Transparent Conductive Ink for Additive Manufacturing

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October 2017
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<tr>
<td>EEE</td>
<td>electrical, electronic, and electromechanical</td>
</tr>
<tr>
<td>IZTO</td>
<td>indium-zinc-tin-oxide</td>
</tr>
<tr>
<td>KSC</td>
<td>Kennedy Space Center</td>
</tr>
<tr>
<td>MSFC</td>
<td>Marshall Space and Flight Center</td>
</tr>
<tr>
<td>TDEL</td>
<td>thick film dielectric electroluminescent</td>
</tr>
<tr>
<td>ICP</td>
<td>inherently conductive polymers</td>
</tr>
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</table>
1. INTRODUCTION

NASA analyzes, tests, packages, and fabricates electrical, electronic, and electromechanical (EEE) parts. Nanotechnology is listed in NASA’s Technology Roadmap as a key area to invest for further development. This research project focused on using nanotechnology to improve electroluminescent lighting in terms of additive manufacturing and to increase energy efficiency. Specifically, this project’s goal was to produce a conductive but transparent printable ink that can be sprayed on any surface for use as one of the electrodes in electroluminescent device design. This innovative work is known as thick film dielectric electroluminescent (TDEL) technology. TDEL devices are used for “backlighting, illumination, and identification due to their tunable color output, scalability, and efficiency” (I.K. Small, T.D. Rolin, and A.D. Shields, “3D Printed Electroluminescent Light Panels,” NASA Fiscal Year 2017 Center Innovation Fund Proposal, unpublished data, 2017). These devices use a ‘front-to-back’ printing method, where the substrate is the transparent layer, and the dielectric and phosphor are layered on top.

This project is a first step in the process of creating a 3D printable ‘back-to-front’ electroluminescent device. Back-to-front 3D-printed devices are beneficial because they can be printed onto different substrates and embedded in different surfaces, and the substrate is not required to be transparent, all because the light is emitted from the top surface through the transparent conductor. Advances in this area will help further development of printing TDEL devices on an array of different surfaces. Figure 1 demonstrates the layering of the two electrodes that are aligned in a parallel plate capacitor structure (I.K. Small, T.D. Rolin, and A.D. Shields, “3D Printed Electroluminescent Light Panels,” NASA Fiscal Year 2017 Center Innovation Fund Proposal, unpublished data, 2017). Voltage is applied across the device, and the subsequent electron excitation results in light emission at the top layer.

Figure 1. Example of TDEL construction.
There have been other developments in the creation of conductive inks with various advantages and disadvantages. For example, NASA’s Kennedy Space Center (KSC) is seeking commercial applications of conductive carbon nanotube inks for inkjet printing technology. This ink combines carbon nanotubes with metallic nanoparticles to use in standard inkjet printing. As stated in the paper, “the conductive materials are composed of electrical conductors such as carbon nanotubes (including functionalized carbon nanotubes and metal-coated carbon nanotubes), graphene, polycyclic aromatic hydrocarbons (such as pentacene and bisperipentacence), metal nanoparticles, inherently conductive polymers (ICPs), and combinations thereof.” The ink has been characterized to have resistance in the kiloohm range and can be printed on surfaces such as paper and textiles. However, the ink is not transparent, and a more complex preparation regimen is required. Figure 2 shows samples of the carbon nanotube ink.
Another conductive ink is one that uses nanometer-size indium-zinc-tin-oxide (IZTO) particles. The IZTO nanoparticles must have an average size of 20–30 nm. A production process similar to that reported here is followed. However, IZTO nanoparticles are challenging to find and purchase, given the novelty of the material. There are few distributors in the market, making it more expensive to obtain. Figure 3 shows an example of IZTO ink.

![IZTO ink](image)

**Figure 3.** IZTO ink.

In contrast to those mentioned previously, the Marshall Space Flight Center (MSFC) produced ink is cost effective, transparent, and a particle free process. MSFC originally worked from reference 4. Experiments were conducted to exactly replicate the process described in the paper. However, this process resulted in less-than-desirable and, in some cases, explosive solutions. Attempts were made to contact the authors to better understand the process, but a response was not received. MSFC decided to conduct experimental trials where certain variables and quantities stated in the paper were altered. Examples of changes included increasing final molar concentrations and evaluating colors seen during the process. A process was developed whereby successful results were obtained. Resistance measurements of films were confirmed in the kiloohm range, the magnitude of which is as good as that reported at KSC for carbon nanotube ink.
2. PROCEDURE

2.1 Substrate Preparation

One-inch glass slides were used as substrates and were prepared according to the process in reference 4. They were prepared using this method to ensure that they were clean. The technique involved sonication for 10 min in acetone, followed by 10 min of sonication in isopropyl alcohol. They were then dried with a nitrogen gas gun and stored in a dust-free flowing nitrogen cabinet for future use.

