Development and Testing of Cathode-type Flexographic Inks

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Printed electronics have been used for some time in RFID (Radio Frequency Identification) circuits and many other aspects of the printing and packaging world. Recent commercial attempts to develop “battery inks” have high manufacturing costs and only produce small nominal voltages. A small paper battery printed by screen-printing has been created but still has a high production cost and a long time to print and assemble. Our recent results, however, can direct us to a functional printable battery capable of, but not limited to, a nominal 1.5 volts, equal to that of a standard AA/AAA battery. The flexographic-printed battery, developed at Rochester Institute of Technology, involves three different ink formulations: the cathode ink, whose main component is manganese dioxide; the electrolyte ink of potassium hydroxide; and the anode ink of zinc. These three formulations represent the same ingredients contained in a standard alkaline battery. This printed battery uses less material in production, is more cost efficient, and is quicker to produce. Unlike a standard battery, it is both compact and malleable.
Introduction

Applications of printed electronics have impacted our everyday lives. They are in the checks you write, magnetic strips in credit cards, and RFID to increase security of merchandise in retail stores. Recent innovations have been in the field of printable batteries. Currently, the technology produces a battery with an output of 1.5 volts, the capacity of a regular AAA or AA battery, and is easily printed using silk-screen-printing (Fraunhofer-Gesellschaft, 2009). Once, printed electronics were mostly seen with the formation of inks containing metallic pigments capable of holding information, and now the printed electronics industry and the science of printing functional products have advanced considerably.

Recent commercial attempts to develop “battery inks” have yielded high manufacturing costs and only produced small nominal voltages. The high costs stem from the usage of screen-printing, which places a cap on the scalability of manufacturing, yielding higher costs to produce and longer times to print and assemble.

The State of Printed Electronics

“Printed electronics” is a broad term that encompasses a large range of applications and processes. Currently, 31.6% of printed electronics produced are focused on conductive inks, sensors, and Organic Light Emitting-Diodes and is predicted to rise to 90.3% by 2017 (Smith, 2007). An advantage of printing electronics and batteries using flexography is that they can be printed inline in order to produce integrated smart packages or novelty electronic products at high manufacturing speeds.

Today, many printing technologies are capable of producing electrical components with functional polymers and materials on flexible media, patterning them in a variety of ways. With the use of specially formulated conductive inks in the screen-printing, flexography, inkjet, and lithography processes, a variety of products are now reproducible. These inks can be formulated for use in such products as sensors, RFID tags, LED lights, solar cells, and fabricated circuits. (Karwa, 2006, p. 18-19) It is only a matter of time before these technologies and applications advance to a level where they can be mass-produced in more complex forms, such as car batteries and portable electronics. Printed electronics offer a potential for high-volume manufacture, driving down production cost and making everything more compact and portable.
As the technology continues to develop, a key issue to keep in mind is that printing defects in these applications would not only degrade the visual quality of the products, but it would also translate into defective units that may not operate as intended, or pose safety concerns for the end user. For non-charged products, these potential defects may not become evident until the unit is first used. However, for printed batteries, a defect can translate into danger during manufacturing, storing, shipping or use. As such, refinements in areas of printability and material quality and performance are essential for researchers to pursue with diligence and care.

**The Design of Batteries**

A battery is a device made up of one or more cells that convert chemical energy directly into electrical energy. An oxidation-reduction (redox) reaction is the means by which these cells convert the active material into electricity (Linden & Reddy, p. 25). A battery’s cell consists of three components: an anode (negative/reducing electrode), a cathode (positive/oxidizing electrode), and an electrolyte bridge (ionic conductor). These three components make up the core foundation of a battery.

![Diagram of a battery cell](image)

**Figure 1. An example of a Galvanic cell. (“Voltaic pile,” 2009)**

Many advantages have been made over primary batteries since the discovery of the voltaic pile, which is “a set of individual Galvanic cells placed in series” (“Voltaic pile,” 2009). This assembly promoted the idea of placing battery cells in arrays to provide additional voltage, which is commonly practiced today (Figure 1). This concept was
invented by Alessandro Volta in the years between 1796 and 1800. During this time, Volta formed the creation of an electric battery using a redox reaction between two metals (Dibner, 1964, p. 65-66).

