate chamber’s temperature and relative humidity are represented by the dotted green and blue lines, respectively. b) The stability of a commercial NTC thermistor (solid black line) and the printed temperature sensor (solid red line) at a fixed temperature of ~30 °C (dotted green line) and at various humidity conditions (dotted blue line).](image-url)
temperature sensor changes from 31.5 kΩ (40 °C) to 2.6 kΩ (140 °C) over a series of 23 cycles spanning 90 h. Remarkably, the output of both the commercially available sensor and the printed temperature sensor were similar and repeatable during heating and cooling cycles.

The sensor’s stability to changing humidity conditions was then determined. For this test, the climate chamber’s temperature was held at 30 °C, while the relative humidity was varied stepwise from 25% to 85% (in steps of 15%) and held at each step for 1 day. This corresponds to a change in absolute humidity from 7.6 to 25.8 g m⁻³. Again, the drift of the printed sensor was evaluated against a commercial NTC thermistor (Figure 3b) as well as an integrated silicon sensor (Sensirion SHT75). The commercial NTC thermistor closely follows the climate chamber temperature, while the printed temperature sensor’s reading was influenced by at most ≈1 °C under these conditions. However, upon returning to lower humidity levels, the printed sensor’s resistance recovered to previous levels. In our experience, and as discussed previously, the choice of binder material is crucial for obtaining stable sensor characteristics, with other systems showing a drastic dependence on humidity (Supporting Information).

To fully take advantage of the printability of the temperature sensor and demonstrate the benefits of the technology, a flexible temperature sensor sheet is fabricated on A4-sized 50 µm thick polyimide substrates. The sensor sheet contains 414 sensors (23 × 18) and has a total thickness of just 285 µm. In the passive matrix sensor sheet, the measured sensor is biased to 1 V while the nonselected sensors are grounded.[35] The measured current is used to extrapolate the resistance of the sensor. The leakage currents through the dielectric bridges are negligible and the wiring resistance is negligible with respect to the resistance of the sensor, e.g., in a A4-sized sensor sheet, the maximum parasitic resistance in series with the sensor amounts to ≈40 Ω, resulting in an ≈0.2% error in the measured current.

At 19.5 °C, the average sensor resistance was 12 kΩ with a standard deviation of just 3 kΩ. The total sensor area was 1.31 cm² (6 mm diameter circle) with an electrode W/L of 145. In Figure 4, a human hand is placed on the sensor sheet and the outline and temperature change caused by the hand can be clearly resolved, showcasing the precision possible with these sensors.

The flexibility of the sensors was verified by bending the sensors on aluminum rods of known radii of 0.8 and 1.0 cm while measuring their temperature response. Indeed, as a matter of strain, the starting resistance of the sensors are also changed, being 51 kΩ (0.0% strain), 124.2 kΩ (0.97% strain), and 239.6 kΩ (1.21% strain), but the temperature scaling remains unaffected (Supporting Information).

In summary, an environmentally stable screen-printable composite temperature sensor has been demonstrated. It was found that careful selection of polymer binders is crucial for obtaining stable sensor characteristics in changing environmental conditions. The sensor has a low overall resistance, good environmental stability, low thickness, and excellent uniformity over large area, as enabled by screen printing.

The development of printable sensors allows for the rapid fabrication of thousands of sensors per square meter, enabling the realization of accurate and reliable electronic skins for a range of applications. The total thickness and flexibility of the sensing surface permits the placement of a large number of sensors in areas and on shapes previously impossible. We anticipate that in the future, the use of other binder materials could be used to realize stretchable and more conformable temperature sensors, especially exciting for growing fields that stand to revolutionize the field of flexible electronics such as soft robotics and electronic skins.