2.2 Chemical Reaction to Create Ink

The inks were prepared first by weighing 1.76 g of indium(III) acetate (99.99%, Aldrich) and 0.24 g of tin (IV) acetate (Aldrich). These acetates were then mixed with 67 mL of acetylacetone (≥99%, Sigma-Aldrich) in a 100-mL glass beaker. The color of the resulting solution had the appearance shown in figure 4(a) when dissolved at room temperature. The acetates were dissolved using a glass stirring rod. Figure 4 demonstrates how color can change in time as the concentration increases. Reference 4 states the final solution should be a reddish-brown color, which could be interpreted as sample color figure 4(c) or figure 4(d).

![Figure 4. Color change of experimental solutions due to concentration increase in time.](image)

A magnetic stirring bar was placed in the beaker, which was positioned on a hot plate with a magnetic stirring accessory. To stir the solution, the magnetic stirrer was set to 300 rpm. The hot plate was set to 165 °C. The paper states that the solution must be maintained at 120 °C. Several experimental runs indicated that the MSFC hot plate had to be set at 165 °C to ensure that the solution was maintained at 120 °C. One observation made during the course of experimentation was that the hot plate temperature decreased as the solution started to evaporate through heat and
fume hood ventilation. To control this, the temperature was constantly monitored using a thermometer clamped to a metal stand and the hot plate adjusted accordingly (fig. 5). A glass titration burette was also affixed to the metal stand above the beaker. The purpose of the burette was to add hydrogen peroxide (30 weight percentage in water, Sigma-Aldrich) to the solution, drop-wise. Reference 4 states, “...added drop-wise in 6 aliquots at 30-min intervals into the solution to prevent phase separation due to a re-crystallization.” Therefore, 1 mL of hydrogen peroxide was added drop-wise to the stirring solution in intervals of 30 min 6 times for a total of 6 mL.

Figure 5. Lab setup.
At this point in the process, color was monitored, and concentration was altered compared to the paper. In one trial, concentration was maintained by adding appropriate amounts of acetylacetone as needed. The maintained concentration, 0.1 M, was reported in reference 4. In other trials, fluid changes from evaporation were permitted resulting in higher concentrations of the acetates. Samples were taken at different time intervals to determine resistance for a given color.

### 2.3 Post-Processing of Ink

Rheology optimization was not part of this experiment, so the ink was not adjusted for inkjet or aerosol jet printing. Instead, a simpler process for depositing the ink was used. Ink was applied onto a glass substrate as one-layer and two-layer specimens. The glass substrate was maintained at 80 °C, as recommended in the paper, by setting the hotplate to 85 °C. Ink was removed from the solution using a 1-mL glass pipet in order to track volume for subsequent concentration calculations. The ink was deposited using a glass dropper, glass pipet, or spray bottle. These applications were used to determine the best material deposition method. After each application of ink, the film was dried in a box oven at 150 °C for 10 min in air to evaporate solvents. The dried films were then annealed in a tube furnace at 500 °C for 2 hr in flowing oxygen to burn off any remaining organic components. Table 1 shows the set points and dwell times of the tube furnace. The ramp rate was ≈8 °C/ min.

<table>
<thead>
<tr>
<th>Set Point Temperature (°C)</th>
<th>Time Held at Temperature (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td>500</td>
<td>25</td>
</tr>
<tr>
<td>300</td>
<td>30</td>
</tr>
<tr>
<td>50</td>
<td>0</td>
</tr>
</tbody>
</table>

For creating two-layer specimens, another layer of ink was added onto the dried film and placed back into a box oven for 10 min. The film was annealed in the tube furnace at 500 °C for 2 hr in a flowing oxygen gas. These two-layer samples were then annealed for 2 hr at 500 °C in a flowing nitrogen gas because data from reference 4 indicated improved results with nitrogen gas annealing. A multimeter was used to measure the deposited film resistance in ohms. The film was probed in different areas of each sample, and the lowest resistance measurement was recorded.
2.4 Preparation of 2- by 2-Inch Slide

Initially, a 2- by 2-in developmental slide was prepared so that four experiments could be compared side by side. It aided in understanding deposition pitfalls and minimized error introduced by different glass substrates, which may be different textures and still have contaminants irreducible by the Fang cleaning process. Additionally, variables such as concentration, thickness, and annealing were tested. To understand concentration effects, the 2- by 2-in glass slide was prepared similar to sections 2.1–2.3. Four distinct samples with different ending time intervals, but after the sixth aliquot, were deposited. The glass slide was marked with a high resistive heat marker to distinguish the different samples. A 1-mL glass pipet was used to add the ink onto the substrate at the different time intervals. Removing the ink at different time intervals resulted in films with different concentrations due to evaporation.