There are two major types of batteries in existence today: primary and secondary batteries. Primary batteries are single-use, disposable batteries, most familiar in AA and AAA formats, providing a 1.5 volts discharge. Secondary batteries are rechargeable and are more widely seen in portable electronics such as laptops and cell phones. Secondary batteries are also produced in the common AA and AAA formats. According to Linden & Reddy (2002, p. 173), the major advantages of primary batteries include convenience and simplicity. It is also easy for manufacturers to design their products to suit these standard formats. Secondary batteries have the advantage of being rechargeable, but come with additional construction and format requirements.

Batteries can be made up of different materials for anodes, cathodes, and electrolytes. This helps define the type of battery and properties such as the discharge capacity and voltage. Major formulations include zinc-carbon (Leclanche cell), zinc-chloride, and alkaline. The research described in this report has been conducted to mimic the functionality of the latter, a primary-type alkaline battery.

**Printed Battery Construction & Functionality Considerations**

The scope of this work is focused on conductive inks, but takes into consideration a single construction model, also being researched and further developed at RIT for final application. The model borrows from commonly found concepts and is presented conceptually in Figure 2.

![Figure 2. Conceptual diagram of the layers of a printed battery.](Image)
A battery’s electrical energy comes from the electron flow of the redox reaction within the cell. Figure 2 shows what Linden & Reddy (2002) describes as the electrochemical operation of a cell. In the construction model used for this research, conductive inks are printed as solid films and are separated by a substrate barrier to form each battery cell.

![Figure 2](image-url)

**Figure 2.** The electrochemical operation of a cell.

![Figure 3](image-url)

**Figure 3.** Example of plate design (layered on top of each other) based on the printed battery concept in Figure 2.

When the anode of a battery is connected to the cathode, electrons are able to flow from the anode to the cathode, producing the electrical charge in the process. This connection is normally provided by a host device, which in turn powers the device through the flow of electrons. The circuit is then completed by the flow of anions to the anode and cations to the cathode (p. 29). The process of connecting the conductors causes a reduction (or oxidization) of the cathode material. The battery will continue to discharge, providing electrical energy until all of cathode material is reduced.

**Conductive Inks & Flexography**

Printing of conductive inks for printed electronics using flexography has been successfully tested using conductive water-based flexographic printing ink containing silver, a conductor. A major disadvantage to the use of silver in conductive inks formulations is that silver by itself is expensive (Sperry & Weisenmiller, 2006).

Conductive inks can come in two forms: carbon-based and metal-based. Although carbon-based conductive inks produce a weaker voltage, and therefore a weaker RFID signal, they are more environmentally friendly and generally more cost effective than metallic inks like silver.
Currently, conductive inks have been developed for use in all forms of print methods except toner based digital printing, and are typically formulated specifically for a certain substrate and printing process (Cole, 2007, p. 27). A great advantage of using flexography for printing electronics and batteries is the speed and potential to producing integrated smart packages or novelty products with inline finishing (Sperry & Weisenmiller, 2006).

**Basic Notes on the Formulation of Flexographic Battery Inks**

In order to produce the previously described battery construction, this research focused on testing two key formulations of cathode inks.

The key component of the cathode ink formulations covered here is manganese dioxide (MnO$_2$), which is the cathode of an alkaline battery, and is considered the ink’s pigment. However, the use of this chemical component requires analysis to identify which additives and other ink components will enable it to function as flexographic printable ink.

Extensive research was conducted to address additives that would:

- Mimic the chemistry of a AA/AAA alkaline battery.
- Replicate the necessary conditions for the ink components to react in the same fashion as the battery components.
- Produce the required flow of electrons between printed cathodes and anodes.
- Provide necessary flexographic ink characteristics for use with a flexographic press.

**FORMULATION OF BETA1— THE BASELINE CATHODE INK**

The first goal was to create a stable MnO$_2$ dispersion. Many trials with different dispersion agents such as E-Sperse, Zeta-Sperse, and Solsperse failed; therefore, solvents were not considered as possible dispersants. Organic solvent blends were also researched, but the pigment would flocculate over time so a new approach was examined. This new approach uses the water-soluble compound potassium permanganate (KMnO$_4$).
By taking potassium permanganate (KMnO₄), a water soluble Mn(VI) oxidizing agent, and putting it in contact with paper (a reducing agent), a redox reaction occurred where the oxidation level of Mn(VI) in the permanganate was reduced to Mn(IV). The presence of MnO₂ was tested and verified by using hydrogen peroxide. MnO₂ is known to be a catalyst for creating a highly exothermic conversion of hydrogen peroxide to hydrogen and oxygen.