**Experimental Section**

**Temperature Sensor Ink Preparation:** The preparation of the NTC ceramic was performed as previously reported. More specifically, Mn₂O₃, NiO, Co₃O₄, CuO, and ZnO in powder form were mixed on a roller bench for 24 h. In order to ensure homogenization, a dispermat bead mill with Zr marbles was done for 6 h. After that, the material was placed in an oven at 80 °C overnight to dry. A mortar and pestle was then used to break up agglomerates and the resulting powder was sieved through a 325 mesh sieve. The powders were then calcined in a high temperature air oven at 950 °C for 2 h and mixed again on the roller bench overnight. Then the powder was mechanically pressed into pellets (∼40 mm wide) and sintered at 1100 °C for 24 h and furnace cooled. The powder was

![Figure 4](image-url)--- Figure 4. a) Calibrated readout of the temperature of a hand placed on a passively addressed A4-sized sensor sheet (23 × 18, 414 sensors). b) Photo of the hand placed on the mat.
obtained by grinding for 5 min using a Fritsch Pulverisette 6 ball mill and sieved with different size meshes, with the smallest being 45 μm. The particles were then passivated by submersion of particles overnight in a 1 M solution of dodecylphosphonic acid, hexylphosphonic acid, or octadecylphosphonic acid (Sigma Aldrich) in isopropanol. The particles were then vacuum filtered over filter paper (MN 85/220 Macherey-Nagel e100) and rinsed with isopropanol. The powder was then dried overnight in an oven at 110 °C. For the ink formulation, the ceramic powder was blended with a commercial binder precursor, cyclotene (3022-35, DOW Chemicals), in a weight ratio of 85:15 and then mixed for 2 min at 2000 rpm in a planetary mixer. Other formulations consisted of particles blended in an 85:15 ratio with either PVDF (Solvay), PDMS (Sylgard 184, DOW Chemicals), or CYTOP (AGC Chemicals Europe) and cured at 100 °C for at least 10 min.

Sensor and Sensor Matrix Fabrication: All layers were screen printed using a Dek Horizon 031 screen printer. For temperature-dependent and humidity and temperature sensor, the layers were screen printed onto 75 μm thick polyimide (DuPont Kapton CR). The Ag layer (DuPont 5025) was printed and cured at 120 °C for 10 min in an oven. For passive matrix structures, dielectric bridges were printed using DuPont 8133 and cured at 120 °C for 10 min in an oven. For the temperature sensor layers, BCB was printed and cured initially at 95 °C for 45 min, followed by a step at 150 °C for 1 h and finally a 2 h cure at 200 °C in an oven. The layer thickness of the sensors was typically ≈45 μm.

Material and Film Characterization: The particle size was defined by laser diffractionometry, using a Malvern Mastersizer 2000. The dispersant solution was water and the obscuration ≈14%. Samples for XRF measurements were prepared by grinding the sample for 5 min in a Fritsch Pulverisette 6 ball mill. A powder pellet was prepared by mixing 6 g of the grinded sample with 3 g of cellulose binding agent. The mixture was pressed into a pellet at a pressure of 300 kN. Measurements were performed using an AxiosmAX-Advanced spectrometer. Quantification was done using the software package “Omnian”. X-ray diffraction was performed on a thin layer of powder which was dusted on a diffusion-free substrate using a Panalytical X’Pert MPD pro diffractometer with Cu-Kα radiation. SEM images were gathered using an FEI Quanta665 in low-vacuum mode at a chamber pressure of 30–70 Pa (pH 2O) to avoid charging of the sample, as the sample was uncoated. The energy dispersive X-ray equipment (EDX) was an Oxford Instruments X-Max20 EDX detector. Film thicknesses were measured using a Bruker DektakXT. XPS measurements were carried out using a Quantera SXMTm from Ulvac-PHI (Q2). The measurements were performed using monochromatic AlKα radiation with a spot size of 1200 × 500 μm (high sensitivity mode). The measurement angle was 45°, leading to a penetration depth of ≈7 nm. Survey scans were used to identify elements present at the surface of the sample, while narrow scans were used to determine the surface concentrations.

Electrical Characterization: The temperature-dependent I–V characteristics of the printed temperature sensors were measured using a Keithley 4200 semiconductor analyzer with the sample placed in a variable temperature probe station and measured at a pressure of <1 × 10−4 Pa. Climate chamber measurements were performed in an Espec SH-641 and the resistance of the sensors was measured at 0.1 V using a Keithley 2612A source measurement unit. In all cases, the printed temperature sensors were measured against a commercial NTC component (Murata NCP15WF104F03RC, wired type, 1 × 0.5 × 0.5 mm, B coefficient = 4250 K) or a Sensirion SHT75 digital humidity and temperature sensor. Matrices were read by a home-built readout circuit. The selection voltage was set at ∼1 V while other lines were grounded.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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