Secondly, testing was conducted to understand effects of the film’s additional layers. The first trial was to deposit a single layer of ink onto the substrate. Then a second layer was added depending on results observed in the first trial. Samples were taken out of the final solution at the same time interval as the first experiment and layered on top of the first film. Finally, the best annealing process was determined. The one-layered film was annealed at 500 °C for 2 hr in flowing oxygen and measured. The two-layered film was placed in a box oven at 150 °C for 10 min in air, then 500 °C for 2 hr with flowing nitrogen gas in a tube furnace.
3. DATA AND ANALYSIS

Valuable data were gathered from the 2- by 2-in developmental slide. Multiple experiments were performed and yielded different results, which provided feedback for optimization. This experiment allowed direct comparison of resistances at different concentrations, thicknesses and annealing.

Figure 6 shows the developmental slide with a one-layer film annealed in oxygen gas for 2 hr. Figure 7 shows sample colors taken in time and images of resulting ink depositions. Box 1 shows a one-layer film after oxygen annealing and box 2 a two-layer film after oxygen and nitrogen annealing.

Figure 6. 2- by 2-in developmental slide image.

Figure 7. Developmental slide results.
There were several observations made during the course of this effort. First, the best product color had to be determined and was observed to be dependent on concentration. An experiment was performed where acetylacetone was added to replace evaporation and maintain a constant 0.1 M concentration. This resulted in an unusable ink that did not change color. However, when evaporation was allowed, volume reduction created a more concentrated solution that eventually turned a darker color in the range that was discussed in reference 4. When assessing if the paper’s description of “reddish-brown” resistance characteristics were in figure 4(c) or figure 4(d), an initial separate experiment confirmed it was not figure 4(c). Although this solution is more of a reddish-brown color, it exhibited high resistance.

Additionally, the ink in figure 4(c) was not stable, which caused it to crumbled off after the 500 °C oxygen annealing process. Therefore, no further testing was performed on solutions removed at this interval. Table 2 shows the best result was obtained with sample D2, which was a brownish-red solution with a concentration of approximately 0.2 M. This concentration was calculated by neglecting the volume error due to evaporation up until the 70-min mark after the sixth aliquot. This volume reduction would tend to increase the concentration.

Table 2. 2- by 2-in slide results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1</th>
<th>A2</th>
<th>B1</th>
<th>B2</th>
<th>C1</th>
<th>C2</th>
<th>D1</th>
<th>D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer</td>
<td></td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Resistance (MΩ)</td>
<td>∞</td>
<td>1.98</td>
<td>∞</td>
<td>∞</td>
<td>∞</td>
<td>∞</td>
<td>8.87</td>
<td>0.01619</td>
</tr>
</tbody>
</table>

Secondly, the paper states that two layers had better conductivity, likely due to linking between conducting islands. This was proven by the A solution and the D solution. It was observed that after adding a second layer to the samples and annealing it in nitrogen gas, a finite resistance was measured. The best resistance was in areas where the film had two, thinly applied layers that were transparent. This was typically near the slide edges where the ink rolled off after application of drops or spray. The transparent film is shown at low magnification in figure 8 and high magnification in figure 9.

Figure 8. Film in low magnification.
Finally, annealing the samples in oxygen gas for 2 hr at 500 °C resulted in multimeter readings that were either infinite (∞) or in the tens of megaohms. However, after the nitrogen gas annealing, A2 was observed to have a new spot that had a slightly lower resistance. This indicated that a nitrogen anneal was beneficial. After application of this anneal for sample D, the resistance was observed to go from megaohms down to kiloohms. Optically comparing square 1 and 2 in figure 7, it was found that the lowest resistance film in square 2 is more transparent.