Unfortunately, MnO₂ alone is not conductive (the cathode of a battery often has a copper rod or graphite to allow the flow of electrons). Carbon black (graphite) was added into the formulation to act as a conductor. Research done by Danilov, Melezhik, and Danilenko (2005) involved the creation of carbon nanotubes (CNT) modified with MnO₂ deposits by a reaction with the CNT and KMnO₄ shown by this formula (p. 1849):

$$4\text{KMnO}_4 + 3\text{C} + \text{H}_2\text{O} \Rightarrow 4\text{MnO}_2(\text{aq}) + 2\text{KHCO}_3 + \text{K}_2\text{CO}_3$$

Adding carbon to the KMnO₄ produced a similar reaction to the one between Mn(VI) and the paper cellulose. The active MnO₂ was now achieved by a redox reaction between Mn(VI) and the carbon surface. However, this reaction happened over the course of a week. To speed up the reaction with the carbon, many different mixtures of carbon + KMnO₄ were tested. The discovery of adding CMC
(carboxymethylcellulose) and KOH (potassium hydroxide, an electrolyte) yielded an instantaneous conversion of KMnO₄ to MnO₂ and added the proper viscosity to the ink. Conclusively, the addition of KOH, and CMC completed the creation of the Beta1 formulation.

**FORMULATION OF BETA2— THE READJUSTED CATHODE INK**

By testing characteristics and performance of Beta1 for flexographic printing, some concerns were identified and readjustments were made to address these concerns, resulting in the readjusted Beta2 formulation.

Beta2 is a modification of Beta1 to remedy noticeable drying problems on press and focuses on the use of an acrylic binder and its effect on the printability of the ink. In the Beta1 testing, after about 30 seconds to 1 minute the ink began to dry on the rollers. Due to this observation, it was concluded that the ink formulation needed modifications, giving rise to Beta2. The major modification to the formulation consisted of the addition of a humectant, a compound that absorbs water from the air, to help aid in the drying. In addition, the binder was changed to an acrylic resin, to potentially provide more stability on press. In Beta2, Joncryl 60, an acrylic resin, replaced the CMC and propylene glycol was added as a humectant.

**Research Objectives**

Through the summarized literature review and preliminary testing outlined above, this research identifies key problems relating to the printability of two cathode inks. Specifically, the combination of the Beta1 formulation with commonly used flexography substrates under normal printing settings has print quality issues, including but not limited to:

- Mottled solid prints and discontinuity of transferred film affecting the safe function of the final product represented by unpredictability of continuous material volume and truthful charge capacity of the product.

- Drying time was significantly long, preventing suitability for inline finishing of complete product due to instability of the film for perceived transport requirements.
The objectives of this study are:

• To further investigate factors that may result in key printing defects, i.e., mottling of printed film and excessive drying time. This is conducted through test prints of both Beta1 ink for solids and tints.

• To investigate the effect of adding acrylic resin, a binder used in the Beta2 formulation, outlining the correlation between the acrylic-to-water content ratios with preferable print characteristics.

• To summarize key concerns regarding the formulations with regards to performance and suitability of use.

**Methodology**

To address the outlined objectives, this study was divided into four distinct tests in three phases: 1) preliminary ink testing, 2) test printing, and, 3) prototype testing. The tests are defined as follows:

• Testing ink characteristics of Beta1 & Beta2 for solid content proportions & rheology to define expected effects of the addition of acrylic content.

• Testing of print characteristics of Beta1 formulation for printing solids and tints with two printing pressure settings (75N & 500N) and on two substrates (coated & uncoated) to identify preferable test settings.

• Testing of print characteristics of the Beta2 formulation for printing solids with three acrylic-to-water ratios, under constant pressure-speed-anilox combinations, with two substrate types (coated & uncoated).

• Testing of functional characteristics for both Beta1 & Beta2 cathode type batteries using temporary anode and electrolyte inks.

• The focus of this report is on the test printing and prototype testing; however, ink characteristics are crucial and will be presented as an integral part of the methodology.
**Formulation and Testing of the Cathode Inks**

For the formulations of Beta1 and Beta2, a few things need to be clarified to properly understand the tests and their results. Foremost, both Beta1 and Beta2 are different formulations, Beta2 being a modification of Beta1 with the use of an acrylic resin as a binder.

Beta1 is intended to show the concept of a printable cathode as well as demonstrate whether it can be functionally formulated to print and, if so, how does it print. Beta2 is intended to ascertain how a change in the acrylic-to-water ratio of the ink can affect how the ink prints.

Both inks were printed on coated and uncoated cover weight stock. To test the voltage of the cathode inks and to further display the concept of a printable cathode as being functional, a temporary ink formulation for the electrolytic and anode inks were used.

It is important to note that the tests and results are not intended compare the cathode inks to determine which ink is better, but intended to display how the two inks behave when printed, relative to their formulation and the substrate they are printed on, and to convey a preference over which ink would likely be used in respect to the conditions.

| Table 1. Percent Solids and Rheological properties of Beta1 and Beta2 formulations. |
|---------------------------------|--------|--------|
| **Formulation**                 | Beta1  | Beta2  |
| Solids                          | 27%    | 24%    |
| C & MnO₂                        | 9%     | 8%     |
| Water                           | 73%    | 76%    |
| **Rheology**                    |        |        |
| Viscosity                       |        |        |
| Low Speed                       | 147.0 cP | 142.5 cP |
| High Speed                      | 8300.0 cP | 9200.0 cP |

Using ASTM-D4713-92(2007), the standards test for nonvolatile content of heatset and liquid printing ink systems, the amount of nonvolatile content in Beta1 and Beta2 formulations was calculated.
The formulation of Beta1 contained 73% water and 27% solids, 9% of which are carbon and MnO$_2$, whereas Beta2 contains 76% water and 24% solids, and 8% of which are carbon and MnO$_2$.

A test of the ink’s rheology, the viscosity of an ink over a given time, was performed using a Brookfield viscometer and #1 spindle across multiple RPM’s 0.3 to 100.

The viscosity of Beta1 in Centipoise (cP) ranged from 8300cP at low speeds to 147cP at high speeds. It can be seen from the data that the ink formulation has sheer thinning properties. Beta2 shares the same properties as Beta1 but with an overall viscosity range from 9100cP at low speeds to 142.5cP at high speeds (see Figure 4).

**Test Prints**

To test the printability of Beta1, a simple flexographic plate consisting of a 100% solid, a 50% solid, and a gradient step patch from 100% to 5% was created (see Figure 5). This plate was used to test the halftone and gradient abilities of Beta1. There was more concern about 100% patches
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than dot size or halftones, so another set of plates was designed for later testing, which consist of 100% solids. An IGT Reprotest Flexography Printability Tester (Model F1, Serial 432.B.033) was used to print at various pressure settings on both coated and uncoated substrates.

The Beta2 formulation focused on the effects of an acrylic resin on print quality of the ink. To compare the effect, multiple formulations with different acrylic-to-water ratios were made. These were then printed using a flexographic plate containing a 100% solid patch on an IGT proofer (Model F1, Serial 432.B.033).

Prototype Construction and Testing

For the purpose of prototype testing of the cathode inks, temporary anode and electrolyte inks were formulated as follows:

- The electrolytic ink was a simple 35% solution of KOH with CMC to modify the resulting viscosity. The anode ink consisted of zinc powder with KOH as an electrolyte, propylene glycol as a humectant, and Joncryl 60.

- Both of these inks are temporary placeholders for final formulations. They may be responsible for some differences in the reported voltage of the tested cathode inks but this is unconfirmed, pending further research and development to improve the circuit.

- Testing of the finished prototypes only covered voltage checking using a simple voltmeter.

Figure 5. Test plate used to test printability of solid 50%, 100% and 5-100% gradient patched on uncoated and coated substrates.
Results & Discussion

Table 2. Printability comparison of Beta1 on coated and uncoated substrates with various pressures.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Printing Pressure</th>
<th>Evenness of Solids</th>
<th>Halftone Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated</td>
<td>500 N</td>
<td>Even (Best for coated)</td>
<td>Smudged</td>
</tr>
<tr>
<td>Coated</td>
<td>75 N</td>
<td>Uneven</td>
<td>Smudged</td>
</tr>
<tr>
<td>Uncoated</td>
<td>500 N</td>
<td>Even</td>
<td>Lost</td>
</tr>
<tr>
<td>Uncoated</td>
<td>75 N</td>
<td>Even</td>
<td>High TVI</td>
</tr>
</tbody>
</table>