### 3.1 Subsequent Experiment

Data from the D2 sample clearly exhibited the best results. To ensure the process was repeatable, a subsequent experiment was performed following the D2 process. Observations directly from lab notes of the D2 repeatability run are shown in table 3. Two 1-in glass substrates were prepared at the 70-min mark when the ink was brownish-red. Two samples were taken out of the solution and deposited on the glass substrates. They were then placed in the box oven at 150 °C for 10 min in air and subsequently layered with ink a second time. After the second layer was applied, the glass slides were placed in the box oven at 150°C for 10 min in air. Both slides were then annealed in oxygen followed by nitrogen.
Table 3. Subsequent experiment lab observations.

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Starting Temperature</th>
<th>Ending Temperature</th>
<th>Observation and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120 °C</td>
<td>117 °C</td>
<td>As the solution gets hotter, it becomes clearer because the solids are dissolving. No reaction when added H$_2$O$_2$. The color is a clear yellow. Hot plate is set at 165 °C.</td>
</tr>
<tr>
<td>2</td>
<td>120 °C</td>
<td>117 °C</td>
<td>Solution is still clear. After adding H$_2$O$_2$, the solution bubbled and fizzed toward the end of the 1mL addition. Hot plate is set to 160 °C.</td>
</tr>
<tr>
<td>3</td>
<td>123 °C</td>
<td>119 °C</td>
<td>Bubbling and fizzing when adding the H$_2$O$_2$. The solution is starting to look like a more concentrated yellow such as lemonade. Hot plate is set at 150 °C.</td>
</tr>
<tr>
<td>4</td>
<td>120 °C</td>
<td>116 °C</td>
<td>Reaction observed when H$_2$O$_2$ is added into the mixture. The color is now a concentrated yellow, but still a lighter version. Hot plate is set at 145 °C. Precipitate is on the walls of the beaker.</td>
</tr>
<tr>
<td>5</td>
<td>120 °C</td>
<td>115 °C</td>
<td>Now an even more concentrated yellow. When adding H$_2$O$_2$ precipitate was observed on the walls and steam came off. Hot plate was set at 140 °C.</td>
</tr>
<tr>
<td>6</td>
<td>118 °C</td>
<td>114 °C</td>
<td>A deeper concentrated yellow with a hint of brown. Reaction observed when H$_2$O$_2$ was added. Hot plate is set at 140 °C.</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Wait 70 min after the sixth aliquot to obtain the brownish-red ink color to take a sample.</td>
</tr>
</tbody>
</table>

The subsequent experiment of D2 produced a 4.88-kΩ transparent film. The actual multimeter reading is shown in figure 10. This second run not only confirmed repeatability but also resulted in the best material produced. When testing the slide, the lowest resistance was found to be in the transparent area. This area was located near the edge of the substrate where the liquid rolled off the side.

![Figure 10. Multimeter measurement.](image-url)
4. CONCLUSIONS

Transparent films were produced with resistances in the low-kiloohm range by deviating concentration from the value indicated in reference 4. The paper stated that a 0.1-M concentration solution should be the final concentration, but experimental data demonstrated that the best concentration was a minimum of 0.2 M. This solution was the darkest observed, exhibited a brownish-red color, and demonstrated the lowest resistance.

Secondly, reference 4 states that two thin layers have better conductivity. Results from this experiment confirmed this statement. This result is most likely due to the deposited material meeting the percolation threshold for conducting islands. The lowest resistance area was found where the ink was layered thinly and near the edge of the slide. This shows that the film must be applied in very thin, but multiple layers in order to have good results.

Finally, the annealing process stated in reference 4 was verified. It suggested to anneal the samples in nitrogen gas after oxygen gas to improve properties. Observations from the A2 and D2 samples indicated this was a necessary step in processing the films. Initial observations showed that oxygen annealing by itself was insufficient to produce the best results.

Future MSFC experiments should follow the D2 method and use a better application method such as aerosol jet printing to achieve thin two-layer films. Aerosol jet printing can produce evenly distributed layers as thin as 600 nm. However, additional studies will have to be conducted to adjust the viscosity of the D2 solution to meet the demands of diverse printing paradigms.
REFERENCES


This project focused on using nanotechnology to improve electroluminescent lighting. Specifically, the goal was to produce a conductive-but-transparent printable ink that can be sprayed on any surface for use as an electrode in electroluminescent device design. Using Mei Fang’s paper entitled, “Particle-free inkjet printing of nanostructured porous indium tin oxide thin films,” attempts at following the paper exactly did not produce desired results. However, by altering certain variables stated in the paper, such as molar concentrations and colors seen during the process, successful results were obtained. Resistance measurements of films confirmed conductivity in the kiloohm range.
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