Battery Halftone Printing

Beta1: First Cathode Ink Formulation

For Beta1, the results can be viewed in Table 2 and were as followed: On the coated substrate at a high pressure of 500 newtons there was a blur in the halftones but a clean 100% solid consistency is achieved. At a lower pressure of 75 newtons, the halftones were printable, though a little smudged, but lack the 100% solid consistency we received in the high-pressure print. On the uncoated substrate at a high pressure,
Battery Patch Printing

**Beta2: Cathode Ink Formulation with Acrylic Resin**

Inking Force: 100N   Printing Force: 30N   Speed: 0.3 m/s

Coated
Acrylic Ratio: 13:15

Uncoated
Acrylic Ratio: 13:15

Coated
Acrylic Ratio: 9:5

Uncoated
Acrylic Ratio: 9:5

Coated
Acrylic Ratio: 5:1

Uncoated
Acrylic Ratio: 5:1

**Figure 7.** Image comparison of 100% solid patches of the Beta2 formulations, varying the acrylic to water ratios across coated and uncoated substrates.
the halftones are completely lost, and a moderately okay density was achieved in 100% solid. At a lower pressure, the halftones print beautifully, but anything above 50% looks the same. The preferred settings outlined from this test were suited using for this run of Beta1 ink, however, may not apply to the Beta2 formulation or with other printing devices. The correlations made through these observations may be useful for future reference.

Referring to the patches in Figure 7, it was observed that as the acrylic concentration in the formulation rises, the print quality increases; conversely, as the acrylic concentration decreases, the print quality decreases. In addition, on the coated substrates, the less acrylic present the more crazing is apparent. Furthermore, the uncoated substrate absorbs ink faster, producing a better print.

Using the placeholder electrolytic and anode inks mentioned prior to the discussion of the Beta1 and Beta2 formulations, a voltage of 1.0 to 1.5 in Beta1 and 0.5-1.1 in Beta2 was achieved using a standard voltage meter. The variation in the voltage is the result of where the point of contact for each voltage meter prong touches on each of the anode and cathode inks. Also, difference in voltage depends on how much moisture is present within the system at the time of the reading.

Table 3. Comparison of the Beta2 formulation with focus on the printability of different acrylic to water ratios.

<table>
<thead>
<tr>
<th>Acrylic Ratio</th>
<th>Substrate</th>
<th>Evenness of Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:15</td>
<td>Coated</td>
<td>Even</td>
</tr>
<tr>
<td>27:15</td>
<td>Coated</td>
<td>Uneven</td>
</tr>
<tr>
<td>75:15</td>
<td>Coated</td>
<td>Even (Best for uncoated)</td>
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<tr>
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<td>Uncoated</td>
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</table>

**Conclusion**

The overall goal of the ink formulations is to demonstrate a cathode ink formulation that can be printed by flexographic means. This cathode ink in combination with an electrolyte and zinc mimics a battery,
ultimately proving the concept of a flexographically printable battery. Beta1 and Beta2 display different functionality depending upon the substrate they are printed on, and change depending upon which binder is used during formulation. Given the results, for most applications it would appear that an uncoated substrate has greater reliability in functionally printing the cathode. Coated substrates are unfavorable due to the difficulty of attaining a quality print on this surface (i.e. crazing), and one key concern in printing the paper battery would be getting the most material down onto the substrate.

The voltage meter clearly shows that Beta2 achieves a lower voltage range than Beta1. This could be due to the inability for electrons to flow within the cathode ink due to the nature of the specific resin. This could cause undesired results in the long run. If printing on a coated substrate, Beta2 would be preferred over Beta1 due to its printing stability on a coated substrate. Furthermore, a Beta2 ink formulated to contain more acrylic resin than water content will produce a stable print, but may lack desired printed matter. However, it may be more desirable to print on the uncoated side of a coated-1-side paper, so the coating can provide a moisture barrier on the back side of the sheet. When using the cathode in a printable battery concept, an externally placed terminal may want to be considered. Future work will be comprised of modifications and additional tests. Tests for voltage and discharge of the printable battery concept will be performed. The electrolytic and anode ink formulations will be modified to perform more efficiently with the cathode ink.

References


